Innovative bio-covers to mitigate the landfill methane emissions under wide seasonally fluctuating conditions

by

Parvin Berenjkar

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Department of Civil Engineering
University of Manitoba
Winnipeg

Abstract

Methane (CH_4) is a potent greenhouse gas (GHG) that can highly contribute to global warming. CH_4 emissions from landfills due to the anaerobic decomposition of organic waste comprise a significant portion of GHGs in the waste sector. When CH_4 mitigation in the landfills is not economically and technically feasible by flaring, the biological CH_4 treatment can be adopted by applying bio-covers filled by composts. Methanotrophs are responsible for oxidizing CH_4 in the bio-covers and reducing its emissions from landfills by converting it to carbon dioxide (CO_2) and water. They need enough moisture content (MC), temperature, CH_4 and oxygen (O_2) supply for their survival. However, climatic conditions such as precipitation, ambient temperature, and frost formation can affect these factors.

Laboratory tests at the University of Manitoba provided the basis for an effective methanotrophic bio-cover design, using a mixture of the yard waste and leaf compost (YLWC) and biosolids compost (BSC) from the City of Winnipeg's composting facilities. The current study is conducted based on findings of previous experiments in three steps. In Step 1 of the current study, a pilot bio-window at a City of Winnipeg landfill investigated since 2017 to 2019 led to the data assessment, including a high seasonal variation of ambient temperature (-20ºC to 35ºC) causing a thick, solid winter frost cover affecting gas exchange in winter, as well as temperatures above 45ºC in late summer within the bio-window. The high fluctuations in the temperature made a shift in methanotrophic populations from mesophiles to thermophiles. Low air diffusion through the bio-window was also measured. Dryness in summer caused low MC at the top layers restricting CH_4 oxidation. The effective methanotrophy under favorable environmental conditions was 80%.

In Step 2 of the study, based on the findings from the *in situ* bio-window, interactive effects of critical environmental factors including MC, temperature, and CH_4 concentration were investigated through batch incubations. Box–Behnken Design (BBD) adopting Response Surface Methodology (RSM) was implemented to develop a statistical model and optimize the conditions for the CH_4 oxidation in the compost mixture. The maximum value of CH_4 oxidation was obtained under optimum MC of 47.42%, temperature of 32.72℃, and initial CH_4 concentration of 23.81%. A parabolic curve for MC and temperature was observed simultaneously, and CH_4 concentration was not a significant controlling factor.

In Step 3, in-depth column tests were conducted to improve bio-cover performance by increasing aeration capacity in deeper layers through the addition of inorganic coarse materials. To increase oxygen (O_2) penetration, two sets of columns were packed with compost and two different sizes of gravel (¼" and ½") at different gravel:compost mixing ratios (1:1, 1:3, and 1:7), established in three consecutive stages. Columns were run for 101 days to find the optimum mixture with maximum CH_4 removal. Results showed that the CH_4 removal mechanisms in the columns were a combination of adsorption and biological treatment. The highest methanotrophic CH_4 removal efficiency was 65% obtained for ¼" gravel to compost (1:7) with the highest portion of compost and the lowest amount of fine gravel.

In this thesis, the applicability of YWLC and BSC (1:4) for CH_4 oxidation in the bio-covers was studied by evaluating the performance of a pilot bio-window with this compost mixture as the substrate layer under a high seasonally fluctuating climatic condition. To enhance the performance, the effect of environmental factors on CH_4 oxidation rate was investigated and the optimum levels for MC, temperature, and initial CH_4 concentration were obtained. To further increase the aeration to the deeper layers of the bio-window and fully exploit its vertical capacity, the addition of limestone gravel to the compost in the deeper layers was investigated at different mixing ratios. This study tries to optimize the application of the bio-windows with compost substrates in the areas with fluctuating climatic conditions of the continental areas.

Declaration

I, Parvin Berenjkar, declare that the thesis, which I hereby submit for the degree of Doctor of Philosophy at the University of Manitoba, is my own original work and has not previously been submitted for any other degrees at this or any other tertiary institution.

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Contribution of authors

Parvin Berenjkar: Conceptualization, Formal Analysis, Investigation, Experimental Operation, Writing-original draft.

Qiuyan Yuan: Supervision, Methodology, Writing-review & editing, Resources, Funding acquisition.

Richard Sparling: Supervision, Methodology, Writing-review & editing, Equipment.

Stan Lozecznik: Conceptualization, Funding acquisition, Writing-review & editing.

Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

1.1. Overview

Methane (CH_4) from municipal solid waste landfills accounts for 20% of national CH_4 emissions in Canada. Bio-covers are a cost-effective alternative that provide the conditions for Methane-Oxidizing Bacteria (methanotrophs) to strive or survive in a landfill's final cover soil, reducing fugitive CH_4 emissions. Many larger landfills are designed with landfill gas collection systems. However, such systems are costly and may not be feasible for small and medium-sized active or closed landfills. Moreover, in large landfills, these systems have a lifespan, and they will require a solution when CH_4 emissions are no longer cost effective to be collected and used. Bio-covers are a cost-effective alternative that optimizes the activity of methanotrophs in a landfill's final cover soil, reducing fugitive CH_4 emissions. Few studies have assessed the efficacy of bio-covers at field scale at sites with high seasonal climatic fluctuations that can affect temperatures and moisture content (MC) within the landfill cover. In Canada, with Humid Continental Climate, this is exacerbated by winter ground frost that alters surface gas exchange. In the case of elevated temperature landfills, heat radiating upwards leads to stressing the methanotrophs in summer. Therefore, the interactive effect of environmental factors on the microbial oxidation of CH_4 can affect the design parameters for optimizing compost-based bio-covers for widespread application. Issues around air penetration and the depth of CH_4 oxidation at different times of the year can also restrict the performance of the bio-covers. Study of seasonal fluctuations in methanotrophic performance in landfill bio-covers in Winnipeg (Manitoba, Canada) is well suited to study these issues, since they face both low (<0°C) temperature stress and winter frost cover. This should significantly impact the efficiency of biological CH_4 oxidation.

1.2. Summary of research in previous phases of the study

Previous laboratory experiments were carried out, at the University of Manitoba, to investigate whether it was possible to detect methanotrophs in compost materials produced on site at the landfill (e.g., through the municipal Yard Waste and Leaf Compost (YWLC) program). Also, an assessment of how to enrich the populations of these bacteria was done in the proposed materials

including YWLC and Biosolids Compost (BSC) as a potential growth matrix for methanotrophs, in terms of CH_4 oxidation potential, before implementation in a bio-cover. The BSC also contained woodchip and has higher porosity than YWLC. The findings from experiments were presented in two reports, prepared by KGS Group to Green Manitoba, a M.Sc. thesis in the University of Manitoba, and a published paper.

As proof of concept, batch incubations of the YWLC under a methane-in-air headspace confirmed that methanotrophic populations were present and could accumulate without the need for additional moisture or nutrients. However, there was competition against aerobic heterotrophs when the YWLC was not sufficiently mature, and the presence of readily degradable BOD (rdBOD) prevented the initial proliferation of methanotrophs. All further batch and column experiments were therefore performed with mature, low rdBOD-YWLC. Initial batch incubation of BSC from the BRRMF did not show methanotrophic activity, and addition of a highly active inoculum to the BSC also was not successful. However, in testing several mixing ratios of YWLC to BSC (e.g., 1:1, 1:4, 4:1), it was found that CH_4 was consumed faster than what was observed in the YWLC alone, indicating the benefit of mixing the two composts.

Engineered columns were constructed to assess CH_4 oxidation rates under conditions more representative of those in the field. The column (Plexiglas; height: 0.90 m, diameter: 0.14 m) was sealed at both ends and fitted with an inlet for synthetic landfill gas (LFG) (50%/50% CH_4/CO_2) at the bottom and an inlet for air and an outlet for effluent gas at the top. The LFG was supplied at Q_{LFG} = 15 mL min^{-1} (470 g CH_4 m^{-2} d^{-1}) while air was passed over the column at Q_{AIR} = 200 mL min^{-1} to mimic the diffusive ingress of O_2 due to a light breeze. Once the column was filled with materials, sampling ports located down the side of the column enabled the sampling of gases. Three column trials were conducted with variables including compost mix ratio, MC, and the addition of inoculum containing active methanotrophs.

From these trials it was conclude that there was a lack of O_2 diffusion down the column due to compost compaction at the high MC of the compost; therefore, no methanotrophy was observed below top 2 cm of the composts when the column was filled with a 1:1 mixture of YLWC and BCS at a MC of 65% g g^{-1} wet basis. Increased porosity using 1:4 mYLWC:BSC at lower MC of 35% g g^{-1} permitted CH_4 removal of upto 40%. Learning from the previous 2 trials, a methanotroph enriched inoculum was added to a 1:4 mixture of YWLC to BSC at a MC of 40% g g^{-1} wet basis.

There was biological activity detected throughout the length of the column, implying that there was O_2 penetration to the very bottom of the column. To confirm that the absence of O_2 was due to methanotrophy and not heterotrophy, the gas was changed at the end of the experiment from 50%/50% CH_4/CO_2 to N_2. Under these conditions, O_2 penetrated the column.

In this thesis, the proposed materials from previous experiments with the optimum mixing ratio will be applied in a pilot bio-window. Field and laboratory investigations will be performed throughout the year to monitor methanotrophic activities in the pilot landfill bio-window by evaluating O_2 consumption, CO_2 production and CH_4 emission rates. The evaluations will consider the effect of climatic factors (e.g., precipitation, ambient temperature, and atmospheric pressure) on the overall performance of the bio-window, and methanotrophs recovery rate in the spring. Eventually, it will be possible to determine if the concept of a biological landfill cover with proposed materials can successfully be applied to fluctuating conditions of continental climates. To enhance the performance of the bio-window, the interactive effect of environmental factors and facilitating air penetration by increasing the porosity will be investigated by laboratory batch and column experiments.

1.3. Objectives of the thesis

Step 1 (To investigate the performance of the bio-window under high seasonally fluctuating climatic conditions): The overall objective of Step 1 is to construct a pilot bio-window based on what was obtained from previous laboratory experiments including general design parameters and the most effective mixture of materials inducing the highest CH_4 oxidation, and to investigate the performance of the bio-window under high seasonally fluctuating climatic conditions through field-scale testing.

The detailed objectives of Step 1 are:

1. Investigate the CH_4 oxidation efficiency of the bio-windows by measuring net CH_4 emission and doing a mass balance.
2. Study vertical concentration profiles of the main gas components, O_2, CO_2, and CH_4, in the pore volume of the bio-windows to determine the depth of O_2 diffusion into the bio-windows and the location of the methanotrophic active zone.

3. Assess high seasonal fluctuations (i.e., soil temperature, moisture, frost line) on bio-window performance and *in situ* population and activity of methanotrophic communities.
4. Investigate the initial methanotrophic activity before multiplication by evaluating the CH_4 consumption rate potential.

Step 2 (To understand the effect of the environmental factors on the methanotrophic activity in the compost matrix): Based on the findings from Step 1, environmental factors including temperature and moisture content (MC) fluctuations could affect CH_4 oxidation by methanotrophs as well as the high CH_4 flux. To clearly understand the effect of the environmental factors on the methanotrophic activity in the compost matrix, a series of batch experiments at a wide range of MC, temperature, and initial CH_4 concentration were conducted.

The detailed objectives of Step 2 are:

1. Investigate the interactive effect of critical environmental factors including MC, temperature, and initial CH_4 concentration on the CH_4 oxidation by methanotrophs through batch incubation tests.
2. Adopt statistical modeling and Response Surface Method (RSM) to maximize the performance of the bio-window in oxidizing CH_4 by optimizing the critical environmental factors.
3. Verify the developed model by conducting supplementary batch incubations.

Step 3 (To improve the bio-window performance by increasing the porosity for better aeration): Field studies need to be supplemented with in-depth laboratory studies. Therefore, the next step of the study is conducting column and batch tests to improve bio-window performance around issues of air diffusion using compost samples collected from the *in situ* bio-window. Step 3 of the study is conducting column and batch tests filled by compost samples collected from the *in situ* bio-window to improve its performance around issues of air diffusion. The experiments investigate if increasing the porosity with focussing on gravel size and mixing ratios can result in high CH_4 oxidation efficiency in the laboratory.

The detailed objectives of Step 3 are:

1. Conduct column tests to assess the use of amendments to enhance performance of the methanotrophs.
2. Study vertical concentration profiles of the main gas components, O_2, CO_2, and CH_4, in the pore volume of the column to determine the depth of O_2 diffusion and the location of the methanotrophic active zone in each of the column setups.
3. Investigate the CH_4 capture efficiency of each column setup by measuring net CH_4 emissions doing mass balance.
4. Examine the effect of different media compositions and compost: gravel mixing ratios on MC, as a controlling factor for CH_4 oxidation, at various depths of each column.
5. Conduct batch incubations to determine the kinetic parameters and the potential activity of methanotrophs at various depths of each column after dismantling the columns.

1.4. Structure of the thesis

This thesis is presented in seven chapters and two appendices.

- *Chapter 1:* Introduction. This chapter includes an overview of the thesis, the previous research that was the basis for the current thesis, the thesis objectives and structure.
- *Chapter 2:* Literature review. A comprehensive review is conducted on the role of environmental factors and climatic conditions on the performance of the bio-based landfill covers. This chapter includes an Introduction section, followed by the principals of CH_4 oxidation in the bio-covers. Then, previous field and laboratory scale studies are presented.
- *Chapter 3:* Methane oxidation in the landfill bio-window was assessed under wide seasonally fluctuating climatic conditions. This chapter includes an Abstract, Introduction, Materials and Methods, Results, and Conclusion sections.
- *Chapter 4:* The interactive effect of environmental factors in a landfill bio-cover at a seasonally fluctuating climate is investigated. The results of batch tests designed by Box-Behnken Design are presented, and the optimum levels of the critical environmental factors are obtained. This chapter includes an Abstract, Introduction, Materials and methods, Results, and Conclusion sections.
- *Chapter 5:* Enhancement of methane oxidation in bio-based landfill covers by increasing aeration is studied. The results of column tests are presented and the CH_4 removal

mechanisms after increasing the porosity by gravel addition are discussed. This chapter includes an Abstract, Introduction, Materials and methods, Results, and Conclusion sections.

- *Chapter 6:* This chapter presents a summary and conclusion of the main findings in this thesis.
- *Chapter 7:* This chapter indicates the engineering significance of the thesis and presents the main findings along with the recommendations for future work. The technical challenges for the design and application of the bio-window are also mentioned and potential solutions are provided.
- *Appendix A:* Additional photos are presented to show the sampling in the *in situ* bio-window and the experimental procedure.
- *Appendix B:* Additional photos are presented to show the experimental set up for column tests and the equipment.

Chapter 2: Literature review: The role of environmental factors and climatic conditions on the performance of the bio-based landfill covers

Abstract

Methane (CH_4) is a potent greenhouse gas (GHG) that can highly contribute to global warming. CH_4 emissions from landfills generated from the anaerobic decomposition of organic waste comprise a significant portion of GHGs in the waste sector. When CH_4 mitigation in the landfills is not economically and technically feasible by flaring, the biological CH_4 treatment is adopted by applying bio-covers usually filled by composts. Methanotrophs are responsible for oxidizing CH_4 in the bio-covers and reducing its emissions from landfills. They need enough moisture content (MC), temperature, CH_4 and oxygen (O_2) supply for their survival. However, climatic conditions such as precipitation, ambient temperature, and frost formation can affect these factors. Numerous field-scale studies on the effect of seasonal variations on biological CH_4 oxidation in landfills were conducted in the cold climate and boreal areas focusing on frost-free seasons. It was revealed that the CH_4 oxidation decreases with the decrease in temperature. The laboratory-scale studies on the effect of multiple environmental factors on CH_4 oxidation showed that temperature, MC, and CH_4 concentration were dominant factors affecting the biological CH_4 oxidation, and the optimum MC in composts was higher than in soils while the optimum temperature was almost similar for both. The CH_4 oxidation enhancement examples are also presented in laboratory-scale studies through nutrient addition, increasing aeration, mixing media, applying CH_4 adsorption, and vegetation. The purpose of this chapter is to provide a thorough insight for the bio-cover implementation in landfills by focusing on challenges regarding climatic conditions and improvement potentials during its performance.

Keywords: Methanotrophs, Moisture content, Temperature, CH_4 oxidation, Compost

2.1. Introduction

Methane (CH_4) is a potent greenhouse gas (GHG) significantly contributing to heat trapping and global climate change (Caulton et al., 2014; Myhre et al., 2013). Having a much shorter atmospheric lifespan than carbon dioxide (CO_2), global warming potential (GWP) of CH_4 is 28-34 over a 100-year time horizon and 85 over a 20-year time span compared to CO_2 (IPCC, 2013). CH_4 is recognized being the second most crucial GHG by the international GHG inventories (IPCC, 2013; NOAA/ESRL, 2018) due to the current annual emission comprising of 10-16% of all anthropogenic GHGs and the increase in the CH_4 concentration in the atmosphere by 2.5x since the industrial revolution, from 715 ppbv to 1803 ppbv in 2011 (IPCC, 2013). The global annual CH_4 concentration was determined to be 1858 ppb on average in 2017 (NOAA/ESRL, 2018).

More than 60% of all CH_4 emissions are anthropogenic, initiating from rice agriculture, animal husbandry, landfilling, composting, anaerobic wastewater treatment, natural gas refineries, and coal mining (IPCC, 2013).

During the methanogenesis phase of the landfill, the organic waste is decomposed under anaerobic conditions inside the landfill and the landfill gas (LFG) is produced. The LFG typically consists of 55–60% v/v of CH_4 and 40–45% v/v of CO_2 (Ayalon et al., 2001; Scheutz et al., 2009). CH_4 emissions from landfills cause the most significant GHG emissions from the waste sector with nearly 500 to 800 Mt-CO_2e·yr^{-1} (Bogner et al., 2007).

Total emissions from landfills continue to increase because of waste generated by increasing populations despite efforts to divert organics away from landfilling (IPCC, 2013), thereby necessitating that effective and practical technologies be developed to reduce emissions. Common procedures to capture and reduce CH_4 emission from landfills include incorporating an LFG collection system, a landfill cover, or a combination of both.

Studies have proved the efficacy of the LFG collection systems, which can vary in the range of 50-95% depending on the landfill cover, whether it is daily, intermediate, or final cover (Spokas et al., 2011; Barlaz et al., 2009). The LFG collection system can be retrofitted by the flaring system, where CH_4 can be combusted and converted to CO_2 with lower GWP. When the energy recovery infrastructure is not feasible in the landfill site, CH_4 combustion can be a simple and feasible method to control CH_4 emission (Chai et al., 2016; Goldsmith et al., 2012). However, flaring is economically feasible when the CH_4 concentration in the LFG is higher than 20-25% with a minimum generation rate of 10-15 $m^3CH_4 \cdot hr^{-1}$ (Haubrichs and Widmann, 2006). In small and

medium-sized active landfills or closed landfills where LFG generation rate is not high enough, flaring or energy recovery are not technically and economically efficient (Spokas et al. 2006; Börjesson et al. 2007; Huber-Humer et al., 2008).

In modern engineered landfills, landfill cover systems are applied to control the fugitive CH_4 emissions that are not adequately captured by gas collection systems. Landfill covers have primarily been implemented to minimize the leachate formation; therefore, low permeable materials such as clay have been used to cover the landfill that could also trap the generated CH_4 without reducing it (Kjeldsen, 1996). However, clay covers can get cracked while being dry, which can appear in the hotspot formation with extensive fugitive CH_4 emissions (Pedersen et al., 2010). Manipulation of landfill covers to maximize the CH_4 oxidation potential offers a promising alternative for flaring to control fugitive CH_4 emissions and reduce CH_4 emission in small and closed landfills. A bio-based landfill cover, known as a bio-cover, is an engineered landfill cover being widely used as a biological treatment method for CH_4 emissions in landfills. The bio-covers employ natural CH_4-oxidising bacteria to oxidize and reduce CH_4 emissions which is a cost-effective and environmentally friendly alternative for flaring.

Previous research has focused on understanding the fundamental processes and controlling factors including pH, material porosity, moisture content (MC), temperature, and nutrient content that govern CH_4 oxidation in landfills to determine how to adequately exploit the process in a biological system (Kightley et al. 1995; Chanton and Liptay 2000; Börjesson et al. 2004; Mor et al. 2006; Wang et al. 2011). Experimental set-ups have shifted from batch tests to determine oxidation rates to column experiments that more reliably replicate landfill dynamics (Kightley et al. 1995; Humer and Lechner 1999; Lou et al. 2011; Pedersen et al. 2011; Mancebo et al. 2012). Field-scale application of the bio-covers have also been widely investigated (Humer and Lechner 2001a, 2001b; Einola et al. 2009; Roncato and Cabral 2012). However, despite the standard conditions in the laboratory experiments, the field-scale application of the bio-covers is not in a controlled environment, and the CH_4 oxidation can be affected by multiple environmental factors. Precipitation, ambient temperature, solar radiation (SR), and frost formation are among the environmental regulators that can affect the MC, temperature, and oxygen (O_2) accessibility in the bio-covers. The CH_4 oxidation rate was the only assessed parameter in most of the field-scale studies, and the effect of climatic factors (e.g., temperature, MC, air flow etc.) on bio-cover performance was missing. Few studies have considered four season and specifically winter. For

instance, Wilshusen et al. (2004) investigated the CH_4 oxidation efficiency in bio-covers under varying climatic conditions in British Columbia, Canada, focusing on summer and spring results. A similar study was carried out by Chanton et al. (2011) that determined CH_4 oxidation in landfill covers at different climate types (i.e., arid, Mediterranean, continental, tropical). During 4 years of investigation, they mostly considered warmest times of the year even in arid and tropical areas, and with very few samplings in northern continental areas in winter. One sampling site, in December indicated only 1.1% fraction of evolved methane oxidized. In a study by Pedersen (2010), the temperature at different depths of the soil cover was measured only in May with ambient temperature fluctuating between 7ºC to 22ºC and soil temperature fluctuating between 18ºC to 30ºC at top layers and 25ºC to 27ºC at deeper layers.

There are several in-depth and short review papers regarding biological CH_4 oxidation in landfill cover systems. Scheutz et al. (2009) have comprehensively described the microbial CH_4 oxidation processes in natural environments and landfills and explained the technologies to mitigate CH_4 emissions from landfills supported by numerous field-scale and laboratory-scale case studies. Chiemchaisri et al. (2012) have a brief review on the process of CH_4 emission reduction in the landfills with the focus on the soil as the cover material. However, in the study by Sadasivam and Reddy (2014), the CH_4 oxidation process in both soil cover and bio-covers are discussed, followed by summarizing published data in previous field-scale and laboratory-scale research. They focused on the challenges regarding the design and operation of these cover systems and listed the advantages and disadvantages of each type of landfill cover system. A similar study was conducted by Majdinasab and Yuan (2017), focusing on the parameters controlling biological CH_4 oxidation and comparing different types of CH_4 bio-mitigation systems.

The purpose of this chapter is to provide a comprehensive background for the bio-cover implementation in landfills while focusing on the potential challenges and improvements influencing its performance. This chapter will provide an insight for the investigators regarding the bio-cover performance under variable climatic conditions. Therefore, first, bio-cover basics are thoroughly presented to be practical for the investigators; the bio-cover design, the process of gas transport in the bio-cover, the biological CH_4 oxidation procedure, and the methods of quantifying bio-cover performance are concisely explained to be understandable. Then, the most significant environmental factors affecting CH_4 oxidation are described, and potential improvement approaches to regulate these factors are discussed. The field-scale and laboratory-

scale studies considering the environmental factors caused by seasonal variations in the climatic conditions are presented, and the specific methods used in each study are compared. Finally, the studies, including approaches for enhancing CH_4 oxidation in the bio-covers, are provided to discuss the potential engineering solutions.

2.2. The principals of CH_4 oxidation in the landfill bio-covers

2.2.1 Bio-cover design

In a bio-cover system, the LFG, coming from inside the landfill, needs to be homogeneously distributed into the substrate material where CH_4 can be oxidized by CH_4 oxidizing bacteria. Therefore, the bottom layer in the bio-cover is the gas distribution layer (GDL) that is typically filled by coarse materials such as gravel, tire shreds, and glass. On top of the GDL, there is oxidation layer that is mainly packed by materials that can support the growth and activity of CH_4 oxidizing bacteria. The thickness of the GDL varies between 10-50 cm, while it is in the range of 50-120 cm for the substrate layer (Gebert and Groengroeft, 2006; Philopoulos et al., 2008; Roncato and Cabral, 2012).

Composts and waste materials such as sewage sludge, biosolids, and yard waste are commonly used in the substrate layers of the bio-covers. However, according to the laboratory experiments in a study by Cabral et al. (2010), compost was found to be more favourable than the waste material for CH_4 oxidation as it required less time than sewage sludge to oxidize CH_4. Moreover, the high MC of 70% in the sewage sludge caused an anaerobic condition leading to CH_4 generation.

Compared to mineral materials, composts have unique characteristics that can be beneficial when applied in the bio-covers. Due to having high organic contents and high specific surface area, composts have high water retention capacity (Scheutz et al., 2009), so they can prevent high levels of infiltration and leachate production into the landfills. The high specific surface area also allows more population of CH_4 oxidizing bacteria adhere to the surface (Huber-Humer et al., 2009). Composts have higher thermal conductivity than mineral materials due to their higher porosity, making them provide a proper insulation effect (Kettunen et al., 2006; Huber-Humer et al., 2009). Coarsely textured composts have a better insulation effect during the winter than fine-textured ones (Huber-Humer 2004), and they are more favourable for CH_4 oxidation (Scheutz et al., 2009). Compost maturity is an essential factor for adequate CH_4 oxidation as in mature composts there is

minimal competition for O_2 between CH_4 oxidizing bacteria and heterotrophs. However, Niemczyk et al. (2021) showed that composts need to be matured beyond the compost stabilization standards to oxidize CH_4 to its full capacity.

While bio-covers are meant to cover the entire or vast areas of the landfills, bio-windows are implemented in small separate segments integrated into the landfill final clay cover. As the clay cover has a low permeability, the LFG tends to pass through the bio-windows containing compost materials. The bio-window system is more profitable when applying a full-scale bio-cover system on the landfill is not economically feasible, especially in landfills with low LFG production rates. Bio-windows are more cost-effective than bio-covers due to comprising smaller amounts of filling materials. The required surface area of the bio-windows is calculated using the ratio of CH_4 load ($kgCH_4.d^{-1}$) from the waste inside the landfill to the CH_4 oxidation capacity of the applied materials ($gCH_4.m^{-2}.d^{-1}$) (Scheutz et al., 2011a). The CH_4 load is usually determined during the baseline investigations before the bio-cover/bio-window installment through different methods, including the static flux chamber, advanced tracer-based plume analysis, double tracer approach, and others. (Scheutz et al., 2011b). The Oxidation capacity of the materials can be obtained from preliminary column experiments conducted to assess the applicability of the materials (Scheutz et al., 2011a). There are numerous studies on the application of bio-cover or bio-window systems in landfills from different regions possessing distinct climatic conditions (Table 2-1).

Table 2-1. Bio-cover and bio-window systems in landfills from different regions with various climatic conditions

Landfill location	Climatic zone	Size (m^2)	Bio-cover filling material	CH_4 oxidation efficiency (%)	Reference
Kentucky, USA	Humid subtropical	2200	Yard waste compost	55	Barlaz et al. (2004)
Hamburg, Germany	Cold and temperate	6 9	Humic topsoil+ crushed clay	62	Gebert and Groengroeft (2006)
Florida, USA	Humid subtropical	7.6 × 7.6 7.6 × 7.6 7.6 × 7.6	Yard waste compost	41-64	Stern et al. (2007)
Alberta, Canada	Continental	9.3 9.3 20.9	Yard waste compost	76 68 35	Philopoulos et al. (2008)
Sydney, Australia	Temperate	3 × 3	Yard waste compost+ 10% woodchips	60	Dever (2009)
		3 × 3	MSW compost+10% woodchips	32	
		3 × 3	Yard waste compost	12	
		3 × 3	MSW compost+20% woodchips	67	
Finland	Boreal	3.9 ha	Peat+sludge compost	89 (max)	Einola et al. (2009
Zealand, Denmark	Temperate	9 × 9. 5	Garden waste compost	28	Scheutz et al. (2011)
Quebec, Canada	Humid continental	2.75 × 9.75	Sand+compost	89	Cabral et al. (2010)
Quebec, Canada	Humid continental	2.75 × 9.75	Sand+compost+gravel	11	Roncato and Cabral, (2012)
		2.75 × 9.75	Sand+compost	72	
Tuscany, Italy	Mediterranean	25 25 25	Organic compost+sand MSW compost+sand Organic+MSW compost+sand	65 56 75	Pecorini and Iannelli (2020)
Winnipeg, Canada	Humid continental	3.5 × 2.5	Yard waste and leaf compost+Biosolids compost	21 (average) 80 (max)	Berenjkar et al. (2021)

2.2.2 Gas exchange in the landfill cover systems

Advection and diffusion are the main gas transport mechanisms regulating gas exchange in the landfill cover system. The diffusive gas transport is caused by concentration differences in the landfill cover and its surrounding environment, while advective gas transport is provoked by pressure gradients (Poulsen and Møldrup, 2006). The variations in the microbial activity inside the landfill producing LFG can alter both the pressure gradient and gas concentration differences (Kjeldsen, 1996; Héroux et al., 2010). Moreover, when the atmospheric pressure drops, the CH_4 emission increases due to the pressure gradient between the landfill and the atmosphere (Héroux et al., 2010). The pressure gradient can also be induced by wind turbulence (Poulsen, 2005).

The physical characteristics of the substrate layer of the landfill cover system, such as porosity, MC, and O_2 permeability, can also affect the gas exchange by both advection and diffusion (Poulsen and Møldrup, 2006). The lower MC in the substrate layer, the more diffusive gas exchange (Scheutz et al., 2009). The MC can increase by precipitation; therefore, the gas permeability reduces due to the limited pore volume and lower gas diffusion coefficient in the water (Héroux et al., 2010). When the MC is high, the wind-induced gas transport can be the dominant mechanism for gas exchange compared to the diffusion. When there is low pore volume in the substrate layer, both diffusive and wind-induced gas exchange are critical, while the latter is the most significant (Poulsen and Møldrup, 2006).

Vegetation can enhance O_2 penetration into the pedosphere and accelerate CH_4 oxidation; however, it can increase CH_4 emissions through gas conduits. Xin et al. (2016) studied the effect of vegetation and SR on CH_4 emission from landfills and observed that vegetation could regulate the diurnal CH_4 emissions based on its type and growing conditions. Vegetation can also increase CH_4 emissions from landfills by convection mechanism caused by the increase in SR. Moreover, the SR causes the internal pressurization of plants to alter the gas transport mechanism from diffusion to convection, accelerating CH_4 emissions in vegetated zones.

2.2.3 CH_4 oxidizing bacteria

CH_4 oxidizing bacteria, known as methanotrophs, are considered as a subcategory of methylotrophic bacteria that can utilize CH_4 as their solely supply of carbon and energy (Hanson and Hanson, 1996). There are three types of O_2 dependent methanotrophs, including Type I, Type

II, and Verrucomicrobial methanotrophs. The physiological and biochemical characteristics of these species are briefly contrasted in this section.

The CH_4 oxidation by methanotrophs occurs stepwise through methanol (CH_3OH), formaldehyde (CHOH), and formate (CHOOH) to CO_2. Methanotrophs use methane monooxygenase (MMO) enzymes to catalyze the oxidation of CH_4 to methanol (Hanson and Hanson, 1996). There are two main pathways of formaldehyde assimilation by methanotrophs, including the ribulose-monophosphate (RuMP) pathway and serine pathway that are used by Type I and Type II methanotrophs, respectively (Figure 2-1.).

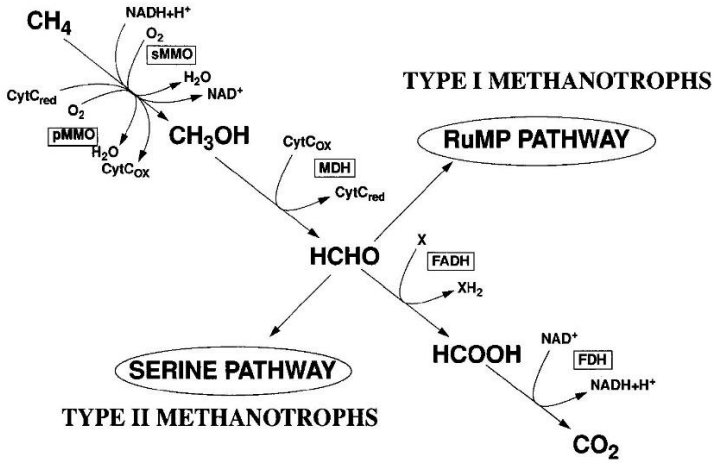

Figure 2-1. Pathways for methanotrophic CH_4 oxidation and formaldehyde assimilation (retrieved from Hanson and Hanson 1996). Note: CytC, cytochrome c; FADH, formaldehyde dehydrogenase; FDH, formate dehydrogenase; NAD: Nicotinamide adenine dinucleotide

Type I methanotrophs belong to the γ -subdivision of Proteobacteria, while Type II methanotrophs belong to the α-subdivision. All methanotrophs can develop a particulate or membrane-bound methane monooxygenase (MMO) (pMMO) should there be copper while their growth. However, in the absence of copper, Types II methanotrophs can synthesise the soluble MMO (sMMO). Growth yields on CH_4 are higher by Cells of methanotrophs containing pMMO than those containing sMMO. High copper availability results in the expression of pMMO, which yields higher growth efficiency than sMMO (Hanson and Hanson, 1996). Type I methanotrophs can better grow when CH_4 concentration is low and the O_2 concentration is near its atmospheric level. They can form cysts and fix inorganic N. On the other hand, Type II methanotrophs prefer to grow at a high CH_4 concentration and a low O_2 concentration, and they can fix N_2 for the cell synthesis (Sadasivam and Reddy, 2014).

On the other hand, the non-proteobacterial methanotrophs were first isolated from geothermal features in areas with hot conditions including a mudpot in the Solfatara volcano in Italy (Pol et al., 2007), a steaming soil at Tikitere, New Zealand (Dunfield et al., 2007), and an acidic hot spring in Uzon Caldera, Kamchatka, Russia (Islam et al., 2008). The most distinguished features of these new methanotrophs were their remarkably acidophilic phenotype, their lack of intracytoplasmic membranes typical for proteobacterial methanotrophs, and their phylogenetic affiliation to the bacterial phylum Verrucomicrobia. They were able to grow at pH <1 and temperature of 65°C that are respectively far below and far above the reported values for proteobacterial methanotrophs.

In a landfill setting, there can be distinct roles for each of the three methanotroph types to play. Knowing that methanotrophs coexist in soils, in a landfill cover soil, it is expected that Type I methanotrophs oxidize O_2 in the upper layers, where they have access to more atmospheric O_2, while in deeper layers due to the low O_2 and high CH_4 concentrations, type II methanotrophs work better (Scheutz et al., 2009; Sadasivam and Reddy, 2014; Meyer-Dombard et al., 2020). To our knowledge, there has been only one study on the existence of Verrucomicrobia methanotrophs on the landfill bio-covers (Berenjkar et al., Under review). Since they are available in thermal zones, it is not expected to find them in the landfills unless the temperature radiating from the degrading waste to the landfill cover is not less than 60ºC.

2.2.4 The CH_4 oxidation reaction and kinetic parameters

The CH_4 oxidation in the aerobic environment of the landfill covers and bio-covers occurs according to the following stoichiometric reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat} \qquad (2\text{-}1)$$
$$\Delta G^o = -780\ \text{kJ.mol}^{-1}\ CH_4$$

The equation indicates that methanotrophs need two moles of O_2 to oxidize one mole of CH_4 and produce one mole of CO_2, two moles of water, and heat.

The CH_4 oxidation kinetics in the bio-covers are typically defined by the Michaelis-Menten equation that is mostly used for enzymatic reactions with single substrate, indicating that the growth of the microorganism can be limited by one substrate. In case of CH_4 oxidation by methanotrophs in the bio-covers, the substrate is the CH_4, while the enzyme is the MMO, and the equation is as the follow:

$$r_{CH_4} = -\frac{V_{max}.[CH_4]}{K_m + [CH_4]} \quad (2\text{-}2)$$

Where r_{CH4} is the CH_4 oxidation rate, V_{max} is the maximum CH_4 oxidation rate, $[CH_4]$ is the initial CH_4 concentration and K_m is Michaelis–Menten (half saturation) constant. K_m indicates the CH_4 concentration at which the removal rate is half of its maximum value. The value of K_m is usually affected by the type of dominant methanotrophs in the reaction.

For applying the Michaelis-Menten equation it is assumed that the reaction is in equilibrium and the produced CO_2 will not be converted to CH_4, the growth and breakdown of the enzyme is in the steady-state phase, and the maximum CH_4 oxidation rate is achieved when the enzyme is saturated by CH_4.

2.2.5 Methods of CH_4 oxidation calculations to assess the bio-cover performance

The fraction of CH_4 oxidized during transport through a bio-cover (f_{ox}) can reflect the performance of the bio-cover. There are three methods to calculate the oxidized fraction of CH_4, including stable carbon isotope technique, CH_4 mass balance method, and the gas concentration ratios in the vertical profile of the bio-cover.

Stable carbon isotopic method described by Chanton and Liptay (2000), Barlaz et al. (2004), Abichou et al. (2006), and Cabral et al. (2010), allows for the *in situ* determination of f_{ox}. This method relies on measuring the difference between $\delta^{13}C$ of subsurface (anoxic) CH_4 and $\delta^{13}C$ of emitted CH_4, where $\delta^{13}C(‰)$ refers to the proportion of a given sample that is ^{13}C in relation to a standard (Eq 3). It is well-known that methanotrophic microorganisms have a preference for the stable carbon isotope of smaller mass, ^{12}C, rather than ^{13}C; as a result, significant isotope fractionation occurs when CH_4 is oxidized. Together with knowledge of the isotope fractionation factors associated with bacterial oxidation (α_{ox}; based on empirical equations using ambient temperature) and gas transport (α_{ox}; equal to 1.0 for advection, >1.0 for diffusion), f_{ox} can be calculated using Eq 3. This method is considered to be the most robust approach available to quantify CH_4 oxidation in the field.

$$\delta^{13}C(‰) = 1000 \text{ x } \left(\frac{R_{sam}}{R_{std}} - 1\right) \quad (2\text{-}3)$$

Where R_{sam} and R_{std} refer to the $^{13}C/^{12}C$ ratios of the sample and the reference standard, Vienna Peedee Belemnite (R = 0.01124), respectively.

$$f_{ox} = 0.1 \text{ x } \frac{\delta_E - \delta_A}{\alpha_{ox} - \alpha_{trans}} \quad (2\text{-}4)$$

Where δ_E and δ_A refer to the $\delta^{13}C$ value of emitted and anoxic CH_4, respectively; α_{ox} and α_{trans} are isotope fractionation factors for bacterial oxidation and gas transport, respectively.

Knowing the CH_4 influx and outflux, the CH_4 mass balance method can be used to determine the fraction of CH_4 oxidized and the CH_4 oxidation efficiency (Eff_{ox}) using the following equations:

$$f_{ox} = J_{in} - J_{out} \quad (2\text{-}5)$$

$$Eff_{ox} = \frac{J_{in} - J_{out}}{J_{in}} \times 100 \quad (2\text{-}6)$$

Where J_{in} and J_{out} are CH_4 influx to the bio-cover and outflux from surface of the bio-cover, respectively. The CH_4 flux in the field can be measured, before and after bio-cover construction, using above-ground micrometeorological and tracer methods, ground-level static or dynamic chambers, or other field-validated methods. While flux chamber methods are single point measurements, the other techniques can be employed to determine the total emissions from landfills. In the existing bio-covers where field measurement of CH_4 influx is impossible or it was not measured in the baseline investigation, the CH_4 influx can be obtained by the carbon mass balance method that has been used by many researchers (Christophersen et al., 2001; Einola et al., 2008&2009; Scheutz et al., 2011a). According to this method, the CH_4 influx corresponds to the summation of CH_4 emission and CH_4 oxidation. It is assumed that there is a direct relationship between the CH_4 and CO_2 influxes, and their concentrations in the waste underneath the bio-cover. Therefore, the CH_4 influx can be calculated according to the following equations:

$$J_{LFG} = J_{in(CH_4)} + J_{in(CO_2)} = J_{out(CH_4)} + J_{out(CO_2)} - J_{resp(CO_2)} \quad (2\text{-}7)$$

$$\frac{J_{in(CH_4)}}{J_{in(CH_4)} + J_{in(CO_2)}} = \frac{C_{in(CH_4)}}{C_{in(CH_4)} + C_{in(CO_2)}} \quad (2\text{-}8)$$

$$J_{CH_4(in)} = \frac{C_{in(CH_4)}}{C_{in(CH_4)} + C_{in(CO_2)}} . (J_{out(CH_4)} + J_{out(CO_2)} - J_{resp(CO_2)}) \quad (2\text{-}9)$$

Where J_{LFG} is the LFG influx (mol $C.m^{-2}.d^{-1}$) composed of CH_4 and CO_2 influxes ($J_{in(CH4)}$ and $J_{in(CO2)}$), $J_{resp(CO2)}$ is the CO_2 emissions due to the respiration ($J_{resp(CO2)}$) in the bio-cover (mol $C.m^{-}$

$^{2}.d^{-1}$), $C_{in(CH4)}$ and $C_{in(CO2)}$ are the CH_4 and CO_2 concentrations (% v/v) in the waste underneath the bio-cover, and $J_{out(CH4)}$ and $J_{out(CO2)}$ are CH_4 and CO_2 outfluxes (mol $C.m^{-2}.d^{-1}$).

Barlaz et al. (2004), Stern et al. (2007), and Cabral et al. (2010) are among studies that have used both stable isotope method and mass balance method through static flux chamber measurements. They have observed rather close agreement between the results of both methods.

In the flow-through column tests and the biofilters that are fed by gas pipes CH_4 flux can be calculated by the following equations:

$$J_{in} = C_{in}.Q_{in} \quad (2\text{-}10)$$

$$J_{out} = C_{out}.Q_{out} \quad (2\text{-}11)$$

Where C_{in} and C_{out} are CH_4 concentrations in the inlet gas and column effluent, respectively, while Q_{in} and Q_{out} are the CH_4 flow rate in the inlet and outlet of the column, respectively.

Gebert et al. (2011) proposed a method to calculate the cumulative CH_4 oxidation at various depths of the bio-cover and biofilter systems and reported a high correlation between the results of this method and that of the CH_4 mass balance method. In this method, it is assumed that one mole of CH_4 is converted to one mole of CO_2 according to the stoichiometry, the total produced CO_2 in the system is due to the methanotrophic CH_4 oxidation and not respiration or heterotrophic activities, the population of the methanotrophs is stable and no transfer of carbon to biomass is expected, the gas and liquid phases of CO_2 are in equilibrium, no CO_2 precipitation is expected, and the entire system is in the steady-state phase. Considering these assumptions, the portion of oxidized CH_4 can be determined at any depth of the vertical profile of the system.

Therefore, the concentrations of CO_2 and CH_4 in the inlet gas (laboratory-scale and biofilters) or LFG (field-scale bio-covers) are obtained, and the ratio of these concentrations is determined. The pore gas concentrations of CO_2 and CH_4 are also measured at any depth of the vertical profile of the system through gas probes, and the ratio of these concentrations is determined. Since the dilution of gases due to the air penetration into the system must be to the same extend, any variations in the ratio of CO_2 to CH_4 concentrations compared to that in the LFG is due to the methanotrophic CH_4 oxidation. Therefore, the volume of oxidized CH_4 is equal to the volume of produced CO_2, and it can be calculated at any depth by the following equation:

$$\frac{C_{CO_2(LFG)} + x}{C_{CH_4(LFG)} - x} = \frac{C_{CO_2(i)}}{C_{CH_4(i)}} \quad (2\text{-}12)$$

$$Eff_{ox} = \frac{x}{C_{CH_4(LFG)}} \times 100 \quad (2\text{-}13)$$

Where $C_{CO_2(LFG)}$ and $C_{CH_4(LFG)}$ are CO_2 and CH_4 concentrations in the LFG (vol%), respectively, x is the share of the oxidized CH_4 (vol%) that is converted to CO_2, $C_{CO_2(i)}$ and $C_{CH_4(i)}$ are CO_2 and CH_4 concentrations at the depth of i (vol%), respectively, and Eff_{ox} is CH_4 oxidation efficiency (%). In case of laboratory column tests, the concentrations of CO_2 and CH_4 in the column inlet can be used instead of those in the LFG in the equation.

Huber-Humer (2004) and Huber-Humer et al. (2009) used soil gas probes along with CH_4 screenings and flux tunnel to evaluate CH_4 oxidation.

Comparing the three methods, the stable isotope method does not require the CH_4 influx and outflux measurements; therefore, when obtaining the CH_4 oxidation rate is the primary purpose of the study, it seems more feasible than the CH_4 mass balance method, requiring flux measurement equipment, especially in the field-scale studies. The gas profile method can only be beneficial in the well-established CH_4 oxidation systems, where the applied filling materials are mature enough to not producing excessive CO_2 or undergoing anaerobic degradation. While this method can be verified using the mass balance method, it can only provide the CH_4 oxidation efficiency without calculating the CH_4 oxidation rate. Overall, the application of these methods depends on the purpose of the study, the equipment availability, and the stability of the bio-cover material.

2.3. Environmental factors influencing the CH_4 oxidation rate in the landfill bio-covers

The microbial CH_4 oxidation in the landfill bio-covers can be either enhanced or inhibited by several controling factors, including temperature, MC, CH_4 and O_2 availability, nutrients, pH, soil texture, etc. (Scheutz et al. 2009; Sadasivam and Reddy 2014; Majdinasab and Yuan 2017). The effect of these factors on microbial CH_4 oxidation can noticeably change by the climatic conditions. Knowing the effect of environmental factors can assist in accomplishing of the optimized design of the landfill soil covers and bio-covers. It has been inferred that in the landfill soil covers, temperature and MC are crucial environmental factors controlling microbial CH_4 oxidation (Scheutz et al., 2009).

2.3.1 Temperature

Several factors can alter the bio-cover temperature affecting the microbial CH_4 oxidation. The variations in the ambient temperature during the day and throughout the year is the most crucial factor affecting the temperature, especially at the upper layers of the landfill covers and bio-covers (Yeşiller et al., 2005; Aït-Benichou et al., 2009; Chiemchaisri et al., 2012). Studies from different cold climate areas have shown that seasonal variations in the ambient temperature can affect CH_4 oxidation in the landfill bio-covers. During the winter, when the bio-cover temperature was below 5°C to 10°C, the CH_4 emission increased, indicating low CH_4 oxidation, while there was low or no CH_4 emission during the summer due to the complete CH_4 removal (Börjesson and Svensson, 1997; Christophersen et al., 2001). The CH_4 oxidation efficiency could drop by 18% even when the temperature was reduced to 12°C in winter (Berger et al., 2005). However, an increase in the temperature of bio-cover over 50°C during the summer could also fully stop CH_4 oxidation in the landfill cover soil (Zeiss, 2006).

In the bio-covers covered by plants, the temperature can be affected in some ways; the surface can be protected from the ambient heat, the heat in the bio-cover can be retained, and water evaporation can result in lower temperatures than the ambient (Chiemchaisri et al., 2012).

In addition to the mentioned factors, the heat generation in the landfill due to the anaerobic decomposition of organic waste (NRC, 2007) can alter the bio-cover temperature. Many researchers have reported that there are spatial variations in the temperature inside the landfill. The decreasing order of reported temperature was in the landfill core, landfill base, and near the surface, with the maximum value of 40°C to 65°C (Houi et al., 1997; Yoshida et al., 1997; Rowe, 1998; Lefebvre et al., 2000; Yeşiller and Hanson, 2003). Dach and Jager (1995) found the maximum temperature of 85°C in the aerobic zones, while in the anaerobic zone, it was in the range of 60°C to 70°C. Yeşiller et al. (2005) studied seasonal variations in the temperature of four landfills from different climatic areas and reported a steady high temperature of 23°C to 57°C in the centre of the landfills despite the shallow depths where the temperature trend followed the seasonal variations of the ambient temperature.

Sustaining desirable temperature for methanotrophic activity during winter, especially in the cold climate landfill bio-covers, can increase CH_4 oxidation rates. Zeiss (2006) implemented a heat extraction pipe and a heat exchanger pipe to conduct landfill heat to the biofilter in a Canadian landfill. Moreover, snow covering can insulate the soils, secure a higher temperature during the

winter and early spring, and reduce CH_4 emissions (Zhao et al., 2016), benefiting CH_4 oxidation in the bio-covers.

The temperature range in an environmental system can regulate whether Type I, Type II, or *Verrucomicrobial* methanotrophs are active. Most of the methanotrophs are mesophiles (Hanson and Hanson, 1996) with the optimum temperature of 25°C to 35°C in the soils (Scheutz et al., 2009). While below the optimum temperature, with an increase in the temperature, the CH_4 oxidation rate increases, research has shown that above 40°C, CH_4 oxidation rates decline and approach to zero (Park et al., 2005; Mor et al., 2006; Zeiss, 2006).

On the other hand, methanotrophs can also be active at the temperatures as low as 1°C to 2°C and as high as 60°C to 70°C (Christophersen et al., 2000; Scheutz and Kjeldsen, 2004; Jäckel et al., 2005; Einola et al., 2007; Op den Camp et al., 2009). All psychrophilic methanotrophs are Type I (Omelchenko et al., 1992; Bowman et al., 1997; Börjesson et al., 2004). Studies on the cold climate landfill soil covers have revealed that Type I methanotrophs can oxidize CH_4 at lower temperatures of 2°C to 10°C, while both Type I and Type II methanotrophs can grow at 20°C (Börjesson et al., 2004; Spokas and Bogner, 2011). Moreover, in a landfill biofilter, Type II methanotrophs had higher optimum temperature (28°C) than Type I methanotrophs (10°C) (Gebert et al., 2003).

Studies from other environmental habitats have also shown the dominance of Type I methanotrophs compared to Type II methanotrophs in tundra soils and the areas with maximum temperature of 9°C (Vecherskaya et al., 1993) and dominance of Type II methanotrophs in meadow soils incubated at 25°C (Horz et al., 2002).

The *Verrucomicrobial* methanotrophs typically favor hot conditions and include thermotolerant (<45°C optimum, > 45°C growth possible), moderately thermophilic (45-60°C), and extremely thermophilic (> 60-70°C) species (Jäckel et al., 2005). Optimum temperature for CH_4 oxidation potential by thermophilic methanotrophs was 45°C to 55°C in a mature compost pile under aerobic conditions (Jäckel et al., 2005). Moderately thermophilic and acid-tolerant methanotrophs from tropical CH_4 seep topsoil environment grew at a temperature range of 30°C to 60 °C (optimum 51–55 °C) (Islam et al., 2016). However, the existence and activity of thermophilic methanotrophs have been only proved in geothermal habitats by community analyses (Op den Camp et al., 2009), and there is a lack of investigations for the landfill covers and bio-covers.

2.3.2 Moisture content (MC)

The MC in the landfill covers and bio-covers can be affected by several aspects, including seasonal precipitations, surface runoff infiltration, leachate recirculation, methanotrophic activity in the cover, SR, high ambient temperature, vegetation, wind, etc. (Tanthachoon et al., 2008; Scheutz et al., 2009; Majdinasab and Yuan, 2017).

Microorganisms require a certain amount of water to remain active by receiving enough nutrients and their metabolic residuals being transferred through water. If the water content decreases, microorganisms can get water stress due to the desiccation that can decrease or stop their growth and activity. On the other hand, excessive water can replace the air in the soil pore volume and limit the activity of some aerobic microorganisms such as methanotrophs; moreover, the CH_4 transport can be limited due to the slow molecular diffusion in water 10^4 times less than in the air (Cabral et al., 2004).

The degree of saturation (DS) in the soils principally depends on the soil MC and it corresponds to ratio of the volume of water to the void volume in the soil. DS can affect the gas transport in the bio-cover medium and regulate the depths where CH_4 oxidation occurs (Ait-Benichou et al., 2009; Bajwa, 2012). The high MC in the soil resulting in the DS higher than 85% can reduce the CH_4 oxidation in the bio-covers since the gas diffusion happens in the liquid phase diminishing CH_4 and O_2 availability for methanotrophs (Cabral et al., 2004).

To ensure the highest molecular diffusion of the gases in the soil voids and sufficient moisture for methanotrophs to stay optimally active, an optimum level for MC is required. This can differ with the soil type, texture, porosity, and water holding capacity (Zeiss, 2006; Chiemchaisri et al., 2012). In the coarse sandy soil, the optimum MC can be as low as 10% (Park et al., 2005), while in the mature yard waste compost it can be as high as 50-65% (Niemczyk et al., 2021). While in the soils, the CH_4 oxidation significantly reduces at the MC below 5% (Stein and Hettiaratchi, 2001, Scheutz and Kjeldsen, 2004), in the composts, it can happen at the MC below 20% (Niemczyk et al., 2021). In the landfill bio-cover systems, the optimum MC in soils range from 10–20%, while for the composts, it is in the range of 30-45% and can be as high as 50% (Scheutz et al., 2009; Sadasivam and Reddy, 2014).

The porosity and the water holding capacity of the media can also regulate the variations in the CH_4 oxidation due to an increase in the MC. For instance, in silty sand soils, a 10% increase in the MC from 32% to 42% could decrease the CH_4 oxidation rate by 35-50% (Sitaula et al., 1995), and

in the mature yard waste compost, a 15% increase in the MC from 20% to 35% could significantly increase CH_4 oxidation rate by approximately 10 times (Niemczyk et al., 2021).

The shortage of MC due to the environmental circumstances such as SR, ambient temperature, and wind can primarily affect the upper layers of the landfill cover and bio-covers by drying them, and it can be more critical in reducing CH_4 oxidation than the substrate limitations (Scheutz et al., 2003; Scheutz et al., 2009). In arid regions or during low precipitation periods, low MC can significantly restrict the CH_4 oxidation in landfill covers and bio-covers (Jones and Nedwell, 1990) because while in the dry soils, LFG can transport from more soil voids and be accessible for methanotrophs, the dryness can inhibit microbial activity (Majdinasab and Yuan, 2017). Implementing the materials such as composts that have high moisture holding capacity and high porosity can be beneficial in maintaining the MC in the bio-cover medium. In the bio-covers with vegetation, the MC can be exchanged with the atmosphere through evapotranspiration, the water infiltration into the underneath waste can be controlled, and methanotrophic colonies can develop. (Levitt et al., 2005; Roncato and Cabral, 2012); moreover, through shading, vegetation can further modulate the temperature and MC in the bio-cover (Hilger and Humer, 2003). Regular irrigation of the bio-cover especially in the arid or low precipitation areas can be beneficial.

On the other hand, the excessive MC can inhibit the O_2 penetration into the landfill covers and bio-covers (Majdinasab and Yuan, 2017). This can be exacerbated f*or bio-covers* in cold climates because high MC from precipitations before winter can cause ice formation in winter, decreasing the overall porosity of the bio-cover, hence the O_2 penetration along the vertical profile. Therefore, some inhibitory measures are required to be accomplished. For instance, application of coarse materials such as gravel in the upper layers of the bio-cover can conduct the excess water to deeper layers which might not be frozen during the winter due to the higher temperature caused by waste degradation in the landfill. Vegetation in the bio-covers can also increase the depth of the methanotrophic active zone by developing roots and conducting the O_2 to the rhizosphere and deeper layers of the bio-cover where more stable MC and temperature is expected (Tanthachoon et al., 2008; Scheutz et al., 2009).

2.3.3 O_2 availability

Methanotrophs are obligate aerobes; therefore, the O_2 concentration is vital in controlling the CH_4 oxidation rate in landfill bio-covers. Literature on landfill bio-covers and paddy fields has shown

that O_2 concentration above 3% does not significantly affect CH_4 oxidation rate while at lower levels, it could drastically drop CH_4 oxidation rate (Czepiel et al., 1996; Scheutz et al. 2011a; He et al., 2012). Similar results were observed by Gebert et al. (2003) investigating the kinetic parameters of CH_4 oxidation in a biofilter; moreover, the value of V_{max} was attributed to 9% O_2 concentration.

The O_2/CH_4 mixing ratio is considered a significant factor controlling the methanotrophic activity (Hrad et al., 2012). While the stoichiometric ratio for CH_4 oxidation by methanotrophs is 2, it seems that an O_2/CH_4 ratio of 3 is required for an efficient CH_4 oxidation especially by Type I methanotrophs, typically existing at the top layers of the bio-covers and sensitive to the O_2 limitation (Chi et al., 2012). Chiemchaisri et al. (2001) investigated various O_2/CH_4 mixing ratios at a given CH_4 concentration in the soil. The optimum ratio was 6.5 yielding the maximum CH_4 oxidation rate while at ratios below or above the optimum value the CH_4 oxidation rate decreased. In the landfill covers, O_2 penetrates passively into the cover medium through diffusion from the atmosphere, and in case of high barometric pressure, it can penetrate by advection (Gebert and Groengroeft, 2006). The O_2 penetration into the landfill covers can be controlled by several factors such as soil texture and porosity, soil MC, LFG flux, the thickness of the cover, frost formation in the soil, and meteorological conditions (Humer and Lechner, 1999; Scheutz et al., 2009; Majdinasab and Yuan, 2017) that can affect the landfill cover performance. Einola et al. (2008) observed 0% to 22% reductions in the CH_4 oxidation efficiency during the winter on a field-scale landfill lysimeter as the frost formation and snow covering limited O_2 penetration.

The depth of O_2 penetration can regulate the optimum CH_4 oxidation zone in the vertical profile of the landfill covers. While many studies have found the oxidation zone at the upper layers of the cover, including 0-10 cm (Jugnia et al., 2008; Niemczyk et al., 2021), 10-30 cm (Jones and Nedwell, 1993), and 15-40 cm (Visvanathanet al., 1999), it can also happen at the deeper layer of 50-60 cm (Börjesson and Svensson, 1997).

On the other hand, active aeration can help to utilize the full potential of the landfill bio-covers and permit CH_4 consumption at deep layers. Moreover, an air injection system at below-freezing depths of the landfill covers can be a promising approach towards CH_4 oxidation during the winter. However, the temperature of injected air in winter should be considered and regulated as it may cause negative impacts on CH_4 removal due to creating colder environment. There are laboratory scale studies on active aeration of biofilters for CH_4 treatment (Streese and Stegmann, 2003; Haubrichs

and Widmann, 2006; Haththotuwa et al., 2012; Farrokhzadeh et al., 2017; La et al., 2018); however, it has not been studied on the landfill bio-cover systems.

While knowing the effect of each controlling factor on CH_4 oxidation is beneficial to improve the landfill bio-cover system designs, it is not enough to enhance their overall performance. In a bio-cover system, multiple environmental factors can be influential; therefore, to find the optimum level for each factor, investigating their interactions can be of importance. In the following sections, the effect of environmental factors in the field-scale bio-covers is presented. Laboratory-scale studies on the effect of multiple environmental factors on CH_4 oxidation are summarized, followed by studies on the enhancement of CH_4 oxidation considering the influence of environmental factors.

2.4. Field-scale studies considering seasonal variation of CH_4 bio-oxidation in landfills

The seasonal variations in the climatic conditions can alter the environmental factors affecting CH_4 oxidation in the landfill bio-covers. This section emphasizes on the fluctuations in the crucial environmental factors, including temperature, MC, and O_2 availability under various climatic conditions in a landfill CH_4 oxidation system and their effect on the CH_4 oxidation rate. Therefore, the field-scale CH_4 bio-oxidations in the landfills of different climatic areas are presented and the treatment materials in the oxidation system are described. Moreover, the trend of variations in the temperature and MC at various depths of the CH_4 oxidation system are explained along with the corresponding CH_4 oxidation rate. This section provides a comparative description of seasonality in CH_4 oxidation in the areas with different climatic conditions.

Gebert and Groengroeft (2006) worked on a field-scale biofilter embedded in the cover of a landfill, located in Hamburg, Northern Germany with maritime temperate climate, that was mainly used for dredged materials. In their study, an upflow biofilter comprised of two chambers was passively vented by LFG originating from two gas wells. The chambers contained 10 cm of humic topsoil with vegetation underlain by 1.5 cm of sand that were placed on top of 1.5 cm of gravel underlain by 0.67 m of porous clay. To drain water, 10 to 30 cm of gravel was placed at the bottom of the biofilter. The biofilter was constructed in the landfill cover and the LFG supply pipes were placed on upper part of the gravel layer. To determine CH_4 emissions from the biofilter, manual and automatic flux chambers were implemented. Around 62% of the annual cumulative CH_4 load

was removed by the biofilter, and the maximum removal of 1920 $g.m^2.d^{-1}$ was achieved when there was 100% CH_4 removal. The CH_4 removal was restricted by low temperature in winter. It was observed that in the depth of 5cm, the measured temperature was equal to -5.7℃. However, due to LFG supply and heat generation from the landfill, the temperature of 7℃ was observed in the deeper layers of the biofilter that was higher than the ambient temperature during the winter while in summer, the maximum temperature was 39.4℃ at the top layer. Moreover, the high CH_4 flux, caused by variation in the atmospheric pressure, restricted O_2 infiltration from the atmosphere into the biofilter and reduced CH_4 removal. On the other hand, due to the flux reversals caused by atmospheric pressure, the air was mixed with LFG, therefore the biofilter was fed with combination of O_2 and LFG that could increase CH_4 removal starting from deeper layers of the biofilter where O_2 penetration from the atmosphere was limited.

Jugnia et al. (2008) studied a passive CH_4 oxidation barrier (bio-window) located in St-Nicéphore landfill, Quebec, Canada with humid continental climate. The plot consisted of 0.8 m mixture of compost and coarse sand (5:1) as the substrate layer underlain by 0.2 m of coarse gravel as GDL, and it was directly placed on the waste. The sampling was conducted in 13 campaigns from July to October. The ambient temperature was in the range of 2.3-22.7℃ that started to gradually decrease from Fall. From July to August, the temperature inside the cover had a decreasing order from surface to the depth, and in September it stayed constant, while in October, it showed an increasing trend. The maximum temperature was in July with a value of 30℃ that only occurred at the upper 10 cm. At the depth of 82 cm, the highest recorded temperature was 22℃ that was observed in the hottest period of the study, while the lowest temperature of 15℃ at the same depth occurred in October. The MC in the cover was between 51-64% that varied with precipitation. In the vertical profile of the cover, O_2 was mostly observed at the upper 10 cm. From July to September, CH_4 was completely oxidized in the entire depth of the cover. From September, the high MC in the cover restricted O_2 penetration resulting in almost no CH_4 oxidation below 10 cm. However, a very low CH_4 emission of 2.5-30 $g.m^2.d^{-1}$ was observed in the cover indicating that CH_4 was mostly oxidized at the depth of 10 cm.

Philopoulos et al. (2008) studied seasonal variations of CH_4 removal rate, MC, and temperature in three pilot biofilters in Leduc, Alberta, Canada with continental climate. Biofilter 1 was located on the slope of a non-active section of the landfill, and biofilter 2 was located on top of the

intersection of active and non-active section of the landfill. There was a gas well 5 m underneath the biofilter 2 that was surrounded by gravel. Biofilter 3 was located on top of the non-active section of the landfill. With the current placement of the biofilters, it was also possible to compare different locations in terms of the top and the slope of the landfill as well as the availability of a gas well. The biofilters were filled by 1.5 m of yard waste compost underlain by 0.5 m of tire shreds as GDL. Monthly monitoring of gas concentrations in the vertical profile of the biofilters, CH_4 removal rate, MC, and temperature was conducted during eight campaigns from October 2005 to May 2006. The average CH_4 influx to biofilter 1, 2, and 3 was equal to 37.4, 53.5, and 1.2 $g.m^2.d^{-1}$, respectively, while the average CH_4 removal was 76, 68, and 35%, respectively. It was observed that CH_4 was mainly oxidized at the top 0.55 cm of the biofilter according to the O_2 concentration in the vertical profile of the biofilters. There was sufficient temperature and MC in all biofilters to support CH_4 bio-oxidation. The MC in the biofilter 2 was higher than others. The ambient temperature fluctuated between -20℃ to 20℃ during the sampling period. From August to May, the biofilters located on non-active sections of the landfill (1 and 3), showed a decreasing temperature from top to bottom with the highest temperature of 45 ℃ in May, while in the biofilter 2, the temperature increased with depth as at the deepest layer of 160 cm, even in winter there was a high temperature between 30 ℃ to 40 ℃. Higher temperature and MC in biofilter 2 than biofilter 1 and 3 were explained by its high CH_4 influx and CH_4 removal. It was assumed that the high influx in biofilter 2 was attributed to the gas well.

Carbal et al. (2010) observed a maximum CH_4 oxidation rate prior to a sharp decrease in ambient temperature in winter in St-Nicéphore landfill, Quebec, Canada with humid continental climatic condition. They also concluded that (1) absolute removal rates were linearly correlated to CH_4 loading; (2) methanotrophs were present in great numbers near the surface; and (3) the oxidation zone was established between 0.6 and 0.8 m.

A series of bio-cover studies were carried out on Fakse landfill, Zealand, Denmark with temperate climate. Pedersen et al. (2010) reported that CH_4 oxidation rates were lower during winter, when the CH_4 oxidation zone in the bio-cover profile shifted upwards and diffusion of O_2 was limited by high water content. In situations where the supply of CH_4 and O_2 was optimum and temperatures were high, CH_4 oxidation rates were higher than values obtained in the preliminary column test study. On the other hand, at the Klintholm landfill in Denmark, Scheutz et al. (2014)

reported very active CH_4 oxidation throughout the winter with the ambient temperature of 5–10°C for long periods. Their study also showed that the bio-cover system had an average mitigation efficiency of approximately 80%.

Kjeld (2013) conducted research on a bio-cover in Fíflholt landfill in Iceland with boreal climatic conditions. The bio-cover soil contained 15-20 cm of chopped wood, a thin layer of gravel and approximately 1 m of excavated soil from the site that was gravelly sand with 7% organic matter. The highest and lowest reported atmospheric temperatures were 12°C and 0-2°C, respectively, and soil temperature in winter was below 3°C at around 1 m depth. There was a high oxidation efficiency of 64%, and it was concluded that temperature was not a significant controlling factor for CH_4 oxidation because the CH_4 influx was low, between -0.6 $g.m^2.d^{-1}$ to 5.4 $g.m^2.d^{-1}$, due to the hot spots in leaching wells. The concentration of O_2 an N_2 in the vertical profile of the bio-cover showed deep penetration of air to the depth of 0.8 m. Therefore, the high efficiency of the bio-cover was due to the low influx and appropriate aeration.

As discussed above, the field-scale studies encountering seasonal variations in CH_4 bio-oxidation mostly belong to the cold climate and boreal areas. CH_4 oxidation mostly happen during the warm season and with the decrease in the temperature the CH_4 oxidation dramatically decreased. The temperature trend in the vertical profile is highly dependant on the climatic area, the location of bio-cover in the active or non-active zone, heat generated from the active zone, fermentation condition inside the landfill, presence of higher than the ambient temperature throughout the year, and application of a biofilter supplied with gas pipes.

Studies on ice covered lakes and in frozen soil CH_4 cycling in boreal regions (Jammet et al. 2015) indicate buildup of CH_4 below the frozen layer followed by a spike in CH_4 emissions in springtime. If this is also observed under landfill bio-cover systems, it will need to be considered in the development of strategies to modulate CH_4 fluxes in early spring. Thus, it is important to determine how deep the soil is frozen, the depths methanotrophs are able to be active in the bio-cover below the frozen soil layer (i.e., CH_4 oxidation zone), and the extent of the oxidation rate would be. This will help to assess the effectiveness of methanotrophy in the bio-cover for CH_4 oxidation as the filling material cools to below freezing in the fall and as it thaws in the spring. This can help investigators adopt appropriate approaches to increase the recovery rate of methanotrophs and

consequently the efficiency of the bio-cover in CH_4 oxidation throughout the year extending the shoulder season for methanotrophic activity.

While majority of field-scale studies on landfill bio-covers typically consider frost-free seasons for CH_4 removal, it can be beneficial to extend the shoulder season by optimizing the bio-cover design for significant environmental factors and to enhance its performance adopting engineering solutions. The following sections will discuss these measures.

2.5. Laboratory-scale studies on the effect of multiple environmental factors on the CH_4 oxidation rate

According to literature, in the laboratory-scale studies on the effect of multiple environmental factors on CH_4 oxidation rate, the various range was considered for MC, temperature, and CH_4 concentrations. This mainly depended on the climatic conditions of the study area where bio-covers were located, or materials were examined to be implemented in potential bio-covers. This section summarizes some of these studies employing composts and soils as the bio-cover filling materials with details in their particular methodology and approach, special considerations during the experiments, and the studied range for different factors. Therefore, it is also possible to make a comparison among different studies in terms of experimental set-ups and outcomes.

Visvanathan et al. (1999) studied the effect of MC, temperature, and CH_4 concentration on CH_4 oxidation rate in tropical landfill cover soils. Batch incubations and column experiments were applied under the conditions typically occurring in the tropical climate. In the column test, 120 cm long acrylic tubes were packed by two different mixtures of sand, silt, and clay at MC 11%. The gas was supplied to the columns with CH_4:CO_2 of 60:40 in the flow rate of 5 ml.min-1 that was further increased to 9 $ml.min^{-1}$ to investigate its effect on the CH_4 oxidation rate. Also, a control column was supplied by N_2 at the same flow rates. In the batch tests, fresh and old column soils were used at MC of 5%, 10%, 15%, 20%, and 25%, at 5°C, 20°C, 30°C, 36°C, and 45°C. Results showed that CH_4 oxidation at MC of 6% was negligible, while at MC of 15-20%, the maximum CH_4 oxidation rate was obtained. Temperature was found to be an essential factor affecting CH_4 oxidation rate with the optimum level of 30-36°C, while at 45°C, the CH_4 oxidation rate was close to zero. The effect of temperature in the column test was assessed based on the diurnal variation of the temperature with 37-40°C during the day and 30°C during the night. The highest CH_4

oxidation rate was observed during the night, while high temperature during the day was a limiting factor. Temperature also had an implicit impact on the column test as it made the top layers of the columns dry, resulting in low CH_4 oxidation. The increase in the gas flow did not significantly increase CH_4 oxidation, and the vertical profile of the columns revealed that maximum CH_4 oxidation occurred at the depth between 15 cm to 40 cm. However, it was concluded that the CH_4 oxidation rate could be higher if MC remains at the optimum level in the topsoil of the tropical landfill covers.

Park et al. (2005) studied the application of coarse sandy soil to reduce CH_4 emission from landfill covers because of their ability on providing better aeration in CH_4 oxidizing zones. The study examined the effect of environmental factors including MC and temperature on CH_4 oxidation rate and the oxidation kinetic parameters in the soil samples collected from a South Korean landfill. To investigate the effect of MC, it was adjusted to 5%, 10%, 15%, and 20% (w/w) in the soil samples, and batch incubation tests were conducted at a constant temperature of 30℃, and the initial CH_4 concentration was in the range of 5%, 20%, 30%, and 53%. Moreover, the effect of temperature was investigated by adjusting the MC in the soil samples at 10% and incubating them at 4℃, 10℃, 20℃, 30℃, and 40℃, under an initial CH_4 concentration of 40%. The results showed that the maximum CH_4 oxidation rate of 19.2 $nmol.g^{-1}.min^{-1}$ to 22.4 $nmol.g^{-1}.min^{-1}$ occurred at 10% MC while there was no significant difference among the oxidation rates under various CH_4 initial concentrations. The increase in MC above 10%, did not make a significant change in V_{max} values, while K_m increased with the increase in the MC. With an increase in the temperature, the CH_4 oxidation rate increased, and the maximum value was obtained at 30℃, while the drop in CH_4 oxidation at 40℃ was lower than that at 20℃. V_{max} and K_m were maximum at 30℃, following a similar trend of the CH_4 oxidation rate. It was concluded that MC was the most critical environmental factor for CH_4 oxidation in the coarse sandy soil covers.

Mor et al. (2006) examined the suitability of different types of compost to be used in landfill bio-covers concerning the CH_4 oxidation rate under various incubation times, MC, and temperatures. They used two different kitchen and garden waste compost mixtures and three garden waste composts collected from compost piles in Belgium. Batch incubation tests were implemented to precisely control the MC in the composts. The initial CH_4 concentration in the batch test bottles was 5%. Composts were not pre-incubated to investigate the effect of incubation time, so they

were incubated for 60 days at 22℃, and the most active composts were determined to be two of garden waste composts (G1 and G3) from this step. To investigate the influence of MC and temperature, the most active composts were first pre-incubated at 22℃ by adding 10% CH_4 periodically. MC in these composts was adjusted to the values in the range of 29% to 110% (w/w), while the incubation temperatures were 7℃, 15℃, 22℃, 30℃, and 40℃. The results showed a different response to MC and temperature by G1 and G3, having 31% and 52% organic matter, respectively. For instance, G1 showed a steady behaviour at 45% MC, the least CH_4 oxidation rate at 29%, and the optimum MC range of 45-85%. On the other hand, with G3, the CH_4 oxidation rate increased with temperature revealing the optimum value of >110%, while there was no significant difference between CH_4 oxidation rates at MC of 85% and 110%. It was observed that the optimum MC in both composts was regulated by the organic matter content. Regarding the temperature effect, G1 showed an increase in CH_4 oxidation rate with an increase in temperature followed by a decrease at 40℃ while there was no significant difference in the oxidation rates at 15-30℃. On the other hand, G3 showed a slow and erratic response to the temperature variations with the highest CH_4 oxidation rates at 40℃. The study concluded that the influence of MC and temperature was time dependent.

Einola et al. (2007) did a similar study investigating the effect of MC and temperature on a boreal landfill cover soil. The studied cover soil was a municipal sewage sludge and chemical sludge compost with volume mixing ratio of (1:2). The samples were collected from 10-30 cm of the soil cover of Tarastenjärvi landfill located in Tampere, Finland in December when the ambient temperature and soil temperature were 3℃ and 5℃, respectively. Samples were mixed and used in the batch incubation tests. The range of studied temperature was 1℃, 6℃, 12℃, and 19℃, while MC values included 7%, 14%, 21%, and 28% under the initial CH_4 concentration of 8% to 9%. Results showed that CH_4 oxidation occurred at all temperature range. It was observed that the CH_4 oxidation at various MCs depends on the temperature variations. When MC increased, the response of CH_4 oxidation to temperature decreased. With an increase in MC, CH_4 oxidation increased at 1℃ to 6℃, while at 12℃ to 19℃, there was a curvilinear response. Moreover, the optimum MC at the temperature range of 1℃ to 6℃ was 27% that was higher than optimum MC of 21% at 12℃ to 19℃. The study concluded that even at low temperature of boreal climates, CH_4 oxidizing bacteria were able to consume CH_4 and grow.

The effect of MC and temperature was also studied by Zhang et al. (2015) on a landfill bio-cover material including aged refuse and sewage sludge collected from a landfill and domestic water treatment plant in China, respectively. Samples were incubated in batch tests under 1% CH_4 concentration. Results showed that the increase in the MC from 18% to 30% and in the temperature from 4℃ to 35℃, significantly increased the CH_4 oxidation rate. The CH_4 oxidation rate showed a parabolic response to both MC and temperature, with the optimum levels of 30% and 35℃, respectively.

Bajar et al. (2013a, 2013b, 2017) conducted several studies implementing statistical modeling to optimize the environmental factors influencing bio-oxidation of CH_4 in open dumpsite soils in Hisar, Haryana, India, considering the interaction among the factors.

Bajar et al. (2013a) studied the interactive effect of MC, temperature, incubation time, and initial CH_4 concentration on CH_4 oxidation rate and obtained their optimum values causing maximum CH_4 oxidation rate. They collected soil samples from the depth of 0 to 30 cm of the dumpsite soil. Samples were air-dried in the laboratory and mixed to provide a homogeneous sample for the batch incubation tests. The samples were pre-incubated for three months under 30% CH_4 in the headspace. The studied environmental factors were optimized using a statistical model developed based on Box-Behnken Design (BBD) of Response Surface Methodology (RSM). The low, middle, and high levels were considered for MC (5%, 35%, and 70%), temperature (15℃, 26℃, and 37℃), incubation time (5, 10, and 15 days), and CH_4 initial concentration (10%, 20%, and 30%), and different combination of the levels was applied based on the BBD. Results showed that the effect of temperature on CH_4 oxidation rate depended on MC. There was a low CH_4 oxidation rate at 5% MC, while at MC of 35% to 45%, the CH_4 oxidation rate was high even at low temperatures. The CH_4 oxidation rate showed a parabolic response to the temperature with the optimum level of 27℃ to 30℃. The optimum incubation time and the initial CH_4 concentration were six days and 10-15%, respectively. Moreover, ANOVA revealed that MC and initial CH_4 concentration had a significant effect on CH_4 oxidation rate so did the interactive effect of initial CH_4 concentration and temperature, while other factors and the interaction among them were insignificant.

Bajar et al. (2013b) studied the effect of CH_4, O_2, and CO_2 concentrations on CH_4 oxidation rate by employing various combinations of the gas concentrations to achieve the optimum levels. In

the study, the soil samples were collected from different locations of the open dumpsite. Samples were mixed and pre-incubated for four weeks under an initial CH_4 concentration of 20-30%. Then, batch incubation tests were conducted at 30°C with soil MC adjusted to 30% considering optimal levels in literature. BBD statistical design of RSM was applied for experimental design with a mixture of gas concentrations including 5%, 15%, and 25% of CH_4, 0%, 15%, and 30% of O_2, and 0%, 5%, and 10% of CO_2 after flushing the headspace with Argon. The results confirmed that O_2 was a limiting factor for CH_4 oxidation as in the absence of O_2, there was no CH_4 oxidation, while 5% O_2 was sufficient to sustain CH_4 oxidation by methanotrophs. There was a rapid increase in the CH_4 oxidation rate with an increase in the CH_4 concentration from 5% to 15%, with O_2 at a sufficient level. The simultaneous increase in O_2 and CH_4 concentrations increase CH_4 oxidation rate. The optimum level of CH_4 concentration was found to be 15%. Moreover, a CO_2 concentration of up to 2% was found to support the CH_4 oxidation rate, while CO_2 levels higher than 7.5%, caused a decline in CH_4 oxidation. According to ANOVA analysis, O_2 and CH_4 concentrations significantly effected CH_4 oxidation rate, while CO_2 concentration was not a significant factor.

Bajar et al. (2017) conducted a similar study with RSM on the interactive effect of CH_4 and O_2 concentrations, temperature, and incubation time on the CH_4 oxidation rate in the same dumpsite soil. The mixed soil sample at MC of 30% was pre-incubated for three months under 30% CH_4 in the headspace. The studied range for the factors included 20%, 30%, and 40% of CH_4 concentration, 10%, 15%, and 20% of O_2 concentration, 2, 5, and 8 days of incubation time, and the temperature of 20°C, 30°C, and 40°C. Results showed that the effect of CH_4 concentration on the oxidation rate was more significant than that of O_2 concentration. At low O_2 concentrations, the highest CH_4 oxidation rate was achieved at the shortest incubation time, while at high O_2 concentrations, longer incubation times were required. Moreover, at high CH_4 concentrations, the highest CH_4 oxidation rate was obtained under the shortest incubation time. Like the previous study, the increase in CH_4 and O_2 concentration increased the CH_4 oxidation rate. The interaction of temperature and O_2 concentration showed that the highest CH_4 oxidation rate occurred at the highest levels of these factors. Under constant MC of 30%, the maximum CH_4 oxidation rate of 69.58 $\mu g.g^{-1}.h^{-1}$ was obtained at optimum values of 40% CH_4, 15% O_2, with two h of incubation at 30°C. ANOVA showed that considering the studied range of the factors, CH_4 concentration and

the interaction between O_2 concentration and incubation time had significant effects on the CH_4 oxidation rate.

Frasi et al. (2020) investigated the effect of MC on CH_4 oxidation efficiency in the biofiltration systems exposed to diluted CH_4 with high O_2 concentrations. Three column experiments were conducted with filter material consisting of compost:sand 5:1 at MCs of 20%, 30%, and 40%, respectively. The CH_4 load also varied from <100, 100-200, 200-300, and >300 $gCH_4.m^{-2}.d^{-1}$. Results showed that the MC of 20% was insufficient for CH_4 oxidation when CH_4 load was below 100 $g.m^{-2}.d^{-1}$, and the MC of 40% favored the heterotrophic activity at the CH_4 load of 100 $g.m^{-2}.d^{-1}$ to 300 $g.m^{-2}.d^{-1}$. However, CH_4 oxidation was inhibited at CH_4 loads higher than 300 $g.m^{-2}.d^{-1}$ while MC was not a controlling factor. The optimum MC was found to be 30% resulting in the highest CH_4 oxidation rate at the CH_4 loads below 200 $g.m^{-2}.d^{-1}$ with the removal efficiency of 80%. The maximum CH_4 oxidation rate in the set-ups was in the range of 49.6-300 $g.m^{-2}.d^{-1}$.

According to the mentioned studies, the following conclusions can be acquired: (1) the MC range for efficient CH_4 oxidation in soils and composts are different, and optimum MC in composts (30-110%) is higher than that in soils (10-20%), while the optimum temperature is almost similar for both of them (30-35℃) (2) the response of different materials, collected from the same study area, to temperature can be different, (3) that the samples collected from tropical climatic conditions does not always show CH_4 oxidation at thermophilic temperatures (40℃ and 45℃). Table 2-2 represents the summary of all mentioned studies regarding the experimental conditions, the optimum values for the environmental factors, and maximum CH_4 oxidation rates.

Table 2-2. Summary of experimental conditions and optimum values for MC, temperature, and CH_4 concentration in the studies on the effect of multiple environmental factors on the CH_4 oxidation rate

Region	Climatic zone	Bio-cover material	Experimental procedure	Optimum			Maximum CH_4 oxidation rate	References
				MC (%)	T (℃)	CH_4 Conc. (%)		
Tropical landfill	Tropical	Sand, silt, and clay	Column and batch tests	15-20	30-36			Visvanathan et al. (1999)
South Korean landfill	Temperate	Coarse sandy soil	Batch incubations	10	30	5-53	19.2-22.4 $nmol.g^{-1}.min^{-1}$	Park et al. (2005)

Compost piles in Belgium	Temperate maritime	Garden waste compost	Batch incubations Samples pre-incubated	45-110	15-30	10 (Incubation)	1.51-2.35 $\mu mol.kg_{dw}^{-1}.s^{-1}$	Mor et al. (2006)
Landfill in Tampere, Finland	Boreal	Municipal sewage sludge+chemical sludge compost (1:2)	Batch incubations	19	21-27	8-9 (Incubation)	2.5 $\mu mol.g_{dw}^{-1}.h^{-1}$	Einola et al. (2007)
Dumpsite in Haryana, India	Tropical	Dumpsite soil	Batch incubations Samples pre-incubated	35-45	27-30	10-15	100% (Efficiency)	Bajar et al. (2013a)
Dumpsite in Haryana, India	Tropical	Dumpsite soil	Batch incubations Samples pre-incubated	30 (Incubation)	30 (Incubation)	15 (CH_4) 5 (O_2) 2 (CO_2)	-	Bajar et al. (2013b)
Landfill and water treatment plant in China		Aged refuse and sewage sludge	Batch incubations	30	35	1 (Incubation)	7.68 $\mu mol.g_{dw}^{-1}.h^{-1}$ (Average)	Zhang et al. (2015)
Dumpsite in Haryana, India	Tropical	Dumpsite soil	Batch incubations Samples pre-incubated	30 (Incubation)	30	40 (CH_4) 15 (O_2)	69.58 ($\mu g.g^{-1}.h^{-1}$)	Bajar et al. (2017)
Landfill biofilter in Siena, Italy	Mediterranean	Compost and sand (5:1)	Column test	30	-	100-300 $gCH_4.m^{-2}.d^{-1}$ (CH_4 load)	49.6-300 ($g.m^{-2}.d^{-1}$)	Frasi et al. (2020)
Landfill in Winnipeg, Canada	Humid continental	Yard waste and leaf compost and Biosolids compost (1:4)	Batch incubations	47.42	32.72	23.81	2.20 ($mgCH_4.g_{dw}^{-1}.d^{-1}$)	Chapter 4

2.6. Laboratory-scale studies on CH_4 oxidation enhancement in biological treatment methods

The enhancement of CH_4 oxidation has been investigated through different approaches, including the addition of more nutrients, increasing aeration, mixing media, vegetation, etc. The following section summarizes the studies in this area that differ based on the purpose of CH_4 enhancement, the application of the biological treatment, and the availability of supplies.

Pariatamby et al. (2015) investigated the potential of CH_4 oxidation enhancement by addition of various types of organic waste to the compost at different mixing ratios. They used the mixture of grass clippings compost and cow manure compost (3:1) and added sewage sludge, saw dust, spent yeast, empty fruit bunch (EFB), spent tea leaves and black soil at waste:compost mixing ratios of 1:4, 2:3, 3:2, and 4:1 through batch incubation tests. Results showed that while spent yeast, spent tea, and sewage sludge produced CH_4 instead of oxidizing it, combination of organic waste and compost was effective in increasing CH_4 oxidation. The shortest time to complete oxidation of CH_4 was obtained by the sawdust and compost mixture, while the mixture of spent yeat:compost 1:4, could completely oxidize CH_4 in 16 days. The mixture of sewage sludge:compost 1:4 took one day to fully oxidize CH_4. Moreover, while sawdust completely oxidized CH_4 in four days, its mixture with compost at the ratios of 1:4 and 2:3 only required two days for 100% CH_4 oxidation. The performance of different waste:compost mixtures in oxidizing CH_4 was in the decreasing order of 1:4 sewage sludge:compost > 1:4 and 2:3 sawdust:compost > EFB:compost > 1:4 spent yeast:compost that were higher than both single waste and single compost.

Farrokhzadeh et al. (2017) conducted column experiments with active aeration for a biofilter system. To enhance the CH_4 oxidation in the biofilter, the O_2 accessibility for methanotrophs was increased by maintaining a proper O_2 to CH_4 ratio according to stoichiometry. Therefore, multiple level air injections were applied in the biofilter design packed by the leaf compost. In column 1, the aeration was conducted at one level located at the bottom, in column 2, two aeration levels were applied, one at the bottom and the other in the 1/3 of the column height, and in column 3, three aeration levels were located at the bottom, 1/3, and 2/3 of the column height. The columns were supplied by CH_4 flow rate in the range of 6-18 $ml.min^{-1}$, increasing in five stages, to investigate the effect of the rise in the CH_4 flow rate. In each stage, the aeration flow rate was10 times higher than the corresponding CH_4 flow rate to secure the stoichiometry requirements. Results showed that over the range of flow rates during the five stages, the performance of the biofilter under two-level active aeration was more consistent, providing the maximum CH_4 oxidation efficiency of 85% during the entire experimental period of 95 days. Moreover, batch incubation tests were conducted to obtain the CH_4 oxidation kinetic parameters in the samples collected from the top, middle, and bottom of the columns at the end of the experiment. The values of V_{max} were the highest at all levels of the column with two aeration levels with the maximum value of 65.3 $\mu g.g^{-1}.h^{-1}$ at the top. However, there was no significant difference among the values

of V_{max} at the bottom and middle levels of the columns with one and three aeration levels. The V_{max} values and their trends adequately conformed to the CH_4 oxidation rates in the columns.

Huang et al. (2020) conducted applied sandy loam landfill top cover soil in three column experiments. In column 1, the entire substrate layer was packed by cover soil (75 cm). In column 2 and 3, the top 10 to 30 cm was amended by 15% (v/v) biochar, while column 3 was also equipped by an active aeration port at the depth of 40 cm with flow rate of 5 $l.d^{-1}$. The columns were supplied with the LFG composed of CH_4:CO_2 60:40 at the flow rate of 10 $ml.min^{-1}$. Moreover, 300 ml of enriched methanotrophic solution was added to the packing materials. Results showed that CH_4 oxidation in the three columns mostly happened at the top 35 cm while biochar amendment and aeration further increase CH_4 oxidation at this depth upwards. The average CH_4 removal efficiency for Column 1, 2, and 3 were 78.6%, 85.2%, and 90.6%, respectively. Biochar amendment improved the properties of the cover soil and caused better aeration in the top 35 cm leading to stimulation of methanotrophs while active aeration provided more O_2 for methanotrophs and further increased CH_4 oxidation. In all three columns, a decline in the CH_4 removal was observed that was mainly due to the nutrient deficiency caused by methanotrophic activity; however, in column 3, more nutrient retention was observed that was also confirmed by the lowest CH_4 removal decline in this column.

Niemczyk et al. (2021) investigated the applicability of two different composts including yard waste and leaf compost (YWLC) and biosolids compost (BSC) for CH4 oxidation in the landfill bio-covers. Different MC of 5%, 20%, 35%, 50%, 65%, and 80% were established in the composts. The study revealed that further maturation of YWLC beyond the compost maturation standards was required to obtain maximum CH_4 oxidation and the optimum MC was 50-65%. However, there was no CH_4 oxidation observed in the BSC, and even the addition of nutrients and inoculum, derived from YWLC, could not stimulate methanotrophic activity in BSC. Therefore, the potential for the enhancement of CH_4 oxidation was investigated through mixing composts at different ratios of YWLC:BSC 1:1, 1:2, 2:1, 1:4, and 4:1. Therefore, short-term and long-term batch incubation tests were conducted. It was observed that mixing two composts more effective on CH_4 oxidation than using the single compost. The results showed that mixing ratios of 1:1 and 1:4 could reach to a comparable level of maximum CH_4 oxidation rate within the range of 360-380 $\mu mol.g^{-1}.d^{-1}$ in long-term. This study was followed by a series of column experiments to optimize the design of

the bio-cover compost to be applicable in the bio-cover (Niemczyk, 2018). Therefore, columns were packed by 1:1 and 1:4 compost mixtures and supplied by CH_4:CO_2 50:50 at the flow rate of 15 ml.min^{-1}. It was observed that the optimum MC obtained in the batch tests from the previous study restricted O_2 penetration into the column and reduced the CH_4 oxidation. The maximum CH_4 oxidation efficiency was obtained by 1:4 compost mixture due to the higher porosity of BSC than YWLC, letting better O_2 penetration into the column, and the practical optimum MC was 40%.

Literature shows that there is expected benefits of long root grass and vegetation on the landfill cover with regards to methanotroph attachment. Hilger et al. (2000) conducted a column test with grass vegetation to simulate the landfill soil cover and observed that the methanotrophic population increased in the rhizosphere. While the vegetation did not significantly increase the CH_4 oxidation for the long term, it could cause a peak in CH_4 oxidation. Stralis-Pavese et al. (2004) applied lysimeters to compare CH_4 oxidation using four different plants and bare tropical soil. The planted lysimeters showed more enhanced CH_4 oxidation than the bare soil one, revealing a relationship between microbial community structure and CH_4 oxidation capacity. Different plants also had a different effect on CH_4 oxidation while having a similar community structure.

It seems that in the landfill covers with vegetation, the roots can excrete exudates in the soil cover and create a beneficial support matrix for methanotrophs making their populations in the rhizosphere more than in soil alone. However, while plant roots can conduct O_2 to the anaerobic zone of the landfill covers, they can compete with methanotrophs for O_2, nutrients and water. Moreover, the roots can make preferred escaping channels for LFG emissions (Hilger and Humer, 2003; Tanthachoon et al., 2008).

One way to enhance the microbial oxidation of CH_4 in landfill covers, when resident methanotrophic populations are low, can be to inoculate the bio-cover materials with a methanotrophic inoculum, enriched from sites expected to contain them (e.g., composts produced in the landfill site itself). Recently, only laboratory-scale studies have been performed to investigate the effect of methanotroph inoculation of the bio-covers on CH_4 oxidation enhancement (Nair et al. 2015; Cáceres et al. 2016; Hu & Long 2016).

The studies mentioned above have provided proof for the practical approaches to enhance CH_4 oxidation in the bio-covers in laboratory-scale. Therefore, they can be considered to be employed to modulate the effect of environmental factors on *in situ* bio-cover performance; for instance,

compost addition can affect the water holding capacity and methanotrophic population, active aeration can overcome O_2 deficiencies, and vegetation can regulate MC, temperature, and O_2 penetration in the bio-cover.

2.7. Conclusion and recommendations

The purpose of this study is to review the bio-cover implementation in landfills by focusing on the challenges regarding its performance under variable climatic conditions and suggesting potential improvement approaches.

Most of the field-scale studies on microbial CH_4 oxidation in landfills are conducted in a cold climate and boreal areas focusing on frost-free seasons. However, with a decrease in the ambient temperature, the CH_4 oxidation was restricted. The temperature trend in the vertical profile of the bio-cover is highly dependant on the bio-cover location, whether it is on the active or non-active zone, and whether the heat generation from the active zone, due to fermentation inside the landfill, is higher than the ambient temperature throughout the year. Moreover, if biofilters are implemented, due to being supplied by gas pipes, the temperature trend is usually increasing, and even in winter, the temperature in the deep layers is higher than the ambient temperature.

Meteorological factors such as barometric pressure and wind-induced pressure can regulate the gas transport in the bio-cover, and they can even make flux reversals leading to air mixture with LFG while flowing through the bio-covers.

While bio-covers can beneficially exploit the solid wastes in an extensive surface of the landfills, biofilters and bio-windows with designed surface areas are easier to control, monitor, implement enhancements, and make modifications. Moreover, due to covering small areas of the landfills and no need for supply gas pipes, bio-windows are more economically feasible compared to bio-covers and biofilters.

Temperature, MC, and CH_4 concentration were dominant variables considered in the laboratory studies investigating the effect of multiple environmental factors on biological CH_4 oxidation. The optimum MC in composts is higher than in soils, while the optimum temperature is almost similar for both.

To enhance the CH_4 oxidation efficiency, different approaches have been studied in the laboratory-scale, including adding more nutrients, increasing aeration, benefiting from mixing media, vegetation, etc. However, such studies are missing for the *in situ* landfill bio-covers. Use of

amendments can be beneficial to enhance *in situ* performance of the methanotrophs in the bio-covers. Therefore, the following measures are recommended:

- Enhancing aeration through aeration pipes in the soil, especially bellow frost line to exploit the whole capacity of the bio-cover throughout the year.
- Increasing the porosity of the filling materials by adding coarse materials such as gravel.
- Re-inoculating with appropriate methanotrophs in response to shifts in soil temperature.
- Modulating the temperature of the bio-cover in early spring and late fall using mechanical means (e.g., thermosiphons) to increase the shoulder season for methanotrophic activity.
- Irrigating the bio-cover during dry season in the areas with fluctuations in the MC level.

Understanding the dynamics of the methanotrophic communities within the bio-cover, relative to *in-situ* temperature, MC, and O_2 penetration, using microbiological methods (i.e., batch/column tests) to test means of enhancing microbial activity is also recommended.

Monitoring the depth of frost, especially in continental climate landfills, is recommended to determine the methanotrophic active zone below the frozen layer in the bio-cover. Therefore, appropriate approaches can be employed to extend the shoulder season for CH_4 oxidation and accelerate the methanotrophic recovery in spring.

Investigating the effect of remaining long-term snow cover on the bio-cover performance is recommended by doing laboratory and field studies in terms of O_2 diffusivity, insulation effects, and trapping CH_4 flux.

Further research is required to assess the *in situ* landfill bio-covers throughout the year and not just frost-free seasons to investigate the effect of environmental factors influenced by seasonal variations on the bio-cover performance not only in the cold climate and boreal landfills but in regions with other climatic conditions such as tropical areas with heavy precipitations and high ambient temperature.

2.8. References

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Chapter 3: Methane oxidation in a landfill bio-window under wide seasonally fluctuating climatic conditions[1]

Abstract

In the current study, a pilot bio-window was constructed in a closed cell of a Canadian Landfill in a Continental Climate, undergoing high seasonal fluctuations in the temperature from -30℃ in winter to 35℃ in summer. The bio-window was filled with biosolids compost amended with yard waste and leaf compost with the ratio of 4:1 as the substrate layer. Two years of monitoring of methane (CH_4) oxidation in the bio-window led to remarkable expected observations including a thick, solid winter frost cover affecting gas exchange in winter, and temperatures above 45℃ in the bio-window in late summer. A high influx compared to the reported values was observed into the bio-window with an average value of 1137 $g.m^{-2}.d^{-1}$, consisting of 64% of CH_4 and 36% of carbon dioxide (CO_2) in the landfill gas. The variations in the temperature and moisture content (MC) of the compost layer in addition to the influx fluctuations affected CH_4 oxidation efficiency; however, a high average CH_4 oxidation rate of 237 $g.m^{-2}.d^{-1}$ was obtained, with CH_4 being mostly oxidized at top layers. The laboratory batch experiments verified that thermophilic methane-oxidizing bacteria (MOB) were present throughout the study period and oxidized CH_4 with a higher rate than mesophilic MOB. The methanotrophic potential of the compost mixture showed an average value of 282 $\mu mol.g^{-1}.d^{-1}$ in the entire period of the study which is in the range of the highest reported maximum CH_4 oxidation rates. The adopted compost mixture was suitable for CH_4 oxidation if the MC was above 30%. The significance of MC variations on CH_4 oxidation rate depended on the temperature range within the bio-window. At temperatures below 2℃, between 29℃ to 31℃, and above 45℃, MC was not a controlling factor for mesophilic CH_4 oxidation.

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Keywords: Methanotrophic activity, Thermophilic condition, Frost formation, Biosolids compost, Methane removal, Batch test

3.1. Introduction

The anaerobic decomposition of organic wastes within a landfill produces landfill gas (LFG) containing among others methane (CH_4), and carbon dioxide (CO_2) (Börjesson et al. 2001; Jugnia et al. 2008; Scheutz et al. 2009b). CH_4 has 28-34 times higher global warming potential than CO_2 over 100 years (IPCC 2013). Globally, landfilling and other waste management activities account for 22.7% (1.7-2.3 $GtCO_2$-eq yr^{-1}) of total anthropogenic CH_4 emissions (IPCC 2013).

Once the landfill is filled, it is usually capped by an impervious conventional cover to minimize leachate generation and control gas migration emissions. However, the cover only captures a portion of the gas generated, and the remainder vents through it as fugitive emissions (Jugnia et al. 2008; Sadasivam and Reddy 2014). Bio-covers are economical or complementary technologies that can be designed to optimize the growth of Methane-Oxidizing Bacteria (MOB) known as methanotrophs and reduce fugitive CH_4 emissions as well as their contribution to global warming (Scheutz et al. 2009a, b; Chiemchaisri et al. 2012; Sadasivam and Reddy 2014; Majdinasab and Yuan 2017). MOB have the unique ability to oxidize CH_4 as their only source of carbon and energy with the only by-products of water and CO_2 (Hanson & Hanson 1996).

A landfill bio-cover typically consists of a gas distribution layer (GDL) that is highly permeable to homogenize LFG fluxes and an overlying substrate or oxidation layer, where oxygen (O_2) diffuses from the atmosphere to be consumed by MOB. The substrate layer is usually composed of suitable materials and amendments that support growth and activity of MOB (Scheutz et al. 2009a; Sadasivam and Reddy 2014). There are on-site sources within landfills, such as compost and organic waste, that could be used as an MOB-friendly substrate layer in the bio-cover, instead of just being disposed of within the landfill. These could reduce CH_4 emissions while reducing costs (Chiemchaisri et al. 2012; Pedersen et al. 2011; Roncato and Cabral 2012).

Bio-covers are typically intended to cover large areas of a landfill, while there is another method called bio-cover-windows (bio-windows) that include small areas excavated inside the existing landfill cover and are more cost-effective than bio-covers due to containing less filling materials (Sadasivam and Reddy 2014; Majdinasab and Yuan 2017).

There have been several studies on the assessment of the efficacy of bio-cover systems in field-scale applications (Humer and Lechner 2001a, 2001b; Einola et al. 2009; Roncato and Cabral 2012); however, limited number of studies are available in wide fluctuating climate conditions.

The effects of seasonal variations on CH_4 oxidation rate in bio-covers have been assessed in areas such as Iceland, Canada, the USA, Germany, Sweden, Italy (Börjesson et al. 2004; Wilshusen et al., 2004; Gebert and Grongroft 2006; Stern et al. 2007; Chanton et al., 2011; Kjeld, 2013; Pecorini and Iannelli 2020). However, the lowest ambient temperature tested in field scale studies was 0°C, with a focus on the ice-free seasons.

Beyond extended periods in spring and fall that the soil temperature is below 10°C, most areas in Canada and Northern USA have Humid Continental Climate. In these areas, in winter, the temperature is between -10°C to -40°C, the soil can freeze at depths greater than 2 m, and snow can be the foremost precipitation. On the other hand, such areas have moderately warm to warm summers with a temperature range of 20°C to 35°C (Yeşiller et al., 2005; Zeiss, 2006). Therefore, deep frost penetration over winter and warm temperature in summer, combined with potential landfill internal rising temperature due to fermentation that can elevate even more the bio-cover temperature (>60°C to 85°C) (Dach and Jager 1995) cause significant seasonal temperature fluctuations within bio-covers. Such temperature variations are expected to affect the activity of MOB and bio-cover performance by through a transition from mesophilic to thermophilic MOB. This issue has never been studied in detail, especially in areas with high CH_4 loads such as landfills.

Although there are some studies on the performance of bio-cover in Canada's Humid Continental Climate, they have focused on the frost-free seasons. Zeiss (2006) studied CH_4 removal by a biofilter in a landfill in Alberta from mid-summer to early winter. However, they used a passive heat exchange from inside the landfill to the biofilter to keep the temperature inside the biofilter above freezing and continue CH_4 removal in winter. In a study on CH_4 oxidation from a landfill bio-cover in Quebec, the investigations were mostly performed during the summer and early autumn when high CH_4 removal was observed due to higher temperatures and low CH_4 load (Jugnia et al. 2008). In another study with seasonal investigations in Alberta (Philopoulos et al. 2008), the CH_4 influx was so low that O_2 could penetrate deep into the substrate layer, and CH_4 could be oxidized. Cabral et al. (2010) also did a study on a landfill biofilter in Quebec during its

operation in summer and fall with increasing CH_4 loads. They observed that there was no correlation between CH_4 oxidation rate and the bio-cover temperature.

Composts have been widely investigated as appropriate materials that can strongly sustain the growth and activity of MOB (Wilshusen et al. 2004; Perdikea et al. 2008; Pedersen et al. 2011; Pariatamby et al. 2015; Pecorini and Iannelli 2020) due to retaining a suitable combination of porosity, moisture retention, temperature regulation, pH value, and nutrient sources (Hilger and Humer 2003; Huber-Humer, 2004). The highest rates of CH_4 consumption were typically observed in mature composts that were homogeneous and coarsely structured (Scheutz et al., 2009a; Niemczyk et al., 2021). Among different compost materials used in bio-cover systems, limited laboratory studies (Humer and Lechner 1999; Kettunen et al. 2006; Einola et al. 2007; Spokas and Reicosky 2009; Mancebo et al. 2012) and very few field studies (Humer and Lechner 2001a, 2001b) have been carried out on Biosolids Compost (BSC).

The overall objective of the proposed research was to construct a bio-window in a closed landfill cell using BSC and Yard Waste and Leaf Compost (YWLC) as a substrate layer. The proposed materials for the substrate layer have already proved to form the most effective mixture with optimum mixing ratio of 4:1 BSC:YWLC as a growth matrix for MOB with the highest CH_4 oxidation rate. Previously, batch- and column-scale tests were conducted in the Environmental Engineering Laboratory and Microbiology Laboratory in the University of Manitoba to provide the basis for designing the landfill bio-window. The YWLC compost was further matured beyond the compost maturation standards. (Niemczyk, 2018; Niemczyk et al., 2021). To our knowledge, the application of this mixture has never been reported in the landfill bio-cover studies.

Two years of monitoring and sampling was conducted in the bio-window (1) to investigate the CH_4 oxidation efficiency by measuring net CH_4 emission and performing a mass balance, (2) to study vertical concentration profiles of the main gas components (i.e. O_2, CO_2, and CH_4) in the bio-window to determine the location of the methanotrophic active zone, and (3) to study and identify the initial rate of MOB activity in the bio-window. The novelties of this study are field-scale application of BSC amended by YWLC that has previously proved to enhance the CH_4 oxidation efficiency in laboratory, to assess high seasonal fluctuations (i.e., soil temperature, moisture, frost line) throughout the year on the bio-window performance and *in situ* population and activity of MOB at field scale despite previous research considering frost-free seasons, and to conduct additional tests with the same compost mixture under lab controlled conditions to

investigate the presence of thermophilic MOB that has not been reported in the landfill environments.

3.2. Materials and methods

3.2.1 Study area and the compost

The City of Winnipeg, in Manitoba, Canada, is representative of a Humid Continental climate (Dfb) according to the Köppen-Geiger climate classification system (Geiger, 1954; Geiger, 1961). It contains a total of 35 closed landfills (City of Winnipeg, 2013). The landfill at Brady Road Resource Management Facility (BRRMF) (100 ha of the existing landfill within 790 ha of the total land available with 5-6 m depth; operating since 1973) (Stantec 2011) is Manitoba's second-largest point source of GHGs (391,587 tCO_2-eq; 2017 value) (Environment and Climate Change Canada, 2020). In 2013, an LFG collection system was commissioned within a closed, northeast portion of the landfill (City of Winnipeg, 2014), and a final clay cap was placed over the waste mass. However, a significant area of the BRRMF landfill currently has no controls for fugitive GHGs.

The BSC and YWLC have been produced on a large-scale in the composting facility of the BRRMF landfill.

3.2.2 Description of the bio-window setup

In October 2016, a bio-window, measuring 3.5 m × 2.5 m, was excavated to the depth of the waste mass (1.3 m) within the existing final clay cover in the BRRMF landfill. The bio-window was filled with 0.75 m of 1:4 mixture of mature YLWC and BSC as substrate layer underlain by 0.55 m of limestone gravel as GDL (Figure 3-1). The chosen surface area and thicknesses of each layer comply with recommended values from literature for compost-based bio-windows (Table 3-1). To avoid lateral movement of moisture due to thermal gradients in the bio-window, 0.15 m thick polystyrene panels were used.

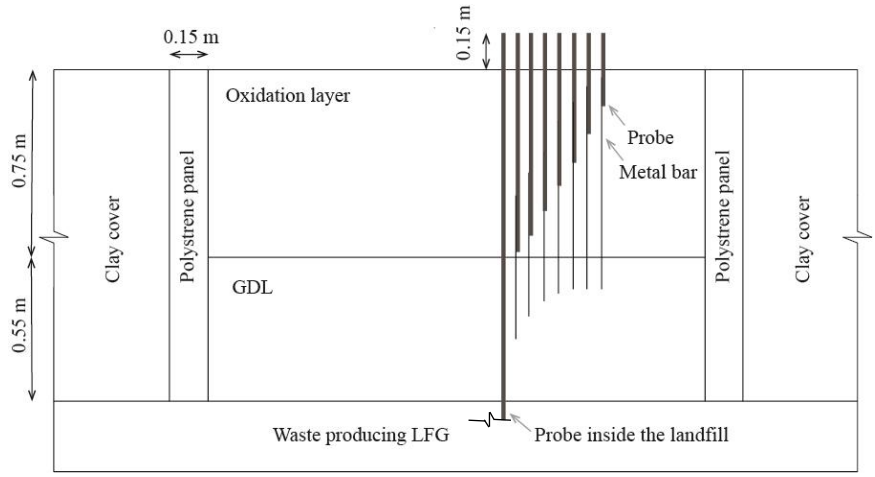

Figure 3-1. The cross section of the experimental bio-window and configuration of the probes at BRRMF

Table 3-1. CH_4 influx, oxidation rate, and oxidation efficiency in landfill bio-window/biofilters around the world

Landfill location	Size (m^2)	Material and depth of oxidation layer	Material and depth of GDL	CH_4 influx ($gm^{-2}d^{-1}$)	CH_4 oxidation rate ($gm^{-2}d^{-1}$)	CH_4 oxidation efficiency (%)	Reference
Hamburg, Germany	6 9	Humic topsoil+ crushed clay (0.77 m)	Gravel (0.3 m)	1114	895	62	Gebert and Groengroeft, (2006)
Florida, USA	7.6 × 7.6 7.6 × 7.6 7.6 × 7.6	Mulsh layer (0.5 m)	Glass (0.1 m)	-6.07 to 330	2	41-64	Stern et al. (2007)
Alberta, Canada	9.3 9.3 20.9	Yard waste compost (0.7 m)	Tire shreds (0.8 m)	37.4 53.5 1.2	28 36 0.4	76 68 35	Philopoulos et al. (2008)
Sydney, Austrailia	3 × 3	Yard waste compost+ 10% woodchips (1.2 m)		168	101	60	Dever (2009)
	3 × 3	MSW compost+10% woodchips (1.2 m)	Gravel (0.5 m)	288	94	32	
	3 × 3	Yard waste compost (1.2 m)		542	62	12	

	3 × 3	MSW compost+20% woodchips (1.2 m)		160	108	67	
Zealand, Denmark	9 × 9. 5	Garden waste compost (1 m)	Gravel (0.15 m)	740	208	28	Scheutz et al. (2011)
Quebec, Canada	2.75 × 9.75	Sand+compost+gravel (0.3 m)	Gravel (0.9 m)	2212	252	11	Roncato and Cabral, (2012)
	2.75 × 9.75	Sand+compost (0.8 m)	Gravel (0.4 m)	408	335	72	
Tuscany, Italy	25	Organic compost+sand (0.7 m)	Gravel (0.2 m)	(460 to 1390)		65	Pecorini and Iannelli (2020)
	25	MSW compost+sand (0.7 m)		(530 to 1170)		56	
	25	Organic+MSW compost+sand (0.7 m)		(530 to 1440)		75	
Winnipeg, Canada	3.5 × 2.5	YWLC+BSC (0.75 m)	Gravel (0.55 m)	1137	237	21 (average) 80 (max)	Current study

3.2.3 Investigating the performance of the bio-window

Once after the placement of the bio-window, field measurements and samplings were conducted either monthly or bi-weekly depending on the weather conditions over two years. Meteorological data, including daily temperature, precipitation, wind speed, and barometric pressure, were obtained from the Richardson International Airport Station in Winnipeg (Government of Canada, 2018).

To have replicates for measurements, the gas samples were collected in duplicate from one location of the bio-window. Moreover, in the laboratory batch experiments, the incubation bottles were prepared in duplicate. To monitor CH_4 and O_2 consumption and CO_2 production in the experiments, gas chromatography was performed using an Agilent 490 Micro GC equipped with Molesieve-5A and PoraPlot U columns.

3.2.4 Flux measurements

The flux of CH_4 was measured to investigate seasonal variability of the flux during sampling period and the CH_4 oxidation due to methanotrophic activity in the bio-window. The measurements were conducted diurnal since the variation of CH4 emissions during the day has been related with weather conditions (Xin et al. 2016; Bian et al. 2019). A static chamber technique was implemented (Stern et al. 2007; Cabral et al. 2010). The flux measurements were first conducted in random spots within the bio-window and different times for a few months at each sampling campaign, and almost similar values were obtained for CH_4 flux in all measurements at each campaign. Moreover, the size of the bio-window is only 8.75 m^2, of which 1.5 m^2 is covered by the gas probe nest; therefore, it was planned to do one placement point of the chamber for flux measurement. A stainless-steel chamber with surface area of 0.152 m^2 and the volume of 0.0262 m^3 (Scentroid SF450 Flux Chamber; IDES Canada Inc.) was installed on top of the bio-window and sealed by bentonite to trap the gas and prevent its dilution. The rate of CH_4 emission was measured by collecting a series of gas samples from the chamber headspace. Gas samples (5 ml) were collected in duplicate using a 60 ml gas-tight sample-lock syringe every 5 min over a 30 min period in sealed tubes. The samples were transferred in a foam box to the laboratory, and the gas concentrations were immediately analyzed through gas chromatography. Total flux was calculated according to Equation (1):

$$J_{out} = \frac{\Delta C}{\Delta t} \cdot \frac{V}{A} \quad (3\text{-}1)$$

where J_{out} is the CH_4 flux ($g.m^{-2}.d^{-1}$), $\Delta C/\Delta t$ is the slope of the plot for the change in gas concentration over time ($g.m^{-3}.d^{-1}$), V is the chamber volume (m^3), and A is the chamber surface area (m^2).

The CH_4 flux into the bio-window (influx), before any CH_4 oxidation takes place, can be determined by considering that CH_4 influx equals the CH_4 emission plus CH_4 oxidation. The Equation 2 to 4 represent the mass balance for carbon with the assumption that there is a direct relationship between the influx of the CH_4 and CO_2, and their concentrations in the waste beneath the bio-window. This method is also implemented and described in other studies (Christophersen et al. 2001; Einola et al. 2008; Scheutz et al. 2011). The oxidation rate and the fraction of CH_4 oxidized in the bio-window were calculated by Equation 5 and 6.

$$J_{LFG(in)} = J_{CH_4(in)} + J_{CO_2(in)} = J_{CH_4(out)} + J_{CO_2(out)} - J_{CO_2(respiration)} \quad (3\text{-}2)$$

$$\frac{J_{CH_4(in)}}{J_{CH_4(in)} + J_{CO_2(in)}} = \frac{C_{CH_4(in)}}{C_{CH_4(in)} + C_{CO_2(in)}} \quad (3\text{-}3)$$

$$J_{CH_4(in)} = \frac{C_{CH_4(in)}}{C_{CH_4(in)} + C_{CO_2(in)}} \cdot (J_{CH_4(out)} + J_{CO_2(out)} - J_{CO_2(respiration)}) \quad (3\text{-}4)$$

$$R_{ox(CH_4)} = J_{CH_4(in)} - J_{CH_4(out)} \quad (3\text{-}5)$$

$$f_{ox(CH_4)} = \frac{J_{CH_4(in)} - J_{CH_4(out)}}{J_{CH_4(in)}} \times 100 \quad (3\text{-}6)$$

Where, $J_{LFG\text{-}in}$ is the LFG flux into the bio-window (mol C.m^{-2}.d^{-1}) including CH_4 influx ($J_{CH_4(in)}$) and CO_2 influx ($J_{CO_2(in)}$), $J_{CO_2(respiration)}$ is CO_2 emission due to respiration in the compost (mol C.m^{-2}.d^{-1}), $C_{CH_4(in)}$ and $C_{CO_2(in)}$ are the concentration of CH_4 and CO_2 (% v/v) in the waste beneath the bio-window, $J_{CH_4(out)}$ and $J_{CO_2(out)}$ are CH_4 and CO_2 flux from surface of the bio-window (mol C.m^{-2}.d^{-1}), $R_{ox(CH_4)}$ is CH_4 oxidation rate (mol C.m^{-2}.d^{-1}), and $f_{ox(CH_4)}$ is CH_4 oxidation efficiency (%).

Primary lab-scale studies showed that the composts were stabilized and there was little competition for O_2 from heterotrophic bacteria (Niemczyk et al., 2021); therefore, the value of CO_2 emission due to respiration in the compost was considered zero to simplify the calculations. The LFG concentrations were obtained from the gas probes described in the following section. The surface CO_2 and CH_4 fluxes were measured by static chamber technique.

3.2.5 Vertical profiles of the gas concentrations

The concentration of O_2, CO_2, and CH_4 in the pore volume of the bio-window was measured at different depths to determine the degree of O_2 diffusion into the bio-window and the location of the methanotrophic active zone. Moreover, the LFG composition pertains to the change in ratio of CH_4 to CO_2 while passing through the bio-window. One gas probe nest (nest diameter = 70 cm) was permanently installed within the bio-window according to the ratio of bio-window to gas probe nest surface areas in literature (Scheutz et al., 2011; Kjeld, 2013). The nest consisted of

probes at seven various depths; 10, 20, 30, 40, 50, 60, 70 cm (Figure 3-1). An additional probe located below the frost line and within the waste (2.5 m) was also installed to obtain the LFG composition.

The probes were manufactured from stainless steel tubes (I.D. = 12.5 mm). To prevent the effect of any possible heave or drop on the probes due to climatic conditions in the study area, long metal bars were attached to the probes and fixed into the gravel in GDL, creating a deep foundation for the probes. Then, samples were manually collected, in duplicate, by taking 10 ml of gas from each probe using the syringe, injecting them into 60 ml sealed glass serum bottles (Fisher Scientific; Toronto, ON, Canada), and then transferring in a foam box to the laboratory. The gas concentrations were immediately analyzed through gas chromatography.

3.2.6 Initial oxidation rate of CH_4

To verify the field measurements, compost samples were also taken for laboratory experiments in every sampling campaign. The initial CH_4 consumption rate was investigated under standardized conditions, in terms of percentages of CH_4 and CO_2 in the air, using samples collected from different depths within the bio-window, but at *in situ* MC.

Compost samples were taken every 10 cm step by step from depths of 0 to 50 cm and collected in sealed plastic bags. A laser thermometer was used to measure the temperature in the bio-window at different depths, so the obtained values were not real-time data due to the air exposure of the compost layers and were less than the real values. Samples were then transferred in a foam box to the laboratory. Immediately after, the compost MC was measured according to the ASTM (2010) standard, and batch tests were conducted. Two g wet weight of compost samples from different depths were added to separate 120 ml serum bottles (Fisher Scientific; Toronto, ON, Canada), that were then sealed with 20 mm blue chlorobutyl septa stopper (Bellco Glass Inc.; Vineland, NJ, USA) and aluminum crimp caps (Wheaton Industries; Millville, NJ, USA). A molar concentration of 20% (mol%) for the proportion of CH_4 to air headspace was established by adding 30 ml CH_4 to each bottle using a gas-tight sample-lock syringe. The batch test procedure was similar to the study by Perdikea et al. (2008) and Niemczyk et al. (2021). The batches were incubated at 22°C and 45°C representing mesophilic and thermophilic conditions, respectively. The initial CH_4 oxidation by MOB, was monitored based on CH_4 and O_2 depletion after 24 hours.

While, before implementing the compost matrix in the bio-window, it was proved that there was little competition for O_2 from heterotrophic bacteria (Niemczyk et al., 2021), to determine the O_2 consumption by MOB and heterotrophs in the compost samples of the *in situ* bio-window, biological oxygen demand (BOD) was investigated by doing the same batch tests with the headspace left undisturbed (i.e., 100% air) in the bottles.

3.3. Results and Discussion

3.3.1. Meteorological and environmental factors

Figure 2 shows the barometric pressure and wind speed fluctuations throughout the study. The barometric pressure fluctuated between 97.08 to 99.97 kPa, in the opposite direction with the wind speed fluctuations, which was also observed by Jugnia et al. (2008) and Aghdam et al. (2019).

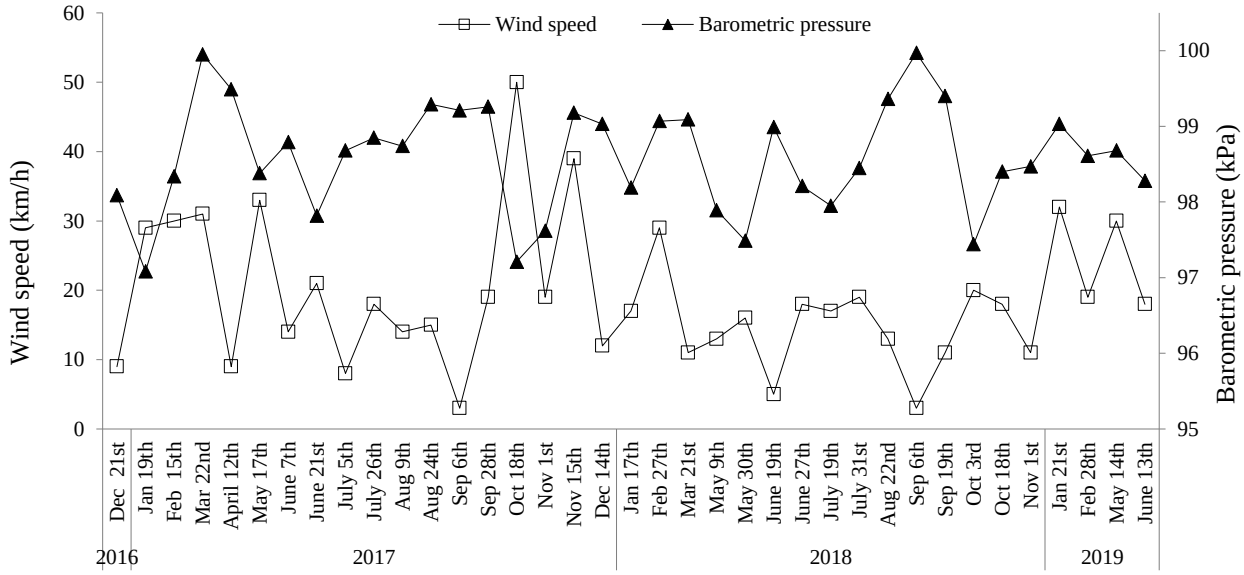

Figure 3-2. Fluctuations in barometric pressure and wind speed during sampling period at BRRMF

It was observed that precipitations, high wind speed and solar radiation could alter MC, especially at top layers. Therefore, at depths of 30 to 50 cm, MC did not fluctuate as much as that at 0 to 30 cm, while it increased with depth and did not exceed 55% (Figure 3-3).

Higher MCs in Figure 3-3 than those reported in the soil for methanotrophic activity (i.e., 10% to 25%) (Scheutz et al. 2009a) were consistent with the previous findings in the field studies with seasonal analyses of the performance of compost filled biofilters (Jugnia et al. 2008; Zeiss, 2006).

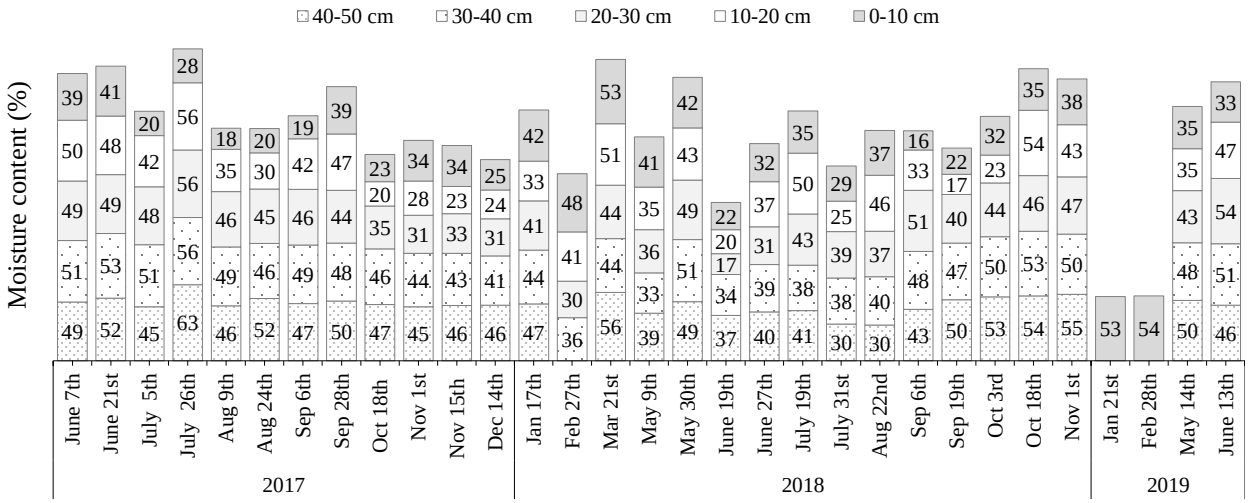

Figure 3-3. MC (%) at different depths of the bio-window (cm) during sampling period

Figure 4 represents the temperature in the ambient and at different depths of the bio-window. The temperature measurements started in late summer 2017 after observing warm compost layers (> 45°C) in the bio-window on a previous sampling campaign. There were days with an ambient temperature of 35°C in summer and < -30°C in winter, while sampling was not conducted due to difficulty of operations.

Despite below freezing temperature from late fall to late winter, at depths deeper than 20 cm within the bio-window, the temperature was > 0°C. It was hypothesized that heat generation due to fermentation inside the landfill elevated the temperature of the bio-window. This was also intensified by snow remaining on the ground throughout the winter and insulating the compost layer that could prevent deeper frost penetration (Molotch et al. 2009). In spring, after all frozen moisture thawed and the snow cover melted, the temperature in the *in situ* bio-window decreased from top to the bottom (Figure 3-4) because the compost at deeper layers contained cold infiltrated moisture (melted ice), while the top layers were exposed to the high ambient temperature.

What was observed in the temperature data, was very close to the study by Zeiss (2006) at similar climatic conditions of Alberta, Canada. The high temperature in deep layers of the bio-covers due to LFG supply and heat generation from the active landfills was observed in similar studies by Philopoulos et al. (2008) and Gebert and Groengroeft (2006).

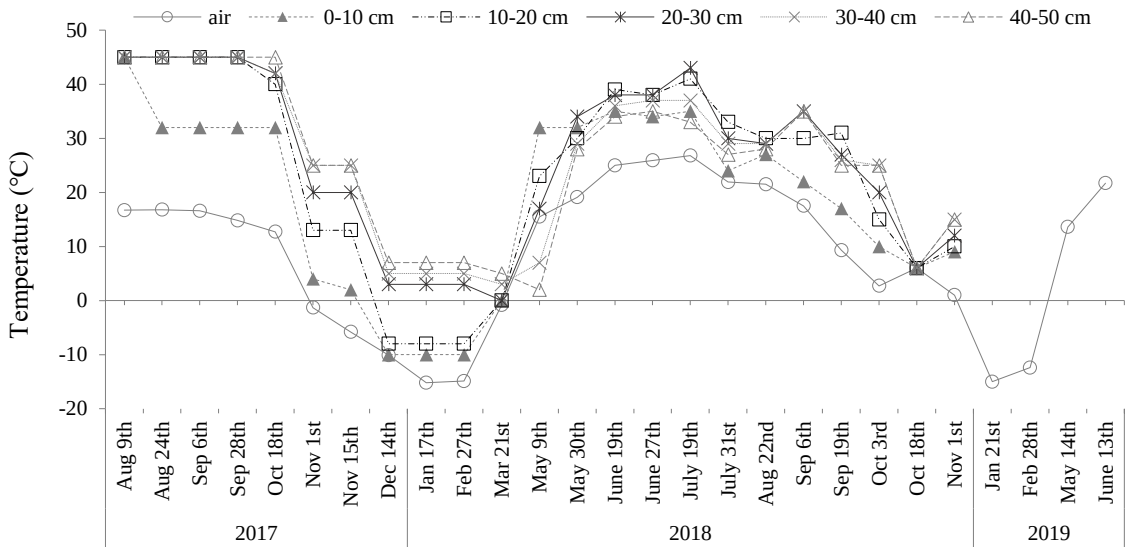

Figure 3-4. Temperature (ºC) at different depths (cm) of the bio-window at BRRMF

Note: Data show the minimum compost temperature due to the air exposure of compost layers during measurements

3.3.2. Flux measurement and CH_4 oxidation efficiency

The high seasonal fluctuation in CH_4 influx, outflux, and CH_4 oxidation efficiency during the sampling period is illustrated in Figure 5. Generally, when there was a high influx, the removal efficiency was low. The flux fluctuated inversely with the wind speed and barometric pressure fluctuations (Figure 3-2 and Figure 3-5) which can be due to the pressure gradient between LFG and the atmosphere (Poulsen and Møldrup, 2006; Aghdam et al. 2019). An extreme drop or increase in barometric pressure and wind speed had an intensive effect on flux and consequently, CH_4 removal (Figure 3-2 and Figure 3-5). Examples are March and April 2017, when a very low flux was observed with high oxidation efficiency. In October 2017, the wind speed was so high that it caused a much higher wind-induced pressure than barometric pressure and decreased the flux while the oxidation efficiency increased. The combined effect of meteorological factors on flux fluctuations and CH_4 removal needs to be further studied to differentiate the significance of each factor.

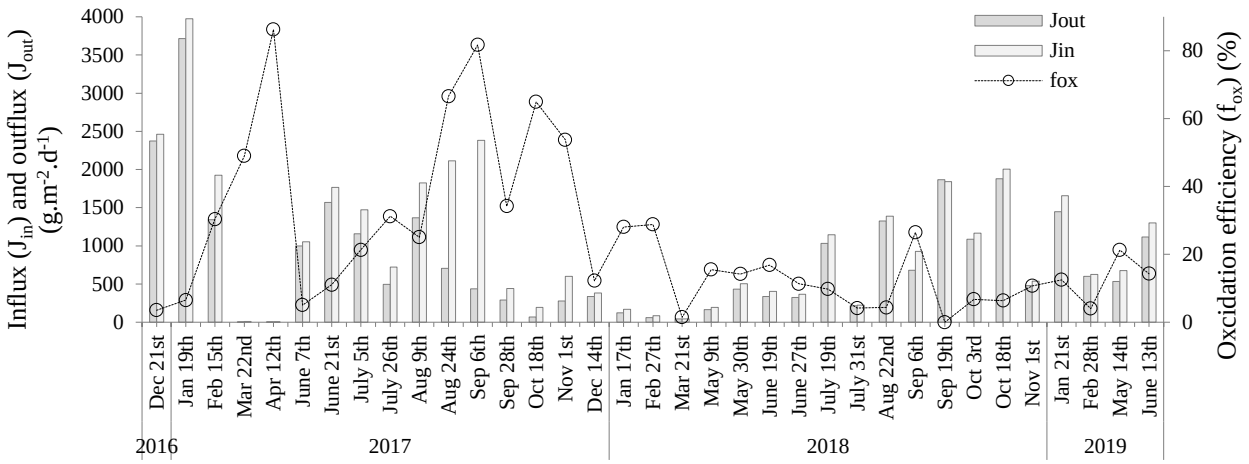

Figure 3-5. CH_4 influx (J_{in}), outflux (J_{out}), and oxidation efficiency (f_{ox})

Precipitations contribute to the MC in the substrate layer and reduce gas migration, while low MC during the dry season can increase it (Topp and Pattey 1997; Scheutz et al. 2009a). High MC in the bio-window after fall precipitations can form the frost layer during the sub-zero winter and affect the gas exchange by reducing both air diffusion to the bio-window and LFG emission. The frost zone in the bio-window can also restrict methanotrophic activity (Zhao et al., 2016). The low flux in winter, despite low barometric pressure and wind speed, could be due to frost formation that was observed in the top layers (Figure 3-2 and Figure 3-5). The high flux in early winter of the first sampling year (Dec 2016 and Jan 2017) was due to the recent construction and not being quite exposed to precipitations. Thus, there was probably low MC in the substrate layer (MC not measured at that date), letting more gas emission and low CH_4 oxidation efficiency. Subsequent compaction and settling of the compost may have led to reduced flux in the following months.

In late Spring, despite much lower CH_4 influx in 2018, the CH_4 oxidation efficiency was close to those in 2017 (June 21st) and 2019 (June 13th) with high fluxes. This could be due to low MC of 22%, in June 2018, since it is a controlling factor for the MOB activity that can dramatically reduce CH_4 oxidation if being much lower or higher than its optimum level (Jugnia et al. 2008; Einola et al. 2007).

Temperature is another factor that can control the activity and community of MOB but requires the induction of temperature appropriate communities. Most well-studied MOB are mesophilic, and their activity increases with the temperature until reaching the optimum range of 25°C to 35°C. With higher temperatures, different MOB communities can be expected to be active. Within the

Methylococcaceae of the phylum Proteobacteria, several species of moderate thermophiles growing optimally between 50°C and 55°C have been more recently isolated from tropical soils (Islam et al. 2016). Thermophilic MOB from the phylum Verrucomicrobia are active at 45°C to 60°C and have been found in surface geothermal features with acidic conditions (Dunfield et al. 2007; Pol et al. 2007; Islam et al. 2008; Carere et al. 2017).

From late fall to early spring in 2018 and 2019, the temperature in the bio-window was very low (Figure 3-4); nevertheless, the CH_4 oxidation sustained at low efficiencies of 20% to 30%.

Comparing the CH_4 oxidation efficiency in late summer in 2017 and 2018, indicated that low MC in the entire depth of the bio-window reduced CH_4 oxidation even with a low influx (August 22th). With comparable meteorological conditions (Figure 3-2), the CH_4 removal efficiency in 2018 (September 6th) was not as high as that in 2017. This can be related to the difference in MC of the top layers (Figure 3-3) where according to the vertical profiles, the majority of CH_4 oxidation occurred. Also, in late summer 2017 and 2018, the temperature of bio-window caused thermophilic and mesophilic conditions, respectively (Figure 3-4). As will be discussed in section 3.5 and Figure 7, thermophilic MOB cause a higher CH_4 oxidation rate than mesophilic MOB.

In mid-fall (November 1st) of 2017 and 2018, the CH_4 influx, MC at different depths, and the ambient temperature were comparable; however, the CH_4 oxidation rate was lower in 2018 than 2017 due to lower temperature in the bio-window. Likewise, this implied for late summer (August and September) 2017 and 2018.

As the bio-window was a small opening in a big landfill cell surrounded by a clay cover (Figure 3-1), large amounts of LFG were funneled through it. This was also observed in the study by Philopoulos et al. (2008). Excluding high removal rates under intense meteorological conditions, the average CH_4 influx and oxidation rate were 1137 $g.m^{-2}.d^{-1}$ and 237 $g.m^{-2}.d^{-1}$, respectively. These values are among the highest range compared to previous studies with similar dimensions for the bio-window/biofilter and compost as the substrate layer (Table 3-1).

When influx was high at approximately 600 $g.m^{-2}.d^{-1}$ (November 1st, 2017) and the temperature was mesophilic, the removal rate of 50% indicated the capacity of the compost to remove CH_4. These results suggest that by expanding the current surface area of the biowindow by four times, it could remove up to 100% of CH_4 emissions.

3.3.3. Main gas concentrations in the bio-window vertical profile

The average CH_4 and CO_2 concentrations in the LFG was approximately 64% and 36% (+/-1.4%), respectively, indicating the value of 1.77 (+/-0.1) for the average CH_4/CO_2. However, data measured on March 22nd, 2017, (42% CH_4 and 58% CO_2) were excluded from the calculations of the average value. While CH_4 and CO_2 concentrations in the LFG were not in the range of the typical concentrations reported in other studies with 55-60% of CH_4 and 45-50% of CO_2 (Ayalon et al. 2001; Börjesson et al. 2001; Jugnia et al. 2008; Scheutz et al. 2009b), similar concentrations were reported in other landfills with similar weather conditions (Roncato and Cabral, 2012) and by USEPA (2006).

The Figure 6-a to 6-h show concentrations of CH_4, CO_2, and O_2 in the vertical profile of the bio-window on selected days with high seasonal fluctuations including, those affected by intense climatic factors including high wind speed and barometric pressure (Figure 3-6-a, 3-6-b, and 3-6-e), those with the highest CH_4 oxidation efficiency (Figure 3-6-c and d), a representative day in winter (Figure 3-6-f), and the wettest and driest samplings (Figure 3-6-g and h).

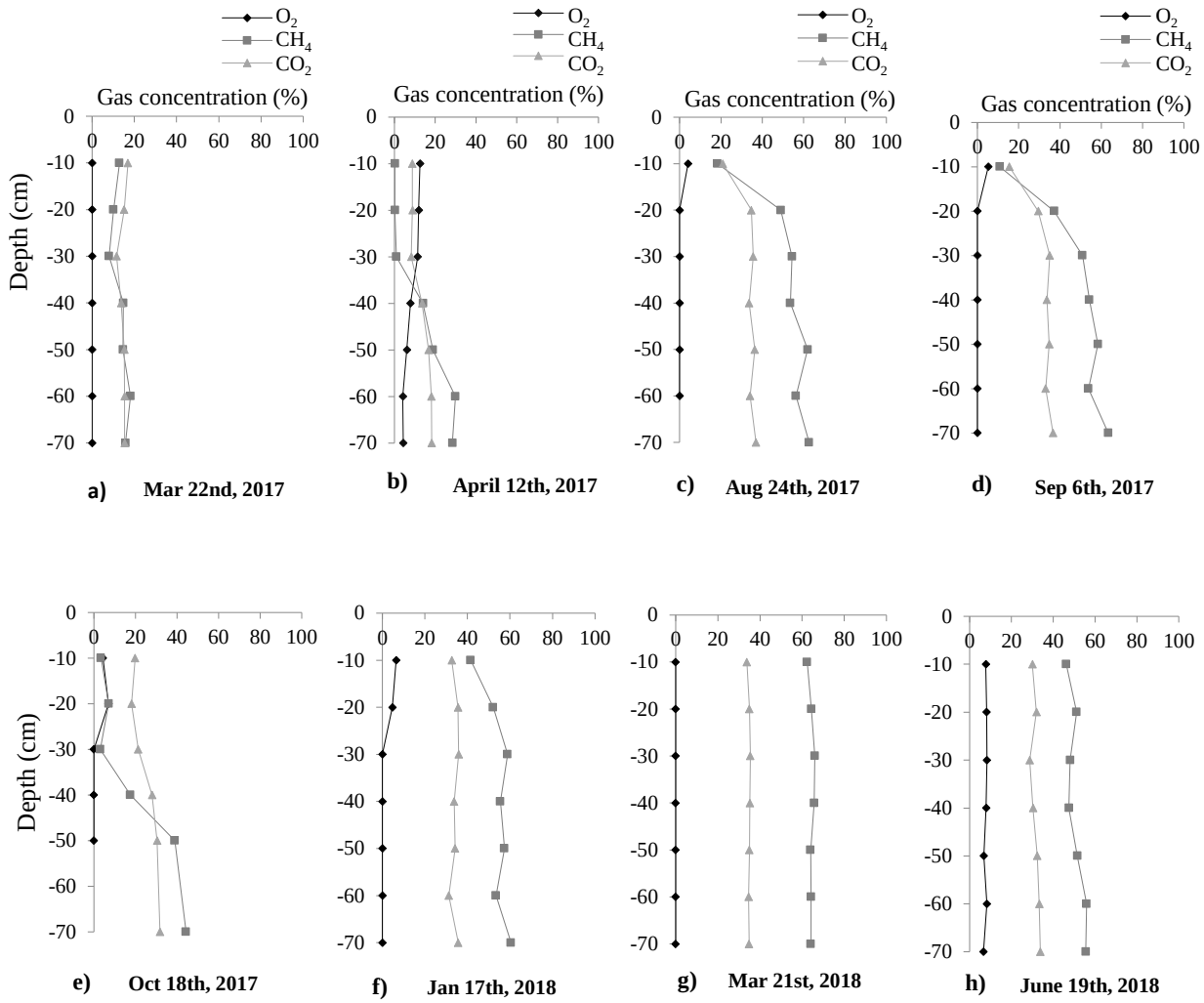

Figure 3-6. Main gas concentrations in the bio-window vertical profile on selected days

Generally, the lower value of CH_4/CO_2 in the vertical profile than that in LFG indicated CH_4 consumption and CO_2 production by MOB. Further reduction of CH_4 and CO_2 concentrations was mainly due to the dilution by air penetration.

It seems that the high barometric pressure and wind speed on March 22nd, 2017 caused advective air penetration and consequently CH_4 oxidation inside the landfill because the value of CH_4/CO_2 was equal to 0.73 which was much lower than that in LFG. Very low CH_4 influx on this sampling day (Figure 3-5) can also be due to the majority of CH_4 being oxidized inside the landfill waste. Further CH_4 oxidation took place in the bio-window between depth 30 to 40 cm (Figure 3-6-a). Similar results were obtained on April 12th, 2017 due to high barometric pressure; however, since there was not very high wind speed, the advective air penetration inside the landfill was not as

much as that in March as CH_4/CO_2 equalled to 1.4. Further CH_4 oxidation occurred from a depth of 60 cm upwards (Figure 3-6-b). However, very high wind speed on October 18th, 2017, did not make observable CH_4 oxidation inside the landfill since the CH_4/CO_2 in the LFG maintained 1.73. The CH_4 oxidation probably started from the GDL as the value of CH_4/CO_2 at 70 cm was equal to 1.4, and it decreased towards the surface of the bio-window, reaching the value of 0.02 at a depth of 10 cm (Figure 3-6-e). Philopoulos et al. (2008) and Humer and Lechner (2001a) also reported similar observations of CH_4 oxidation in the GDL and landfill waste. From the aforementioned sampling results, the advective air penetration inside the landfill waste and bio-window increased due to a combination of barometric and wind-induced pressure > high barometric pressure > high wind speed.

In late summer 2017, CH_4 was oxidized in the entire vertical profile of the bio-window, and at upper layers, CH_4 and CO_2 were also diluted by air (Figure 3-6-c and d). However, from section 3.4, low MCs of 20% and 16% at the top 10 cm, remarkably restricted methanotrophy.

On January 17th, 2018, CH_4 oxidation started from a depth of 30 cm upwards. Although the temperature at the top layers of the bio-window was below freezing, the considerable activity of mesophilic MOB in upper 10 cm layer (Section 3.3.4.), low CH_4 influx to the bio-window (Figure 3-5), and better air penetration in upper layers can explain low CH_4/CO_2 with the values of 0.81 and 1.27 at 10 cm depth of vertical profile in November 2017 (figure not shown) and January 2018, respectively (Figure 3-6-f).

On March 21st, 2018, no O_2 concentrations and dilution of LFG was found in the bio-window indicating no air penetration. Therefore, no CH_4 oxidation occurred in the entire depth of the substrate layer as the concentration of CH_4 and CO_2 in the LFG did not change passing through the bio-window (Figure 3-6-g). On this sampling day, there was a high MC at all layers of the bio-window (Figure 3-3) that restricted air diffusion and reduced the influx due to frost formation (Figure 3-5). The air diffusion was even further restricted by the thick snow-cover on top of the bio-window.

On June 19th, 2018, there was a low influx to the bio-window (Figure 3-5), so O_2 could penetrate deep into it (Figure 3-6-h); however, a mild CH_4 oxidation was observed in the vertical profile as the value of CH_4/CO_2 at depth of 10 cm was 1.54, while it was 1.78 for the LFG. Although the temperature in the bio-window was appropriate for the high activity of mesophilic MOB (Figure

3-4), it seems that very low MC restricted that (Figure 3-3), which was confirmed by limited methanotrophic potential in the compost samples (Section 3.3.5).

3.3.4. ANOVA on CH_4 oxidation rate

According to the entire field-scale results, it can be inferred that the temperature, MC or both, not being within their optimum range for methanotrophic activity was the main reason for low CH_4 oxidation efficiency even when the flux was low due to meteorological factors, or there was sufficient O_2 diffusion into substrate layer of the bio-window.

The regression tool in Design-Expert software (Stat Ease, 12.0 trial Version), intended for response surface method (RSM), was applied to historical data. In the study, from August 2017 to November 2018, data points of MC, temperature, CH_4 influx, and CH_4 oxidation rate were collected simultaneously; therefore, only these values were used in the analysis. A two-factorial statistical model was the best fit for the data, so the impact of CH_4 influx, MC and temperature on CH_4 oxidation rate with both their single impact and interaction was examined. The final response equation representing a proper model for CH_4 oxidation rate is given below:

$$Y = 1170.86 - 2.61 * A - 24.53 * B - 9.7 * C + 0.053 * A * B + 0.028 * A * C - 0.013 * B * C \quad (3\text{-}7)$$

Where, Y is CH_4 oxidation rate, A, B, and C are CH_4 influx, MC, and temperature, respectively.

The goodness of the fit of the model was checked by the determining coefficient R^2 (0.83), which indicates that 83 % of the total variation in methane oxidation rate can be explained by the model. Also, ANOVA was employed for the determination of significant factors and interactions. ANOVA results showed that while MC and temperature had an statistically significant effect on CH_4 oxidation rate ($P<0.05$), their interaction effect was insignificant ($P>0.05$). The effect of CH_4 influx was also insignificant while its crossover interaction with MC and temperature was significant with $P<0.05$ and $P<0.0001$, respectively.

These findings can confirm previous results from section 3.2. indicating that MC and temperature fluctuations affected CH_4 oxidation efficiency, MC altered gas migration as high MC at the bottom layers of the bio-window restricted CH_4 influx, and CH_4 influx increased during the winter when the temperature in the bio-window was low due to low ambient temperature. In contrast, variations

in CH_4 influx throughout the year did not show any change in CH_4 oxidation efficiency (e.g. September 6th, 2017 and 2018) (Figure 3-5).

3.3.5. CH_4 consumption rate potential

To tease out the actual impact of MC and temperature, the response of MOB to the MC under mesophilic and thermophilic temperature was further investigated. Batch microcosm experiments were done to investigate the methanotrophic potential of the compost samples in terms of the initial rate of CH_4 oxidation.

According to Figure 3-7, there was a high seasonal fluctuation in the initial CH_4 oxidation rate due to the cycles of precipitations, dryness, and frost. The variations and migration of CH_4 oxidation potential among different layers explained the impact of MC and temperature more specifically.

When sampling started in fall 2016, a high methanotrophic activity was found at all depths despite low CH_4 oxidation efficiency in the *in situ* bio-window (Section 3.2). This may be due to the recent construction of the bio-window, which may represent methanotrophic potential of the compost itself (Niemczyk, 2018; Niemczyk et al., 2021), which was mixed as it was placed in the bio-window. This may also be related to the fact that microbial populations in the bio-window was not yet well developed, established, and adapted to field conditions. However, the continuance of the cold weather led to a gradual decrease in methanotrophic activity potential at different depths with minimum values in mid to late winter (February and March).

Generally, in spring, when the ambient temperature started to increase and the top layers of the bio-window started to thaw, MOB became more active in the upper layers. As spring reached to the last month MOB furtherly recovered to the deeper layers.

Temperature had a dominant impact on MOB activity in summer 2017 (July 5th), when the CH_4 removal rate started to decrease, then, from mid-summer to fall (August 9th to October 18th), a long lag in the methanotrophic activity was noticed at all depths even though methanotrophy had been observed *in situ* (Section 3.2). This can be explained by very high temperature of >45ºC observed at different depths of the bio-window inducing thermophilic methanotrophs. However, there was an increase in the MOB activity after a favorable mesophilic temperature appeared in the *in situ* bio-window in fall 2017 (November) (Figure 3-4).

The impact of MC on MOB activity was dominant in the following samplings. In December 2017, the MOB activity in the samples migrated deeper, while the negligible CH_4 oxidation at top layers was due to the low MC of 25% to 31%. With an increase in the MC to 42% in January 2018, CH_4 oxidation recurred at that depths. The end of spring (June 19th), 2018, was the driest sampling date (Figure 3-3). The low MC reduced CH_4 oxidation to the end of summer, while an increase in the MC in fall, recurred it (On October 3rd).

The difference in the activity of thermophilic MOB at different layers and sampling dates was also due to variations in moisture level (Figure 3-3, 3-4, and 3-7). Although in 2018, the temperature in the *in situ* bio-window was mesophilic, laboratory experiments showed thermophilic MOB being equal or more active in most of the samplings. However, their activity was minimum during winter and it completely stopped in the entire profile in February. While thermophilic MOB showed a rapid recovery at the end of winter, it was gradual for mesophilic MOB. On the other hand, despite the rapid decline in the activity of mesophilic MOB due to temperature drops in the mesophilic range, a gradual decrease in thermophilic MOB activity was observed (e.g., from October to November 2018). Generally, the most active zone for CH_4 oxidation was found at the depths of 0 to 20 cm under mesophilic conditions, and the depths of 0 to 10 cm and 20 to 30 cm under thermophilic conditions. Being exposed to more O_2 diffusion at these depths, MOB were more active at top layers. While the removal rate in the *in situ* bio-window was low during the field measurements, the laboratory-scale batch experiments showed that there was methanotrophic potential in compost samples for the entire sampling period. Depending on the temperature of the bio-window, different cultures were active, while their activity also varied with temperature variations within their operating range and MC fluctuations. That depending on the temperature, selective MOB populations can be active was also reported by Börjesson et al. (2004); however, their study focused on psychrophilic species. The average initial CH_4 oxidation rate was equal to 282 $\mu mol.g^{-1}.d^{-1}$. This is in the range of the highest maximum CH_4 oxidation rates in the compost-based bio-covers obtained by batch tests in previous studies including 259.5 $\mu mol\ g_{dw}^{-1}\ d^{-1}$ in sewage sludge compost (Börjesson et al. 1998), 214.5 $\mu mol\ g_{dw}^{-1}\ d^{-1}$ in yard waste compost (Streese and Stegmann 2003), 186 $\mu mol\ g_{dw}^{-1}\ d^{-1}$ in Woodchip compost**,** 373.5 $\mu mol\ g_{dw}^{-1}\ d^{-1}$ in municipal solid waste compost (Wilshusen et al. 2004), and 157.5 $\mu mol\ g_{dw}^{-1}\ d^{-1}$ in garden waste compost (Mor et al. 2006). Therefore, the adopted compost mixture can be applied in large scale bio-covers since MOB have shown to be active in different layers in wide seasonally fluctuating

weather conditions. Implementing enhancement measures, through better temperature regulation and increasing air diffusion in the deep layers while maintaining desirable MC for MOB, can even better exploit the bio-cover to its full capacity.

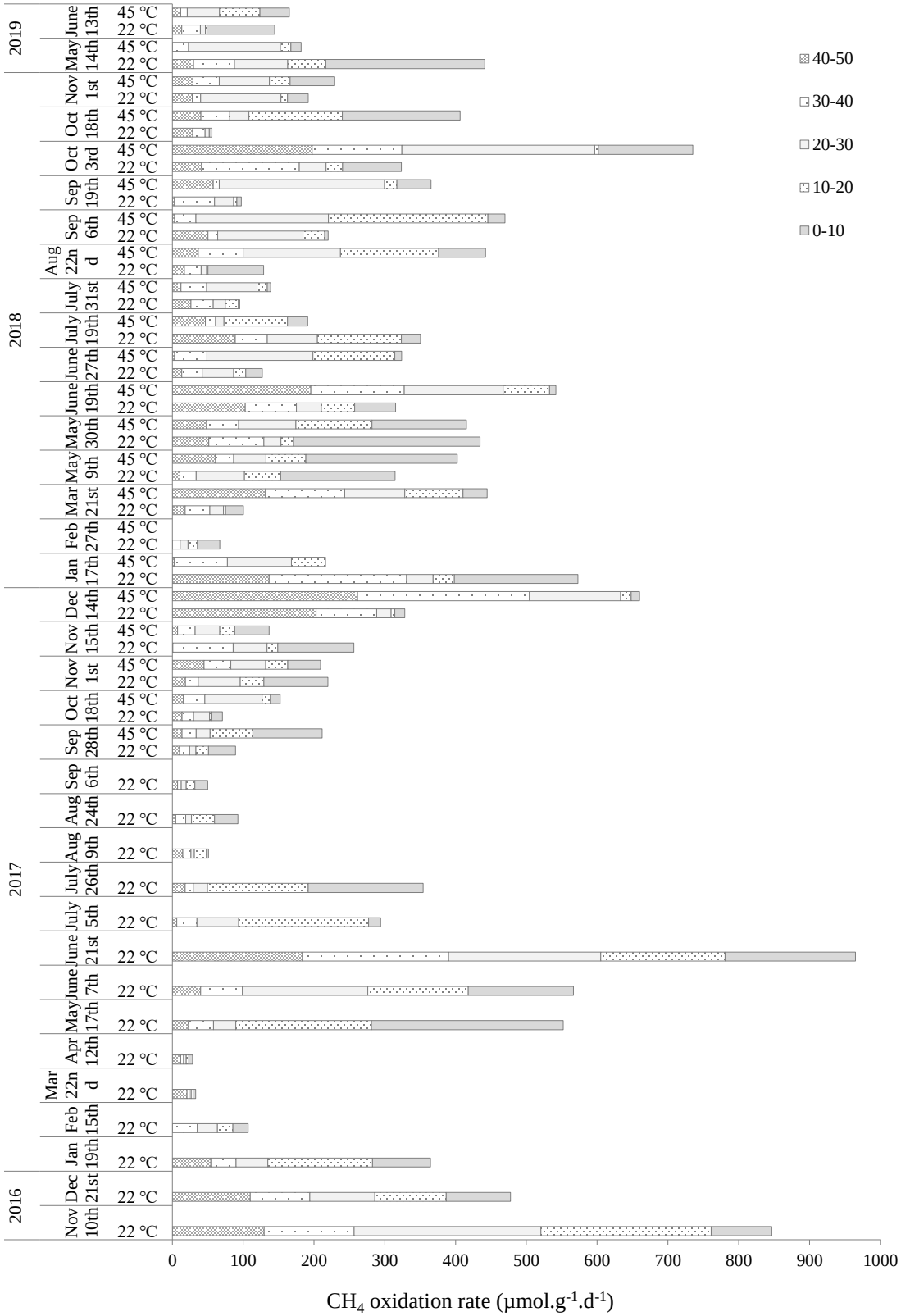

Figure 3-7. Initial CH_4 consumption rate at different depths incubated at 22ºC and 45ºC

Considering compost samples, collected from all depths of the *in situ* bio-window, the following meaningful relationships among values of MC, temperature, and CH_4 oxidation rate can be inferred.

At MCs below 30%, both MOB cultures activity dramatically dropped; however, the level of their response to the variations in the MC was different. At below 2℃, the effect of low temperature on CH_4 oxidation was more dominant than MC as CH_4 oxidation rate was low regardless of the level of MC. From 3℃ to 13℃, an increase in temperature and MC increased the CH_4 oxidation rate. However, at 5℃ and 6℃ no clear link was detected among these factors. This can be due to the insufficient number of samplings at 5-6℃, limiting a clear conclusion.

From 15℃ to 23℃, the highest CH_4 oxidation rate was attributed to the MC between 30% to 40% that was also previously stated by Niemczyk (2018). The variations in MC significantly altered the CH_4 oxidation rate at 32℃ to 33℃ while it did not seem to be a controlling factor at 29℃ to 31℃. The highest CH_4 oxidation rate was observed at 5, 7, 25, and 32℃, with MCs above 40%. In a study to investigate the applicability of different types of compost as landfill cover, the highest CH_4 oxidation rates were observed at MC of 45-110%, while the optimum temperature ranged from 15 to 30℃ (More et al. 2006). It seems that the optimum MC at 34℃ to 45℃ was equal to 40% because CH_4 oxidation rate decreased at MCs above that level. In a study on CH_4 oxidation in subtropical landfill soil, an optimum condition with MC of 35-45% and temperature of 30-35℃ was observed (Bajar et al. 2013). However, the maximum CH4 oxidation in a sandy landfill cover soil was obtained at 10% of MC at 30℃ (Park et al. 2005).

It can be inferred that the significance of MC variations on CH_4 oxidation rate depended on the temperature range. Due to the fluctuations in MC, it is challenging to find its optimum range and the accurate association between CH_4 oxidation and various temperatures. Under controlled lab conditions, the effect of temperature at different MCs should be studied to find a model for CH_4 oxidation in the landfill bio-cover based on MC and temperature variations. The current field measurements can be used to verify the model.

3.3.6. O_2 consumption by compost respiration

Since the bio-window matrix consisted of a mixture of biomass residues and woodchips, some background BOD in the compost was expected. The initial O_2 consumption at the entire depth of

the bio-window by heterotrophic bacteria in the absence of added CH_4 was compared to that by MOB and heterotrophic bacteria with 20% CH_4 in the air (Figure not shown). In most of the samplings, O_2 consumption by heterotrophs was less than that by both. The average initial O_2 consumption by heterotrophs at each depth varied between 59 µmol $O_2.g^{-1}.d^{-1}$ to 77 µmol $O_2.g^{-1}.d^{-1}$. The highest BOD occurred in January 2018, when also a high methanotrophy was detected. It also recorded the highest reading for upper 10 cm only. There was an insignificant difference between O_2 consumptions from August to October 2017 due to the dominance of thermophilic MOB that were not able to consume O_2 at the incubation temperature of 22°C. Despite by MOB, O_2 consumption by heterotrophs did not significantly vary with MC and temperature. While heterotrophs in the compost compete with MOB for O_2 consumption, the bio-window matrix, based on these measurements, contained only a small amount of readily oxidizable biomass.

3.4. Conclusion and recommendations

This pilot study was conducted to assess the seasonal variation in CH4 oxidation due to climatic conditions. Over two years of fieldwork showed that there were large temperature variations in the bio-window due to the heat radiation from the landfill and high seasonal fluctuations of temperature that resulted in a shift in methanotrophic populations. Dryness in summer, causing low MC (<20%), resulted in a low methanotrophic activity. The highest CH_4 oxidation potential was observed in top layers where more O_2 could diffuse. Under intense meteorological conditions, high barometric pressure and high wind speed, CH_4 oxidation started from deep layers and inside the landfill.

To our knowledge, this is the only study on landfill bio-covers that included thoroughly cold winter results. Issues surrounding frost formation, such as modifying gas exchange in the bio-window and the temperature of top layers in winter and deep layers in early spring are critical to discuss as they can incredibly affect the activity and recovery of MOB. Likewise, the unexpected finding of thermophilic methanotrophy in the landfill. All these points have seldom been reported in the landfill literature.

Although high influx reduced CH_4 oxidation efficiency, the CH_4 oxidation rate was in the range of high values in literature. This shows the high potential of the adopted compost mixture in

oxidizing CH_4 that was further confirmed by batch microcosm experiments representing a high average value for methanotrophic potential compared to maximum values in literature.

Laboratory experiments on compost samples showed that mesophilic and thermophilic MOB selectively responded, within their respective temperature ranges. There was an interaction among activity of either group, MC, and temperature.

Potential future work can be extending shoulder season by irrigating the bio-window to secure MC in dry season, oxygenation below the frost line in winter to use the full potential of the bio-window, and re-inoculation by proper MOB population to fasten MOB recovery.

3.5. References

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Chapter 4: The interactive effect of environmental factors in a landfill bio-window in a seasonally fluctuating climate

Abstract

In the current study, the environmental factors including moisture content (MC), temperature, and initial CH_4 concentration were optimized to achieve maximum CH_4 oxidation in a bio-cover material including Yard Waste and Leaf Compost (YWLC) and Biosolids Compost (BSC) (1:4). The optimum mixing ratio of the composts and the most significant environmental factors were previously determined in the preliminary studies. While the effects of individual environmental factors on biological CH_4 oxidation have been studied, their interactive effects in bio-cover compost materials still need to be explored. Therefore, interactive effects of environmental factors were investigated with Box–Behnken Design (BBD) adopting Response Surface Methodology (RSM) to develop a statistical model and optimize the conditions for the CH_4 oxidation in the compost mixture. To do so, 17 batch incubations were conducted at the MC of 20, 40, and 60%, temperatures of 15, 30, and 45℃, and initial CH_4 concentrations of 10, 20, and 30%. The maximum value of CH_4 oxidation rate obtained from the model was 2.20 $mgCH_4.g_{dw}^{-1}.d^{-1}$ with optimum MC of 47.42%, temperature of 32.72℃, and initial CH_4 concentration of 23.81%. The optimum values from the model corresponded with those from the experiments with no significant differences. A parabolic curve for MC and temperature was observed simultaneously, and there was no significant difference between CH_4 oxidation rates at 20% and 30% initial CH_4 concentration. The developed statistical model was also validated by 15 supplementary batch incubations at the constant temperature of 22℃.

Keywords Box–Behnken Design, Interactive effect, CH_4 oxidation rate, Compost, Landfill methanotrophy

4.1. Introduction

Methane (CH_4) has a greater ability to absorb infrared radiation than Carbon Dioxide (CO_2). Having a Global Warming Potential (GWP) of 28-34 over 100 years and 84-86 over 20 years, CH_4 significantly threatens global climate change (IPCC, 2013). The waste sector is the third largest anthropogenic contributor of global CH_4 emissions with a raise of 4% in 2000 and 12% in 2010 (Ciais et al., 2013). Emissions of CH_4 from landfills generate significant greenhouse gas (GHG) emissions from the waste sector ranging from 500 to 800 Mt-$CO_2e \cdot yr^{-1}$ (Bogner et al., 2007).

Many modern sanitary landfills are retrofitted with engineered LFG collection systems, in which captured LFG can be flared or used for energy recovery (Jugnia et al. 2008; Barlaz et al. 2009). However, implementing such systems is costly and may not be feasible for small and medium-sized active landfills or closed landfills (Spokas et al. 2006; Börjesson et al. 2007; Sadasivam and Reddy 2014). Therefore, to capture the fugitive CH_4 emissions within these landfills, biological treatment methods can be adopted (Chiemchaisri et al., 2012).

To minimize CH_4 emissions, considerable research has focused on applying bio-based covers and/or bio-windows on landfills instead of conventional impervious covers. The bio-covers are designed and filled with suitable materials such as soil, compost, sewage sludge, etc. to facilitate CH_4 oxidation by providing a favourable habitat for naturally existing methane-oxidizing bacteria known as methanotrophs (Scheutz et al., 2009; Chiemchaisri et al., 2012; Sadasivam & Reddy, 2014). Methanotrophs, in the presence of bio-cover filling materials, can consume CH_4 produced in the landfill as their only carbon and energy source by oxidizing it with oxygen (O_2) from the atmosphere and convert it to CO_2, water, and biomass (Hanson & Hanson 1996) with lower GWP. There are significant environmental factors such as temperature, moisture content (MC), soil texture, O_2, and CH_4 supply that can regulate microbial CH_4 oxidation (Scheutz et al., 2009; Sadasivam & Reddy, 2014; Majdinasab & Yuan, 2017). Knowing the influence of these factors on CH_4 oxidation in various bio-cover materials and investigating their optimum range can be helpful to adequately exploit the bio-cover potential in promoting CH_4 oxidation, and thereby making it an optimized methanotroph habitat.

CH_4 oxidation rates in soils and composts have been documented in the last decades monitoring the effects of various environmental factors, including MC, temperature, and CH_4 concentration individually (Dunfield et al., 1993; Boeckx and Van Cleemput, 1996; Whalen and Reeburgh, 1996; Christophersen et al., 2000; Gebert et al., 2003; Scheutz and Kjeldsen, 2004; Börjesson et al., 2004;

Zeiss, 2006; Perdikea et al., 2008; Wang et al., 2011). In the above-mentioned studies, MC typically reflects a parabolic curve and its optimum level in the soil mainly remains within 10 to 20% w/w, while higher range of 30 to 50% w/w is typically found for composts due to the higher water holding capacity, high organic content, and larger specific surface area. Furthermore, the optimum temperature was around 25–35°C considering that air-filled pore volume in composts results in a higher insulating effect.

While the maximum temperature caused by the heat generation due to the active fermentation in the landfills can vary in the range of 30°C to 65°C (Yeşiller et al., 2005), higher temperature ranges from 60°C to 85°C have also been reported (Dach and Jager, 1995). This can affect the bio-cover temperature in conjunction with the heat generated due to the microbial CH_4 oxidation (Scheutz et al., 2009). Some studies reveal that temperature in the bio-covers can reach greater than 45°C in summer and affect the bio-cover performance by inhibiting microbial CH_4 oxidation (Zeiss, 2006) or make a transition in the microbial community from mesophiles to thermophiles, especially in regions with a high fluctuating seasonal climate (See Chapter 3: Berenjkar et al., 2021).

The interaction of environmental factors regulating CH_4 oxidation rate has been studied in tropical landfill cover soil (Visvanathan et al., 1999), sandy soil of a South Korean landfill (Park et al., 2005), cover soil of a boreal landfill (Einola et al., 2007), kitchen and garden waste compost (Mor et al., 2006), and aged refuse and sewage sludge (Zhang et al., 2015). However, in these studies, the interactive effect of factors on each other and on CH_4 oxidation is disregarded and the focus is primarily on the change in a single environmental factor while keeping other factors at a constant level which is typically close to the optimum range. Moreover, numerous batch experiments are typically required to be performed, and the effects are depicted by several figures that require concurrent interpretation and analyses, making it extremely time-consuming.

More recently, a series of recent studies have optimized environmental factors, such as MC, temperature, and substrate concentrations, by considering the effect of factors, alone or in combination, on the microbial CH_4 oxidation with a minimum number of experiments (Bajar et al., 2013a; 2013b; 2016; 2017). To do so, they have employed Response Surface Methodology (RSM), a multivariate method that mathematically fits the experiment domain examined in the theoretical design through response function. These studies mainly investigated subtropical Indian dumpsite soil, and the chosen range of temperature (30°C to 50°C) and MC (35 and 70%) were higher compared to tropical climate bio-cover with the typical upper limit of 45°C for temperature

and 25% for MC (Visvanathan et al., 1999). On the other hand, in cold and boreal climate conditions, the responses of CH_4 consumption to temperature variations has been determined in the temperature range from 1℃ to 20℃ (Chistophersen et al., 2000; Börjesson et al., 2004; Einola et al., 2007).

To our understanding, there have been limited studies on the effect of complex system of environmental factors on CH_4 oxidation using composts and under a Humid Continental Climate with seasonally fluctuating climatic conditions as is typical, in certain parts of southern Canada and the Central part of the USA. Therefore, in the current study, a compost mixture composed of yard waste and leaf compost (YWLC) and biosolids compost (BSC) is used with a mixing ratio of 1:4 that was found to be the optimum ratio in feasibility batch and column experiments (Niemczyk et al., 2021; Niemczyk, 2018). The interactive effect of MC (20 to 60%), temperature (17℃ to 45℃), and initial CH_4 concentration (10 to 30%) on CH_4 oxidation rate is examined using RSM to investigate their optimum levels. These factors significantly influenced CH_4 oxidation rate according to the literature (Park et al., 2005; Mor et al., 2006; Einola et al., 2007; Bajar et al., 2017; Frasi et al., 2020) and bio-cover study discussed in Chapter 3. The purpose of this study is to evaluate the multiple environmental factors that affect the CH_4 oxidation in a bio-window and substrate similar to Chapter 3 using a statistical model.

4.2. Materials and methods

4.2.1. Experimental material

Active methanotrophic compost samples were collected from a pilot bio-cover constructed in September 2016 in a closed landfill cell in Brady Road Resource Management Facility (BRRMF), which has been operating in Winnipeg, MB, Canada since 1973. The study area is representative of a Humid Continental climate (Dfb) according to the Köppen-Geiger climate classification system (Geiger, 1954; Geiger, 1961). The pilot bio-cover was filled with 0.75 m of 1:4 mixture of mature YLWC and BSC while substrate layer is underlain by 0.55 m of ½" limestone gravel as the gas distribution layer. Samples were obtained at various depths of the substrate layer from 10 to 50 cm and transferred to the lab in plastic bags. Then, they were mixed and used as a composite sample in the batch experiments. The physical and chemical characteristics, as well as the methanotrophic activity of the compost were reported in the previous studies (Niemczyk et al.,

2021; Niemczyk, 2018). The composite sample was taken in October 2018 after two years of the bio-cover operation and had possessed methanotrophic activity at both 22℃ and 45℃ (See Chapter 3: Berenjkar et al., 2021). MC of the composite sample was determined gravimetrically by drying at 105℃ for 24 h.

4.2.2. Experimental design and optimization method

RSM is a combination of several statistical and mathematical procedures to determine the relationship among design variables and helps develop, improve, and optimize a process. Furthermore, the concerned response is examined orderly and efficiently to achieve a more reliable perception with the least number of experiments. A mathematical model is generated based on the experimental methodology to define the interaction of factors. Box–Behnken Design (BBD) of RSM is a fractional factorial design obtained by combining three-level factorial designs. BBD was adopted to optimize the level of environmental factors, including MC, temperature, and initial CH_4 concentration, that significantly affect microbial CH_4 oxidation in the bio-cover (See Chapter 3: Berenjkar et al., 2021) and evaluate the CH_4 oxidation response under the interactive effect of these factors. Therefore, the BBD matrix consisted of three levels for three environmental factors, coded as (-1), (0), and (+1), indicating the low, middle, and high level, respectively. The corresponding values included 20%, 40%, and 60% for MC, 15℃, 30℃, and 45℃ for temperature, and 10%, 20%, and 30% for the CH_4 concentration. Therefore, 17 experimental runs were conducted with five replicates at the middle level (Table 4-1). The range of factors were selected according to the most frequently observed values in the field-scale pilot bio-cover throughout two years in a high seasonal fluctuating climatic environment (See Section 3: Berenjkar et al., 2021).

Table 4-1. BBD matrix to optimize environmental factors that affect CH_4 oxidation rate

Run	MC (%)	T (°C)	Initial CH_4 concentration (%)	Actual CH_4 oxidation rate ($mg.g^{-1}.d^{-1}$)	Predicted CH_4 oxidation rate ($mg.g^{-1}.d^{-1}$)
1	40	30	20	1.99	1.97
2	40	45	10	1.43	1.42
3	20	30	30	0.34	0.50
4	60	45	20	1.52	1.70
5	40	15	10	0.58	0.35
6	60	15	20	0.56	0.95
7	20	15	20	0.21	0.03
8	20	30	10	0.09	0.49
9	40	15	30	1.14	1.15
10	40	45	30	1.50	1.72
11	60	30	30	2.29	1.89
12	20	45	20	1.29	0.91
13	40	30	20	1.70	1.97
14	60	30	10	0.96	0.80
15	40	30	20	2.20	1.97
16	40	30	20	1.85	1.97
17	40	30	20	2.13	1.97

A polynomial quadratic equation describing CH_4 oxidation rate as an interactive function of environmental factors was fitted as Eq 1:

$$Y = b_0 + b_1A + b_2B + b_3C + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 + b_{12}AB + b_{13}AC + b_{23}BC \quad (4\text{-}1)$$

Where Y (CH_4 oxidation rate) was the dependent variable, A (MC), B (Temperature), and C (Initial CH_4 concentration) were independent variables, b_0 was the constant, b_1, b_2, and b_3 were the linear coefficients, b_{11}, b_{22}, and b_{33} were quadratic coefficients, and b_{12}, b_{13}, and b_{23} were the interactive coefficients. The response surfaces of the independent variables inside the experimental domain were analyzed using Design Expert software (Stat Ease, USA 11.0 trial version).

4.2.3. Model validation

To validate the developed statistical model, a series of supplementary batch incubations were conducted at the room temperature (22°C), which were not incorporated in the design matrix previously. In the incubations, the MC values were 20, 30, 40, 50, and 60%, while the initial CH_4 concentrations were 10, 20, and 30%. The MC of 30% was added to the validation tests while it was not included in the design matrix. The CH_4 oxidation rates obtained from these confirmation tests were employed to validate the statistical model.

4.2.4. Batch incubation procedures

The active compost mixture mentioned above was oven-dried at 30°C for 72 hours while the MC of dried compost was measured gravimetrically. This desiccation event was not expected to significantly impact subsequent methanotrophic activity (Ho et al., 2016). The calculated volumes of Milli-Q® water was added to adjust the MC of dry compost to 20, 40, and 60% w/w. The batch incubations were performed in 120 ml glass serum bottles (Fisher Scientific; Toronto, ON, Canada) with 2 g (w/w) of compost mixture at adjusted MC. The bottles were air tightened with 20 mm blue chlorobutyl septum stoppers (Bellco Glass Inc.; Vineland, NJ, USA) and aluminium crimp caps (Wheaton Industries; Millville, NJ, USA).

To establish the initial CH_4 concentrations of 10, 20, and 30%, the CH_4 volumes of 13.3, 30, and 51.4 ml, respectively, were injected into the sealed bottles by a gas-tight sample-lock syringe. The batch incubations were performed at 15, 30, and 45°C in the corresponding incubators.

Daily gas sampling from the headspace of the bottles and gas chromatography (GC) analysis were conducted to observe the concentration of gases until the entire O_2 was consumed in the bottles. Then, the bottles were unsealed, allowed to equilibrate with laboratory air, and re-sealed, and the initial concentration of CH_4-in-air headspace was re-established. A Varian (Agilent) 490 Micro GC with Molesieve-5A and PoraPlot U columns was used to analyze the gas concentrations in the headspace.

It is assumed that microbial CH_4 oxidation in the steady-state phase represents the long-term application of compost in the bio-cover. Therefore, the CH_4 oxidation rate was calculated and applied in the BBD model after establishment of CH_4 oxidation at a constant level for at least 14 days.

4.3. Results and discussion

In all the batch incubations, CH_4 consumption reached the steady-state phase after 2 to 3 days and sustained for 14 days. Table 4-1 presents the CH_4 oxidation rates acquired from experiments of BBD matrix as a function of MC, temperature, and the initial concentration of CH_4. Based on the combination of values of environmental factors and the obtained CH_4 oxidation rates from the experiments (Table 4-1), a multiple regression analysis was conducted to determine the coefficients in the polynomial equation (Eq 4-1) that were employed to predict the CH_4 oxidation rates by the model. The final model is depicted as the following equation:

$$Y = 1.97 + 0.43A + 0.41B + 0.28C - 0.66A^2 - 0.42B^2 - 0.39C^2 - 0.03AB + 0.27AC - 0.12BC \quad (4\text{-}2)$$

The coefficients of R^2 and adjusted R^2 were used to examine the goodness of the fit of the model. The value of R^2 was 0.88, indicating a strong correlation between actual and predicted CH_4 oxidation rates. The value of R^2 is corrected by adjusting R^2 for the number of factors in the model and the sample size. The value of adjusted R^2 could be visibly less than R^2 if the model has numerous factors, and the sample size is not large. The adjusted R^2 was 0.73, which is close to the value of R^2, reveal that the model is properly fitted to express the impact of all environmental factors on the CH_4 oxidation rate. The predicted values by BBD model for CH_4 oxidation rates are also shown in Table 4-1 that are in good agreement with actual values. To further substantiate this claim, a paired t-test was conducted in Microsoft Excel with the Null hypothesis that the mean difference between actual and predicted values in is zero. According to the paired t-Test, the test statistics (2.17E-15) was not less than -2.12 or larger than 2.12 (t Critical) so the Null hypothesis cannot be rejected. Moreover, no significant difference between the means of two groups (two tail p-value=1) was found at the confidence level of 95%. Therefore, there was no statistically significant difference between actual CH_4 oxidation rates and predicted values by BBD.

According to the signs in Eq 4-1, the factors represent positive or negative effects on the CH_4 oxidation rate, and the interaction between them can be synergistic or antagonistic. To determine the statistical significance of the impact of each factor on CH_4 oxidation and the significant interactions, ANOVA was employed with the confidence level of 95% (Table 4-2). The low p-value of the model (0.015) and the F-value of 5.76 show that the cumulative effect of all the factors in the model is significant. The lack of fit examines the adequacy of the model, and the p-value of 0.05 indicates that the model fits well, and there is no need for a more complicated model.

According to Table 4-2, A, B, and A^2 were the significant factors in the model (p-value < 0.05); MC and temperature were the most crucial factors affecting the CH_4 oxidation rate, while their interaction was the least significant (p-value = 0.87). The initial concentration of CH_4 within the studied range was not a statistically significant factor and indicates the sufficiency of CH_4 concentrations in the studied range to create a substrate-saturated environment.

Table 4-2. ANOVA for the impact of environmental factors and interactions on the CH_4 oxidation rate in BBD model

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value	
Model	7.31	9	0.81	5.76	0.0154	significant
A-MC	1.45	1	1.45	10.27	0.0150	
B-T	1.32	1	1.32	9.40	0.0182	
C-CH_4 Conc	0.61	1	0.61	4.33	0.0761	
AB	0.00	1	0.00	0.03	0.8736	
AC	0.29	1	0.29	2.08	0.1928	
BC	0.06	1	0.06	0.43	0.5308	
A^2	1.83	1	1.83	13.00	0.0087	
B^2	0.74	1	0.74	5.22	0.0562	
C^2	0.65	1	0.65	4.64	0.0683	
Residual	0.99	7	0.14			
Lack of Fit	0.82	3	0.27	6.59	0.0500	not significant
Pure Error	0.17	4	0.04			
Corrected Total	8.30	16				

R^2: 0.88; Adj R^2: 0.73; if p-value < 0.05, factors or interactions in the model are significant and if p-value > 0.05, are non-significant.

To optimize the environmental factors to obtain the highest CH_4 oxidation rate, the partial derivatives of the equation were set to zero for the corresponding factors. The actual CH_4 oxidation rates obtained from the experiments varied between 0.09 to 2.29 $mgCH_4.g_{dw}^{-1}.d^{-1}$. The highest value of CH_4 oxidation rate was attributed to MC of 60%, temperature of 30°C, and initial CH_4 concentration of 30%. This was followed by the rate of 2.20 $mgCH_4.g_{dw}^{-1}.d^{-1}$ at MC of 40%, temperature of 30°C, and initial CH_4 concentration of 20%.

To illustrate the interactions among environmental factors and the optimum level of CH_4 oxidation rate, the 3D response surfaces and iso-response contours obtained from the quadratic equation are plotted. The contour shapes reflect the extent of the interaction among environmental factors;

elliptical and circular contours indicate strong and negligible interactions, respectively. The response surface plots for the CH_4 oxidation rate are displayed in Figs. 4-1 to 4-3. To demonstrate the interactions among environmental factors and their combined effect on the CH_4 oxidation rate, one factor is held constant at its middle level (level 0) in the plots, and the other two factors were changed within their designated range as expressed in section 2.2.

The interactive effect of MC (A) and temperature (B) on CH_4 oxidation rate (Y) at constant initial CH_4 concentration of 20% is illustrated in Figure 4-1. The CH_4 oxidation rate with both MC and temperature shows a parabolic curve with optimum value around 50% and 33°C, respectively, that are in congruence with similar studies of different compost materials (Mor et al., 2006; Perdikea et al., 2008; Pedersen et al., 2011).

At higher values of MC and temperature, the CH_4 oxidation rate slightly decreased; however, at lower values, the decrease was more substantial, indicating that low MC and temperature had more negative effect on CH_4 oxidation rate than their higher values. The simultaneous parabolic behaviour with MC and temperature was reported in previous studies on soils at lower range of MC but similar range of temperature (Visvanathan et al., 1999; Park et al., 2005) and on composts with similar range of MC and temperature (Mor et al., 2006). It can be concluded that, with the current compost mixture, the response of CH_4 oxidation rate to temperature increases with MC until it reaches the optimum level, and the lowest CH_4 oxidation rate occurs at the lowest levels of MC and temperature. However, opposite patterns were reported in other studies on subtropical dumpsite soils with similar range of MC, temperature, and initial CH_4 concentration (Bajar et al., 2013a), and on cover soil of a boreal landfill with lower range of MC (7-34%) and temperature (1-19°C) (Einola et al., 2007).

Results indicate that the CH_4 oxidation rate at high MCs with the current compost mixture can support CH_4 oxidation recovery in the early spring in the study area, having long-lasting high snow precipitation in winter that infiltrates into the bio-cover in early spring and causes a high MC of 40% to 50% in the compost matrix at the temperature of 15°C to 30°C (See Chapter 3: Berenjkar et al., 2021). This resilience has been observed in methanotrophic communities from rice paddies accustomed to cycles of desiccation and rewetting (Ho et al., 2016). Moreover, knowing that composts have a high moisture-holding capacity (Perdikea et al., 2008; Pedersen et al., 2011) and microbial CH_4 oxidation is a water producing process, the compost mixture shows the ability to achieve high CH_4 oxidation rate under high MC in summer, when there is an increase in the bio-

cover temperature up to 45°C due to the increased ambient temperature and heat generation from the landfill (See Chapter 3: Berenjkar et al., 2021).

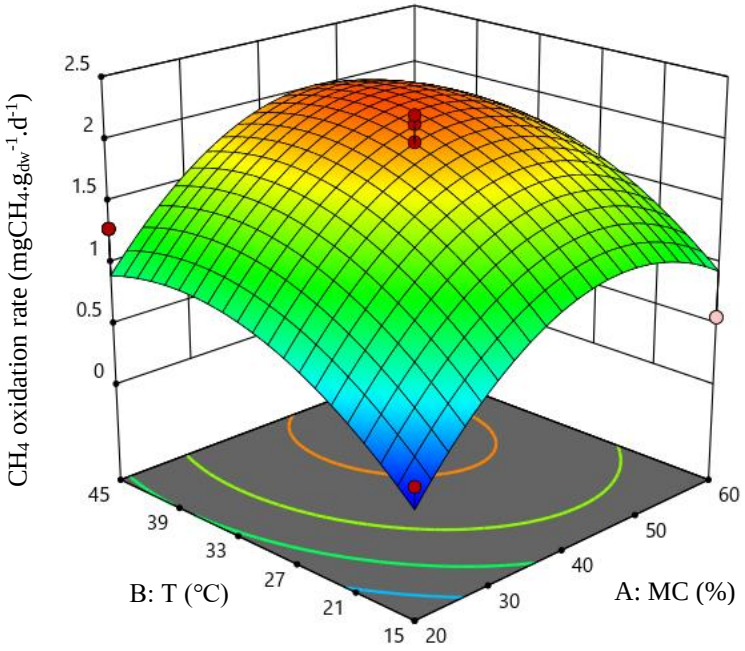

Figure 4-1. Response surface plot illustrating the interactive effect of MC and temperature on CH_4 oxidation rate at constant initial CH_4 concentration of 20%.

The interactive effect of MC (A) and initial CH_4 concentration (C) on CH_4 oxidation rate (Y) at constant temperature of 30°C is illustrated in Figure 4-2. The compost mixture can sustain gas-filled porosity at high MC as previously reported in other studies (Huber-Humer 2004; Perdikea et al., 2008; Pedersen et al., 2011). The current results show that an increase in MC and initial CH_4 concentration increases CH_4 oxidation rate. This increase is accelerated at high initial concentrations of CH_4 (>25%) as an increase from 10% to 30% can increase the CH_4 oxidation rate to 136% at MC of 60% and temperature of 30°C. However, at low MCs, CH_4 oxidation rate showed a horizontal function indicating no significant difference in CH_4 oxidation rate under various initial CH_4 concentrations and MC of 10%, which was enough to sustain CH_4 oxidation by methanotrophs in the compost mixture. The high CH_4 oxidation rate established at an elevated initial concentration of CH_4 reveals that the current compost mixture can be a potential carbon sink in the study area with high CH_4 flux (See Chapter 3: Berenjkar et al., 2021). ANOVA confirmed that MC is a more significant factor than the initial CH_4 concentration. In addition, Figure 2 shows that the effect of a decrease in the CH_4 oxidation rate caused by low MC was a higher contributor

than that caused by the low initial concentration of CH_4, and the contribution of MC is more significant. Moreover, the circular contour plots confirm the poor interaction for the entire range of MC and initial CH_4 concentration.

In the similar study, a high rate of CH_4 oxidation in subtropical dumpsite soils was reported at CH_4 concentration of 10% and MC of 50% (Bajar et al., 2013a), while in their latest studies, with and without adding agricultural amendments, the highest CH_4 oxidation rate was observed at the highest level of CH_4 concentration (30% to 40%) at the fixed MC of 30% (Bajar et al., 2016; 2017).

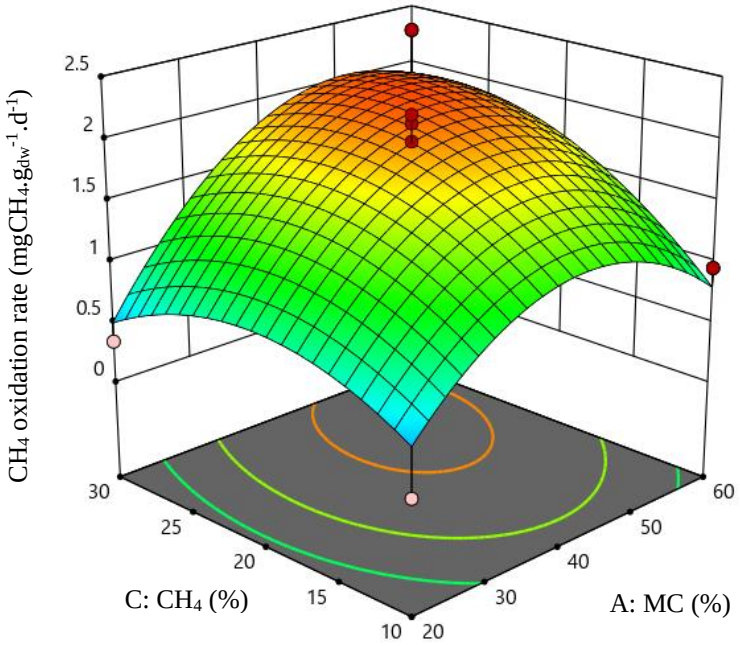

Figure 4-2. Response surface plot illustrating the interactive effect of MC and initial CH_4 concentration on CH_4 oxidation rate at constant temperature of 30°C.

The interactive effect of temperature (B) and initial CH_4 concentration (C) on CH_4 oxidation rate (Y) at constant MC of 40% is illustrated in Figure 4-3. The increased CH_4 oxidation rate can be explained by the increased methanotrophic activity with the temperature further promoted by the CH_4 concentration supply. While there was a rapid increase in CH_4 oxidation rate with an increase in the initial CH_4 concentration from 10% to 30%, there was no significant difference in CH_4 oxidation rate with initial CH_4 concentration shifting from 20% to 30%. At high initial CH_4 concentrations, the impact of temperature on methanotrophic activity was substantial, resulting in an elevated CH_4 oxidation rate. This finding was also reported with a similar range of temperature elsewhere (Zhang et al., 2000; Börjesson et al., 2004; Park et al., 2005). The highest CH_4 oxidation

rate is observed at middle range of initial CH_4 concentration and the optimum temperature range of 30℃ to 35℃ (Börjesson et al., 2004; Bajar et al., 2017). However, a further increase in temperature up to 45℃, slightly decreased the CH_4 oxidation rate, which is a different outcome from previous studies showing that at temperatures beyond 30℃ there was a declining trend in CH_4 oxidation rate. Park et al. (2005) reported a 33% decrease in CH_4 oxidation rate with temperatures increasing from 30℃ to 40℃. Spokas and Bogner (2011) and Bajar et al. (2017) also reported an increase in methanotrophic activity up to 30℃ followed by a decreasing phase at higher temperatures up to the maximum tested values of 55℃ and 40℃, respectively. This finding proves that the current compost mixture can sustain CH_4 oxidation in landfills at their active fermentation phase when there is heat generation with high CH_4 flux, confirming the observations from the studied area (See Chapter 3: Berenjkar et al., 2021). Moreover, further studies on the community analyses of the methanotrophs in the compost mixture are required to verify the availability of thermophilic methanotrophs in the landfill environment. While most of the well-studied methanotrophs are mesophiles (Hanson & Hanson, 1996), various species of moderate thermophiles growing optimally between 50℃ and 55℃ have been recently isolated from tropical soils (Islam et al., 2016). Thermophilic methanotrophs from the phylum Verrucomicrobia are active from 45℃ to 60℃ and have been found in surface geothermal features with acidic conditions (Dunfield et al., 2007; Pol et al., 2007; Islam et al., 2008; Carere et al., 2017).

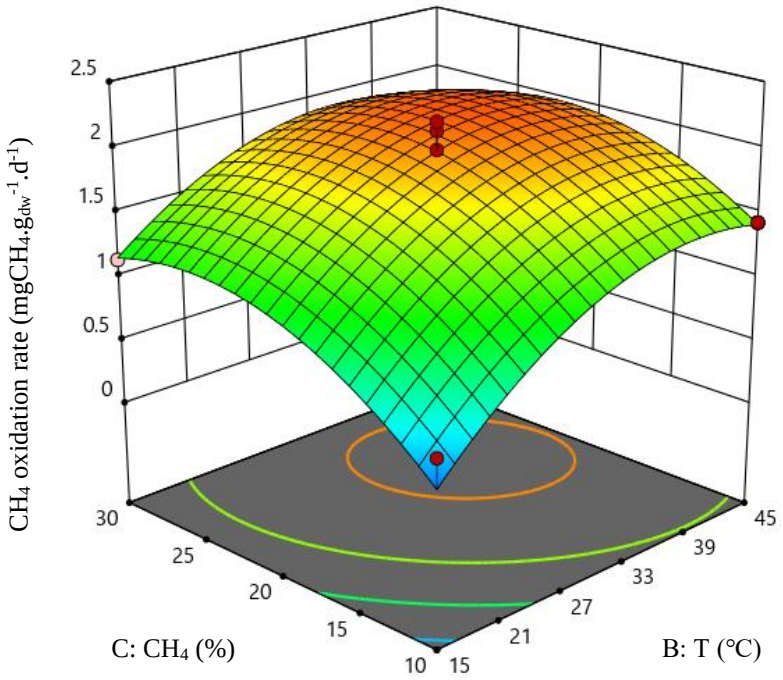

Figure 4-3. Response surface plot illustrating the interactive effect of temperature and initial CH_4 concentration on CH_4 oxidation rate at constant MC of 40%.

The maximum value of CH_4 oxidation rate obtained from the design model was 2.20 $mgCH_4.g_{dw}^{-1}.d^{-1}$ at the optimum MC of 47.42%, temperature of 32.72°C, and initial CH_4 concentration of 23.81% that are close to the values obtained from the experiments (Table 4-1). Table 4-3 compares the maximum CH_4 oxidation rate in the current compost mixture under optimized environmental conditions with other recent studies that have used different types of compost. The CH_4 oxidation rate in the current compost mixture is within the range obtained by previous research and higher than half of the reported values.

Table 4-3. Maximum CH_4 oxidation rate in different types of compost used in the bio-covers

Compost type	CH_4 oxidation rate ($mgCH_4.g_{dw}^{-1}.d^{-1}$)	Reference
YWLC and BSC (1:4)	2.20	Current study
Garden waste compost (passively aerated)	1.13	Mor et al. (2006)
Garden waste compost (intensively aerated)	2.53	Mor et al. (2006)
Leaf/manure compost	0.12	Perdikea et al. (2008)
Raw compost (1 year old)	0.60	Pedersen et al. (2011)
Fine compost	1.10	Pedersen et al. (2011)
Screening compost (1 year old)	0.45	Pedersen et al. (2011)
Sewage sludge compost	3.41	Pedersen et al. (2011)
Mature and Stable compost	0.36	Scheutz et al. (2011)
Sewage sludge compost	5.78	Zhang et al. (2015)

To validate the model (Eq 1), 15 supplementary batch incubations were conducted to obtain the CH_4 oxidation rates at 22℃, considering the MC and initial CH_4 concentrations within the experimental range. The experimental results of MC, temperature, and initial CH_4 concentrations obtained from the batch incubations were then used in the model (Eq 1) to compare with the predicted rates. A paired t-Test was used to investigate statistically significant differences between the experimental results and predicted values.

The interactive effect of MC and initial CH_4 oxidation rate at 22℃ is illustrated in Figure 4-4 comparing the CH_4 oxidation rates obtained from experimental batch incubations with predicted values by the model. As previously shown, the CH_4 oxidation rate shows a parabolic curve with the increase in MC. Moreover, there is no significant difference in CH_4 oxidation rates at 20% and 30% initial CH_4 concentrations, and at low MC of 20%, the initial CH_4 concentration does not significantly affect the CH_4 oxidation rate.

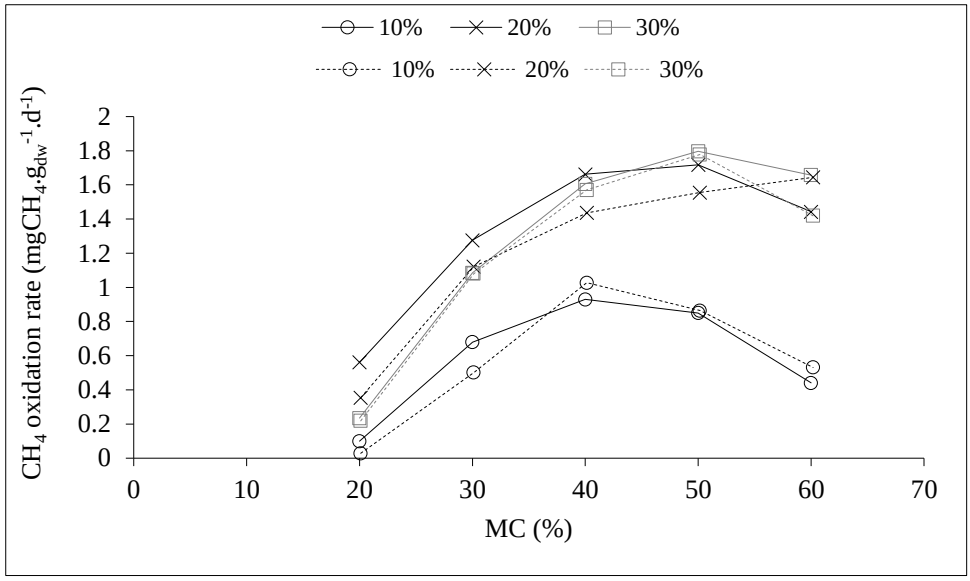

Figure 4-4. The interactive effect of MC and initial CH_4 concentration at 22°C for experimental CH_4 oxidation rate (dashed line) and predicted values by model (solid line).

The experimental and predicted values showed a good agreement with an R^2 of 0.99, indicating the high accuracy of the model. Moreover, according to the paired t-Test, the mean difference between experimental and predicted values was zero, and with the confidence level of 95%, there was no significant difference between the means of two groups (two tail p-value=0.95). Therefore, there was no statistically significant difference between CH_4 oxidation rates obtained via supplementary batch incubations and the predicted values.

4.4. Conclusion and recommendations

The interactive effect of significant environmental factors, including MC, temperature, and initial CH_4 concentration, on CH_4 oxidation rate in the compost mixture of yard waste and leaf compost (YWLC) and biosolids compost (BSC) with the mixing ratio of 1:4 was studied through batch incubations. To optimize the environmental factors and maximize the CH_4 oxidation rate, Box–Behnken Design (BBD) of Response Surface Methodology (RSM) was employed, and a statistical model was developed based on the experimental results of batch incubations. Successful results from supplementary batch tests confirmed to the validity of the model.

MC and temperature were the most significant factors influencing CH_4 oxidation rate. However, the initial CH_4 concentration and the interaction between factors was not significant. High CH_4 oxidation rate was found at high MC and high initial CH_4 concentration. The increase in

temperature from the optimum level slightly reduced the CH_4 oxidation rate. Furthermore, the lowest CH_4 oxidation rate occurred at the lowest MC, temperature, and initial CH_4 concentration. The optimum predicted values for MC, temperature, and initial CH_4 concentration were 47.42%, 32.72℃, and 23.81%, respectively, yielding CH_4 oxidation rate of 2.20 $mgCH_4.g_{dw}^{-1}.d^{-1}$.

Therefore, the current mixture is suitable for bio-covers in landfills at the early stages of fermentation and where the bio-cover is subjected to high temperature and high CH_4 flux. Moreover, it seems that the current compost mixture, as it was obtained from a pilot bio-cover accustomed to fluctuations in temperature (15℃ to 45℃) and MC (20% to 60%), selected for a mixture of methanotrophs capable of effective operation at a wide range of temperatures and MCs, and it can fairly support CH_4 oxidation recovery in the early spring under high MC and low temperature. Overall, this study showed the suitability and applicability of the investigated compost mixture in a high seasonally fluctuating climate condition and provided the maximum CH_4 oxidation potential under optimum levels of environmental factors.

For future work, the community analyses and investigation on the existence of thermophilic methanotrophs in the compost matrix of the bio-cover is recommended. Moreover, conducting flow-through column tests filled by the compost matrix implementing optimum values for MC and temperature obtained from the current study is recommended. The effect of increasing O_2 accessibility in the deeper layers of the compost matrix can also be explored in the column tests to adequately exploit the entire depth of the bio-cover.

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Chapter 5: Enhancement of methane oxidation in bio-based landfill covers by increasing porosity

Abstract

To simulate an increase in the oxygen (O_2) penetration to the deeper layers of a methanotrophic landfill bio-cover, two different sizes of gravel (¼" and ½") were added to a compost and applied as packing material in the flow-through column tests employing synthetic landfill gas of 50/50 v/v methane to carbon dioxide (CH_4/CO_2) ratio with flow rate of 12 $ml.min^{-1}$. The mixing ratios of gravel to compost (1:1, 1:3, and 1:7) were established in three consecutive stages (I, II, and III) in series instead of running separate columns for each mixing ratio. The performance of the bio-cover varied with gravel size and mixing ratio. At ¼" gravel to compost ratio (1:1) and ½" gravel to compost ratios (1:3 and 1:7), 100% CH_4 removal occurred by CH_4 adsorption as there was 0 $g.m^2.d^{-1}$ CO_2 production and no change in the moisture content (MC) at the end of the stage. While a sudden increase in the CH_4 flow rate at the end of the experiment for ½" gravel to compost ratio (1:7) stimulated the methanotrophic activity, the CH_4 removal rate did not exceed 55%. However, in other packings, CH_4 removal achieved by methanotrophs allowed an increase in the MC in the packing material, and higher CO_2 production than the stoichiometric ratio for CH_4 oxidation indicating heterotrophic activity. The highest methanotrophic CH_4 removal rate of 248 $g.m^2.d^{-1}$ corresponding to the removal efficiency of 65% was obtained for ¼" gravel to compost (1:7) with the highest portion of compost and the lowest amount of gravel. The kinetics of CH_4 oxidation demonstrated the maximum value of V_{max} to be 3.98 $mg.g^{-1}.d^{-1}$, which was also obtained for (1:7) ¼" gravel to compost mixture.

Keywords Methanotrophs, Column test, CH_4 removal rate, Compost, Gravel

5.1. Introduction

Waste industries and landfilling are responsible for 22.7% (1.7-2.3 $GtCO_2$-eq yr^{-1}) of global human-made methane (CH_4) emissions (IPCC, 2013). Landfilling has been extensively used for waste disposal as a low cost and simple method. After organic waste placement in the landfill, the biodegradation processes start, and under anaerobic conditions landfill gas (LFG) is produced that typically consists of 55-60% v/v CH_4 and 40-45% v/v carbon dioxide (CO_2) (Ayalon et al., 2001; Börjesson et al., 2001; Jugnia et al., 2008).

CH_4 oxidation in the landfill covers can significantly reduce CH_4 emissions. CH_4 emission to the atmosphere can be reduced extensively by promoting CH_4 oxidation in the landfill cover soils. As a low-cost method with minimal environmental impacts, bio-treatment of CH_4 in the landfill covers has recently been implemented in old and low CH_4 flow landfills, where gas collection and flaring are not cost-effective and unfeasible (Scheutz et al., 2009a). CH_4-oxidising bacteria or methanotrophs are broadly used in biotreatment technologies to remove fugitive emissions of CH_4 (Perdikea et al., 2008; Farrokhzadeh et al., 2017; La et al., 2018; Niemczyk, 2018). Methanotrophs are aerobic bacteria that consume CH_4 as the sole carbon and energy source and generate CO_2, water, and biomass as by-products of the bio-oxidation process (Hanson and Hanson, 1996).

Establishing bio-cover systems on top of the landfills is another bio-treatment technology that can facilitate CH_4 oxidation, reducing GHG. In the bio-covers, aerobic methanotrophs existing in the substrate layer can oxidize the CH_4 from the LFG with oxygen (O_2) from the atmosphere. The layer is placed on top of a gas distribution layer (GDL) normally consisting of coarse materials (Gebert and Groengroeft, 2006; Stern et al., 2007; Philopoulos et al., 2008; Roncato and Cabral, 2012; Pecorini and Iannelli, 2020; Chapter 3: Berenjkar et al. 2021).

In the landfill bio-covers, O_2 penetration typically occurs by passive aeration, which is controlled by the pressure difference between the bio-cover and atmospheric air as well as diffusion (Scheutz et al., 2009b). However, there could be restrictions for air penetration, due to frost formation, pressure drop, high influx, material compaction, water logging, clog formation, etc., which can decrease bio-cover efficiency (Hilger et al., 2000; Wilshusen et al., 2004; Poulsen and Møldrup, 2006; Chapter 3: Berenjkar et al. 2021).

Despite the top layers in a bio-cover that are exposed to drying by wind and solar radiation, deeper layers have more stable moisture content (MC) and temperature. Therefore, air penetration to the deeper layers of the bio-cover can be beneficial in improving CH_4 oxidation (Scheutz et al., 2009a).

Moreover, increasing air diffusion at below-freezing depths of the bio-cover can be a promising approach towards CH_4 oxidation during the treatment season in cooler continental climates, especially in active high temperature landfills.

Numerous studies report that composts are valuable bio-cover substrates to support the growth and activity of methanotrophs because of their porosity, water holding capacity, temperature regulation ability, and nutrient abundance (Hilger and Humer, 2003; Huber-Humer, 2004; Perdikea et al., 2008; Pedersen et al., 2011; Zhang et al., 2015). However, composts are less structurally stable and more susceptible to compaction than granular materials when utilized in bio-covers. Therefore, the porosity of the compost can reduce over time, restricting O_2 diffusion to the bottom layers of the bio-cover. Addition of coarse materials as amendments can reduce compaction and clogging of substrate layers (La et al., 2018).

Gravel is an inert inorganic coarse material that can increase the porosity of the substrate material and transfer more O_2 to the deeper layers. It can also impact moisture holding capacity, modulate MC, and increase aeration. Gravel has mostly been used as a GDL in the bio-covers to homogenously distribute LFG (Gebert and Groengroeft, 2006; Stern et al., 2007; Roncato and Cabral, 2012; Pecorini and Iannelli, 2020; Berenjkar et al., Under review); however, to our knowledge, it has not been used for increasing the porosity in the substrate layer to facilitate the air penetration. Few laboratory scale studies on active aeration of biofilters have been carried out to enhance biological treatment of CH_4 emissions in composts or granular media using flow-through column tests (Streese and Stegmann, 2003; Haubrichs and Widmann, 2006; Haththotuwa et al., 2012; Farrokhzadeh et al., 2017). However, due to the propensity of such systems to high O_2 availability and bio-oxidation processes, EPS formation and biomass production is observed that can impede gas penetration and reduce the performance of the biofilter (Farrokhzadeh et al., 2017; La et al., 2018).

The current study intends to incorporate gravel with the biosolids compost (BSC) and yard waste and leaf compost (YLWC) mixture (4:1) as a substrate layer within a landfill bio-cover to mitigate CH_4 emissions; thus, column experiments are employed in the laboratory to evaluate the potential enhancement of CH_4 oxidation at deeper layers within the bio-cover.

This study will be phase four of a continuing body of work. The preliminary laboratory-scale studies revealed the benefit of mixing the two composts and their optimum mixing ratio which is 4:1 BSC to YWLC (Niemczyk et al., 2021; Niemczyk, 2018). The field application of the

optimized compost mixture revealed significant seasonal fluctuations in temperature and soil MC in addition to a high CH_4 load affecting the performance of the bio-cover (See Chapter 3: Berenjkar et al., 2021). Therefore, the interactive effect and the optimum values of environmental factors were investigated to maximize CH_4 oxidation rate (See Chapter 4). Moreover, in the *in situ* bio-cover, low air diffusion into the bio-cover, a thick, solid winter frost cover affecting gas exchange, and cold ambient temperature in winter were influencing the efficiency of CH_4 oxidation. The concentrations of the gases in the vertical profile of the bio-cover showed that CH_4 oxidation was mostly occurring at the top 20 cm due to low O_2 diffusion, indicating that the entire capacity of the bio-window was not being used (See Chapter 3: Berenjkar et al., 2021). Therefore, such field studies need to be supplemented with in-depth laboratory studies to establish high CH_4 loads and increase O_2 access for methanotrophs throughout the entire depth of the substrate layer to increase the bio-cover performance and adequately exploit its CH_4 removal efficacy. While batch incubations can evaluate parameters influencing CH_4 oxidation in a short time, longer term column tests can better replicate landfill dynamics, thereby assessing long-term performance of bacterial CH_4 oxidation (Niemczyk et al., 2021; Niemczyk, 2018).

In the current study, column and batch tests are conducted using compost samples collected from the *in situ* bio-cover to improve its performance pertaining to air diffusion. The experiments will investigate if increasing the porosity in terms of gravel size and mixing ratios can result in high CH_4 oxidation efficiency in the laboratory.

It is anticipated that the results of this study will provide valuable design parameters for the optimization of compost-based bio-covers for widespread application in terms of the optimum mixing ratio for compost and gravel and the depth of placing the mixture in the bio-cover layer.

5.2. Materials and methods

5.2.1. Column filling materials

In October 2016, a bio-window, measuring 3.5 m × 2.5 m, was excavated to the depth of the waste mass (1.25 m) within the final clay cover of an existing landfill at the Brady Road Resource Management Facility (BRRMF), Winnipeg, MB, Canada. The bio-window was filled with 0.7 m of 1:4 mixture of mature YLWC and BSC as substrate layer underlain by 0.55 m of limestone gravel as GDL. Compost samples were collected from the bio-window at various depths and mixed

to achieve a compound sample. Limestone gravel in two different sizes of ¼" and ½" were added to the collected compost and the mixtures were used to fill the columns.
The physical and chemical characteristics of the compost were reported in the previous studies (Niemczyk et al., 2021; Niemczyk, 2018; Berenjkar et al., Under review).

5.2.2. Description of column tests

Two different column tests were operated to provide better aeration for the deep layers of the column. The first column trial, Column 1, was packed with a mixture of collected compost at an *in situ* MC of 47% and ¼" clean limestone gravel to increase the overall porosity and permeability of the compost to gas flow. The second column trial, Column 2, was packed similarly with ½" clean limestone gravel. The results of control column, containing only compost, was reported in a separate study (Niemczyk, 2018), and will be compared to the results of the current column design. For the efficient use of time, sources, and operational conditions, the experiments were performed under three different stages in series; the gravel addition started with 1:1 gravel to compost volume ratio and after reaching steady-state conditions for at least 14 days (La et al., 2018), the volume ratio was decreased to 1:3 and then 1:7 by replacing 50% of the medium by fresh compost. Operation, dismantling, and medium replacement for each column was repeated until the system became unstable for a total of three stages (i.e. when it is no longer possible to achieve steady-state CH_4 oxidation for at least 14 days).
Column experiments in preliminary studies with the packing material of 4:1 BSC to YWLC mixture showed that air penetration was prominent at the top 15 cm where most of the CH_4 oxidation occurred (Niemczyk, 2018). Furthermore, the field-scale measurements of the vertical profile of the gases in the bio-window showed air penetration to the upper 20 cm layer (Berenjkar et al., Under review). Therefore, in the current column work, the top 15 cm only contained the compost, and gravel was added at the depth below 15 cm. Thus, the MC of the top layer was not affected by gravel addition.

As gravel can affect the water holding capacity of the filling materials, at the end of each stage, MC was measured gravimetrically by drying the sample at 105°C for 24 h that were collected every 10 cm from vertical profile of the columns. This can further substantiate the relationship among gravel to compost mixing ratio, MC, and CH_4 oxidation efficiency.

5.2.3. The design and setup of the column tests

The columns were constructed from PVC tubing (B. A. Robinson Co. Ltd; Winnipeg, MB), which was 90 cm high, 15 cm in diameter, and 0.6 cm in thickness. A removable lid with 6" Stainless Steel Clamps (Everflow EVERCONNECT 1760) was applied to guarantee a gas-tight seal at the top of the columns. The bottom of the columns was permanently glued to a PVC plate.

In the vertical profile of the columns, 14 sampling ports were situated every 5 cm and were equipped with 3/8"-thick silicone septa (Cole-Parmer) to facilitate gas sample collection by a syringe needle. The packing of the column included 12 cm of ½" limestone gravel as gas distribution layer (GDL) stacked by 45 cm of compost and gravel mixture in the middle of the column and 15 cm of compost at the top. At the interface of each layer, a stainless-steel fine wire mesh was used to prevent mixing. The filling material was compacted by hand in 5-10 cm layers. The synthetic LFG containing 50/50 v/v CH_4/CO_2 (Praxair Canada Inc.; Mississauga, ON) was supplied from a port located below the GDL. To homogeneously deliver the synthetic LFG to the GDL, a stainless-steel coarse wire mesh was installed 1 cm above the base of the column providing an empty space for synthetic LFG to accumulate before going up to the GDL. The flow rate of synthetic LFG was 12 $ml.min^{-1}$, which corresponds to a CH_4 flux of 372 $g.m^{-2}.d^{-1}$ that is higher than the reported range fluxes in the field (Bogner et al., 1997), and within the range of reported high CH_4 loads of 280 $gCH_4.m^2.d^{-1}$ (Hilger et al., 2000), 300 $gCH_4.m^2.d^{-1}$ (Frasi et al., 2020), and 520 $gCH_4.m^2.d^{-1}$ (Wilshusen et al., 2004) in the column tests.

At the top of the columns, an inlet for air and an outlet for effluent gas were positioned. Air was passed tangentially over the column at a flow rate of 200 $ml.min^{-1}$ to simulate a light wind blowing over the cover, promoting the diffusive ingress of oxygen into the compost.

The synthetic LFG and air flow to the column and the outflow of the gas at the column outlet were controlled using valved variable area flowmeters (Omega Environmental; St-Eustache, QC). The plastic hose with 3/8" internal diameter was used for the tubing. Figure 5-1 shows the schematic of the column setup.

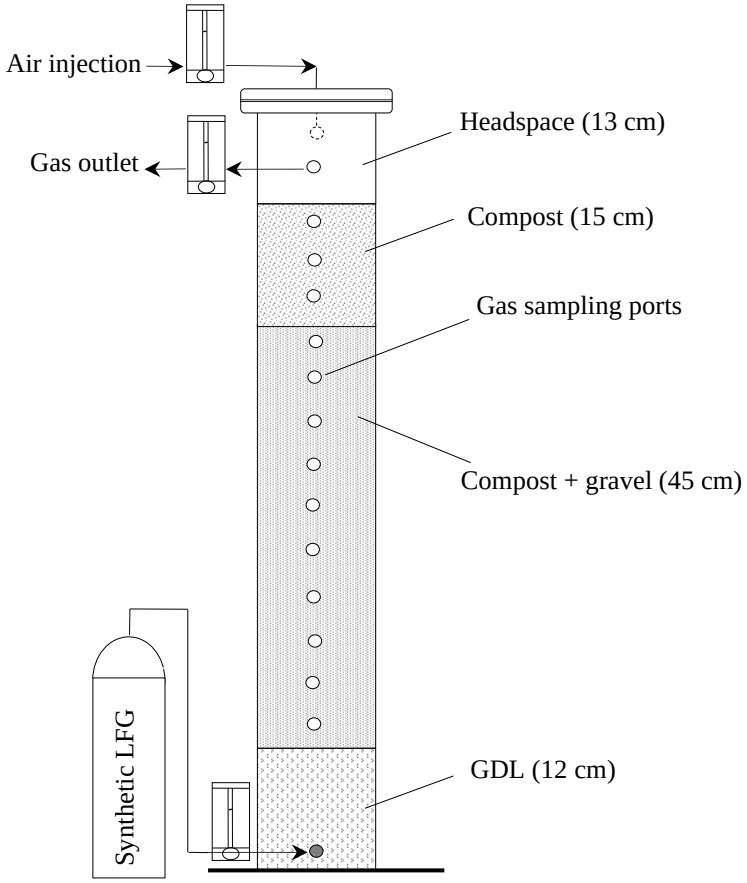


Figure 5-1. Schematic of the column experiment set-up

5.2.4. The experimental process of the column tests

The column experiments were performed at a standard laboratory temperature of 22°C under a fume hood to secure proper gas ventilation in the Environmental Engineering and Microbiology Laboratories at the University of Manitoba.

At the beginning of each stage of the column experiment, the columns were flushed with the synthetic LFG at the flow rate of 12 $ml.min^{-1}$. Then, gas samples were taken from the ports in the vertical profile of the columns. Once there was no air detected in the pore volume of the filling materials, the columns were solely filled by the synthetic LFG and the accurate gas concentrations were acquired in the entire vertical profile of the column before introducing tangential air. Then, the air was injected with flow rate of 200 $ml.min^{-1}$, and gas sampling was conducted daily, starting from the day 1, from the column outlets and all sampling ports.

The gas samples were analyzed through gas chromatography using a Varian (Agilent) 490 Micro GC with Molesieve-5A and PoraPlot U columns to determine the variations in the concentrations of CH_4, CO_2, and O_2 due to the microbial activity in the vertical profile of the columns. The summation of concentrations of these gases plus N_2 should add up to 100%, which was used to calculate the concentration of N_2.

The performance of the columns in terms of CH_4 removal efficiency (R.E.) (%), CH_4 removal rate (R.R.) ($g.m^{-2}.d^{-1}$), and CO_2 production rate ($g.m^{-2}.d^{-1}$) was evaluated using the following equations (Perdikea et al., 2008; La et al., 2018):

$$CH_4R.E. = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100\% \quad (5\text{-}1)$$

$$CH_4R.R. = \frac{Q_{in}.[CH_4]_{in} - Q_{out}.[CH_4]_{out}}{A} \quad (5\text{-}2)$$

$$CO_2Prod.R. = \frac{Q_{out}.[CO_2]_{out} - Q_{in}.[CO_2]_{in}}{A} \quad (5\text{-}3)$$

Where $[CH_4]_{in}$ and $[CH_4]_{out}$ are the CH_4 concentrations at the inlet and outlet of the columns, respectively ($g.m^{-3}$), $[CO_2]_{out}$ and $[CO_2]_{in}$ are the CO_2 concentrations at the outlet and inlet of the columns ($g.m^{-3}$), Q_{in} and Q_{out} represent the flow of synthetic LFG entering the bottom of the column and the gas flow in the column effluent, respectively ($m^3.d^{-1}$), and A is the cross section of the column (m^2).

5.2.5. Determining kinetic parameters and MC

After completion of each stage of the experiment, the columns were dismantled, and compost was sampled every 10 cm. The samples were mixed, and then examined in batch incubations considering several proportions of CH_4 to air headspaces of 1%, 2%, 4%, 6%, 8%, 10%, and 12%. Therefore, the kinetic parameters and the potential activity of methanotrophs in the compost was determined. The procedure to conduct the batch tests was adopted from Niemczyk et al. (2021) and Chapter 3.

The methane oxidation kinetics is commonly described by the Michaelis–Menten equation, which is widely used to model the single substrate enzyme kinetics. The equation is:

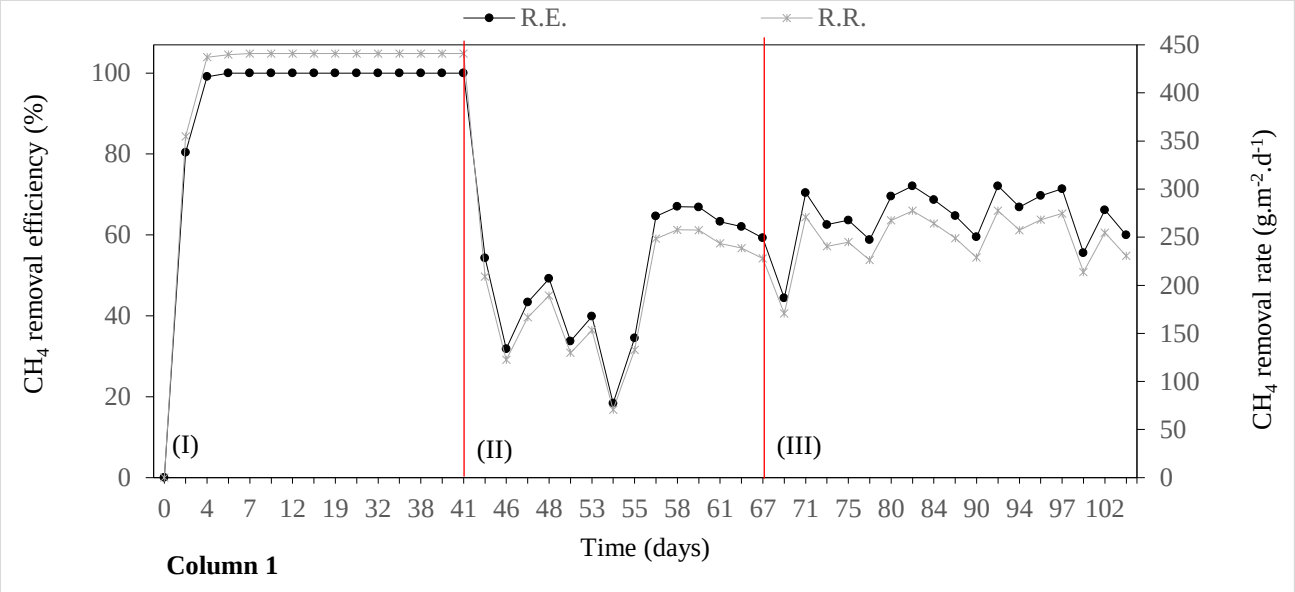
$$r_{CH4} = -\frac{V_{max}.[CH_4]}{K_m + [CH_4]} \quad (5\text{-}4)$$

Where r_{CH4} ($mg.g^{-1}.d^{-1}$) is CH_4 oxidation rate, V_{max} is maximum CH_4 oxidation rate ($mg.g^{-1}.d^{-1}$), $[CH_4]$ is CH_4 concentration (ppm), and K_m is Michaelis–Menten (half saturation) constant (M). K_m indicates the CH_4 concentration at which the removal rate is half of its maximum value. To calculate the r_{CH4}, linear regression of CH_4 consumption with time was adopted, while V_{max} and K_m were obtained by employing a nonlinear regression in Microsoft Excel.

5.3. Results and Discussion

5.3.1. The effect of gravel size and gravel to compost mixing ratio on CH_4 oxidation

The effect of gravel sizes (¼" and ½") and volume mixing ratios for gravel to compost was investigated at three consecutive stages as shown in Figure 5-2. Stage (I) included gravel to compost ratio of 1:1 that was performed from day 1 to 41, Stage (II) included gravel to compost ratio of 1:3 that was performed from day 43 to 67, and Stage (III) included gravel to compost ratio of 1:7 that was performed from day 69 to 103. The description of the results is presented in the following sections.



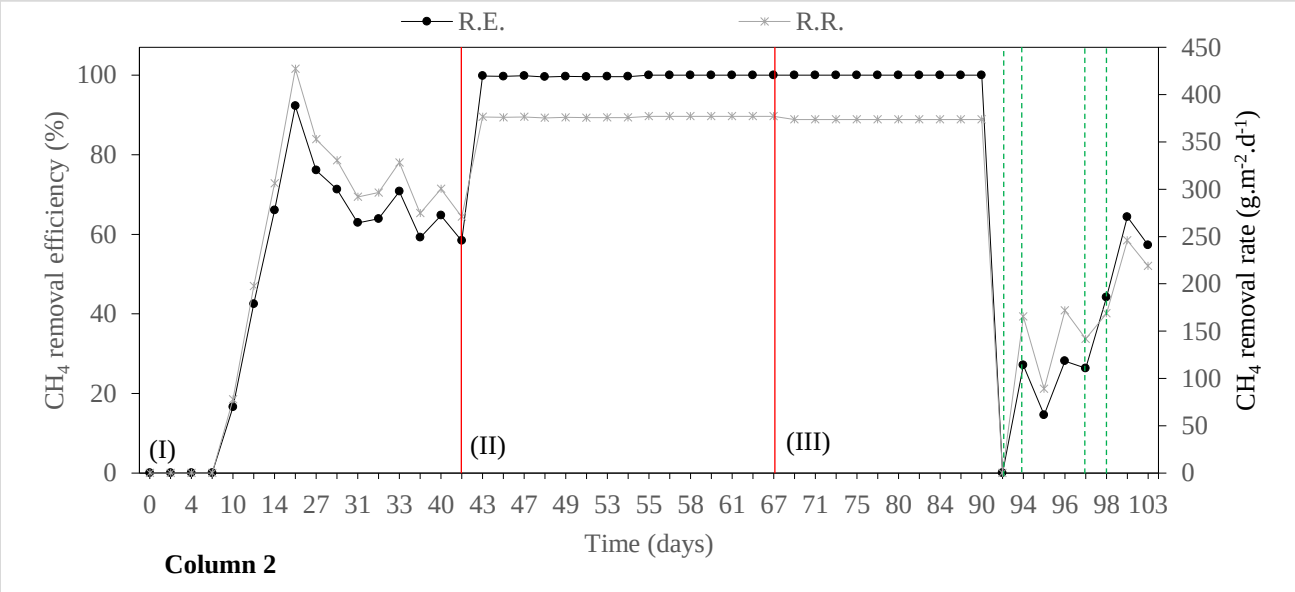


Figure 5-2. CH_4 removal efficiency and removal rate during the three stages of the experiment in Column 1 (¼" gravel and compost mixture) and Column 2 (½" gravel and compost mixture). Solid lines show the end of each stage. Dashed vertical lines show the days when CH_4 flow rate was set to 25, 20, 18, and 12 $ml.min^{-1}$ in order.

5.3.1.1. Stage (I): column testing of 1:1 gravel to compost mixing ratio from day 1 to 41

According to Figure 5-2, in Column 1, CH_4 removal started from day 1, and after a lag time of three days, CH_4 oxidation efficiency reached the maximum of 100% and remained steady until the end of Stage (I). However, in Column 2, no detectable CH_4 oxidation was observed during the first four days, and the maximum oxidation rate of 92% was achieved on day 19, when condensation

at the headspace of the column was observed and sustained nearly to the end of Stage (I). The condensation adversely affected the CH_4 oxidation efficiency that decreased from day 19 to 31 and slightly fluctuated until day 41 henceforth. The condensation can implicitly reflect the methanotrophic activity in Column 2. The CH_4 oxidation by methanotrophs is an exothermic process producing heat and water (Jugnia et al., 2008; Pawłowska, 2010). The reduction in CH_4 oxidation efficiency can be due to the saturation of the packing material by produced water and condensed water vapor that filled the pore space of the packing material and restricted mass transfer of CH_4 in the biofilm. However, it was observed that a considerable volume of the condensed water vapour started to discharge from the outlet of the column from day 31, causing slight fluctuations from 60% to 70% in CH_4 oxidation efficiency until the end of Stage (I) that can be due to the restoration of the pore space. In a study conducted by La et al. (2018), condensation in the column test also reduced the performance of a biofilter while using active aeration with the packing material of 1:1 mixture of compost and lava rock/biochar.

5.3.1.2. Stage (II): column testing of 1:3 gravel to compost mixing ratio from day 43 to 67

The columns were dismantled on day 41, and samples were taken every 10 cm from the medium for kinetic test and MC measurements. Half of the volume of the compost and gravel mixture was removed, and fresh compost was added to establish the volume mixing ratio of 1:3 gravel to compost indicating 25% of gravel by volume. The upper 15 cm compost layer was returned to the column after adding fresh compost to restore the initial volume of the column. The columns were repacked, sealed, and the experiments continued from day 43 for another 25 days.

In column 1, CH_4 removal efficiency decreased compared to Stage (I) and fluctuated from day 43 to day 55 with the average removal efficiency of 38%. Condensation was observed on day 54 to the end of the experiment in Stage (II) reflecting methanotrophic activity.

MC in the packing material increased (Section 3.3.) due to water production by methanotrophic activity and saturation by condensed water vapor that did not discharge in Stage (II). Composts have high water holding capacity, and in the preliminary batch incubation studies, it was confirmed that the increase in the MC to the optimum MC of 50% in the current compost could increase the methanotrophic activity (See Chapter 4). Therefore, having more compost in the mixture led to an increase in the MC and thereby increased the methanotrophic activity after day 56 and thereafter stayed almost stable to the end of Stage (II) with an average removal efficiency of 64%. After

dismantling Column 1 on day 67, a little white powder was observed on top of the compost layer close to the last sampling port that alludes to biomass development. Such substance was also reported in a high magnitude by Hilger et al. (2000), Wilshusen et al. (2004), and La et al. (2018). Despite Stage (I), in Column 2, 100% CH_4 removal started from day 1 and sustained to the end of Stage (II).

5.3.1.3. Stage (III): column testing of 1:7 gravel to compost mixing ratio from day 69 to 103

Once the columns from Stage (II) were dismantled, samples were taken for MC measurements and kinetic parameter tests from the gravel and compost mixture and the 15 cm upper compost layer. Fresh compost was added to the compost layer to restore the initial volume before returning it to the column. To establish the gravel to compost mixing ratio of 1:7, half of the medium was replaced by fresh compost for an estimated 12.5% of gravel by volume. The columns were repacked, sealed, and the experiments continued from day 69 for another 35 days.

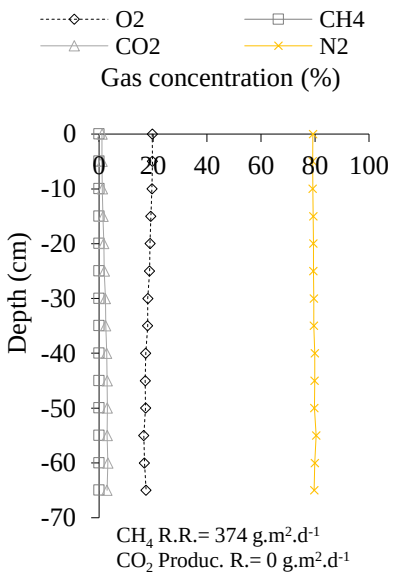
In Column 1, after three days, CH_4 removal reached to the steady-state phase and sustained to the end of the experiment as removal efficiency fluctuated between 60% to 70% with an average value of 66% and removal rate ranged from 214 $g.m^2.d^{-1}$ to 277 $g.m^2.d^{-1}$. Condensation started on day 84 and disappeared by day 94, denoting that the condensed water vapor transferred to the packing material and increased its water content.

Similar to Stage (II), Column 2 started to remove 100% of CH_4 from day one until the end of the experiment. Since Stage (III) had the lowest contribution of gravel with 100% removal efficiency, to investigate its performance under higher CH_4 fluxes, the synthetic LFG inflow was increased to 25 $ml.min^{-1}$ on day 91 and then gradually decreased by day 103. This increase in the inflow and returning to the initial flow rate can also imitate the occasional pulsive increase of LFG flux in the field. On day 91, CH_4 removal efficiency was 0% probably due to the very high flow rate and acclimatization of methanotrophs to the new conditions. On day 94, the inflow was adjusted to 20 $ml.min^{-1}$. Therefore, there was a shift in CH_4 removal efficiency to 27% along with condensation. On day 97, the inflow was reduced to 18 $ml.min^{-1}$, but the CH_4 removal efficiency did not change significantly. From day 98 to the end of the experiment, the inflow was reverted to 12 $ml.min^{-1}$; however, the average CH_4 removal efficiency was 55% and never reached 100% again. Condensation started from day 94 until day 103, reflecting methanotrophic activity, and a considerable volume of water was discharged from the column outlet.

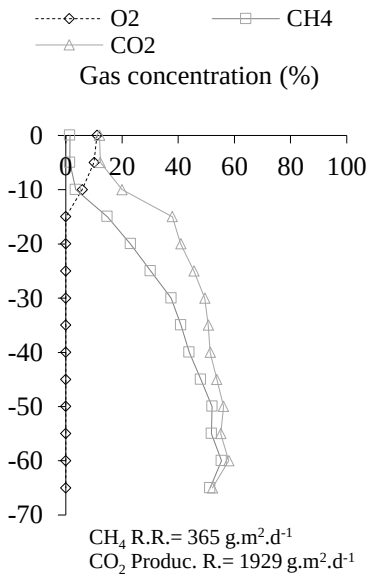
According to Figure 5-2, in such condition of a pulsive increase of LFG flux, the performance of the packing material in Column 2 in removing CH_4 decreased to half compared to initial CH_4 removal of 100%. However, its removal efficiency of 55% was in the range of the highest values obtained for CH_4 removal in Column 1 packed with ¼" gravel.

5.3.1.4. The effect of gravel size and gravel to compost mixing ratio on CO_2 production rates

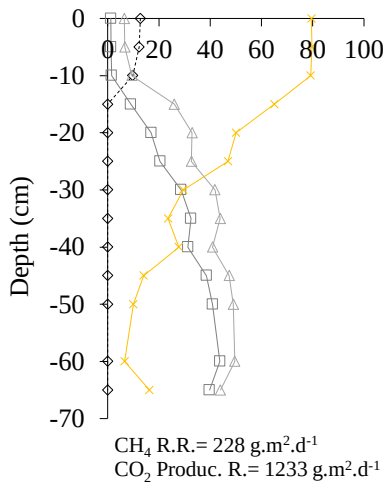
Figures 3(A) to (C) show the gas concentrations in the vertical profile of the Column 1 and Column 2 on selective days with inflow rate of 12 $ml.min^{-1}$, and Fig. 5-3(D) represents the concentrations in Column 2 on the days that inflow rate was changed along with the corresponding CH_4 removal and CO_2 production rates. The vertical profiles of all the three stages show that CH_4 removal started from the very bottom of the columns and very little CH_4 removal was attributed to the upper 15 cm compost. This can be ascribed to lower MC of the upper layer that was exposed to the air (Section 3.3.). However, these findings were dissimilar to the results from the control column reported by Niemczyk (2018) where CH_4 oxidation was mostly observed in the upper layer and O_2 penetration below 15 cm was negligible. The addition of gravel to the compost facilitated O_2 penetration throughout the depth of the columns (Figure 5-3) and prohibited excessive biomass development in the packing materials while it was detected in the control column (Niemczyk, 2018).



(A) Column 1-day 41

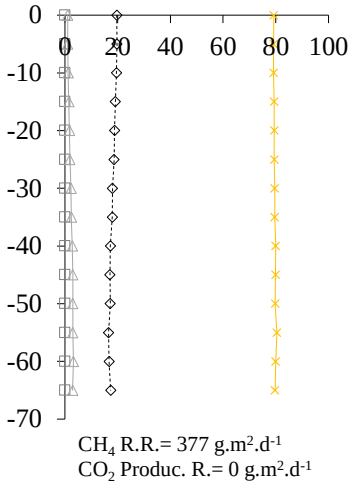


(A) Column 2-day 19



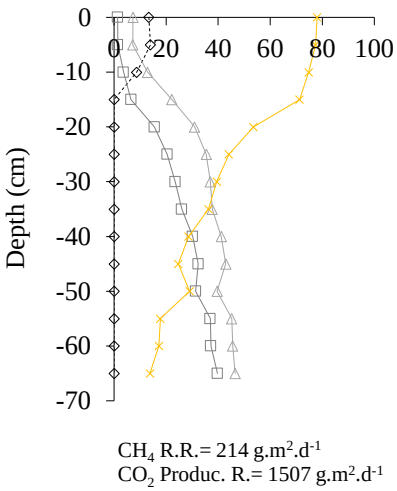
CH_4 R.R.= 228 g.m^2.d^{-1}
CO_2 Produc. R.= 1233 g.m^2.d^{-1}

(B) Column 1-day 67



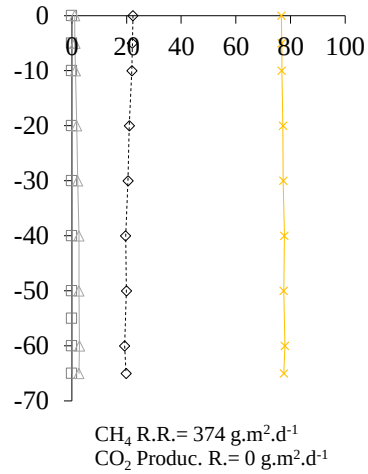
CH_4 R.R.= 377 g.m^2.d^{-1}
CO_2 Produc. R.= 0 g.m^2.d^{-1}

(B) Column 2-day 67



CH_4 R.R.= 214 g.m^2.d^{-1}
CO_2 Produc. R.= 1507 g.m^2.d^{-1}

(C) Column 1-day 98



CH_4 R.R.= 374 g.m^2.d^{-1}
CO_2 Produc. R.= 0 g.m^2.d^{-1}

(C) Column 2-day 90

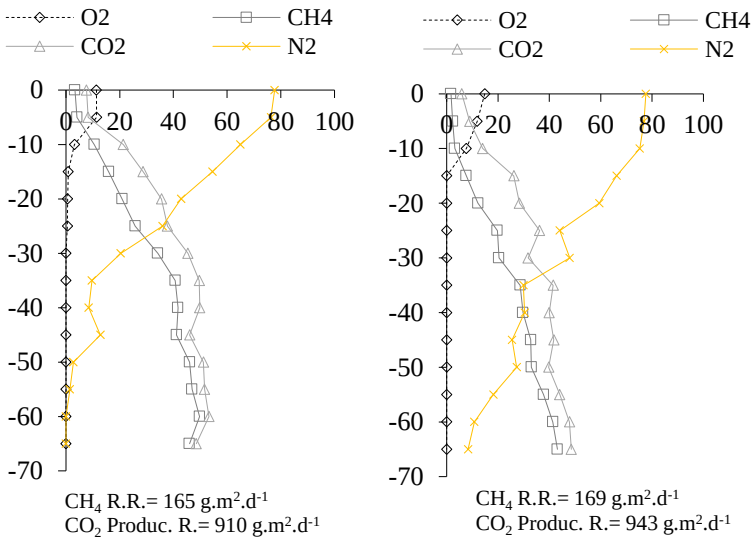


Figure 5-3. Concentration of gases in the verical profile of the columns in A) Stage (I), B) Stage (II), C) Stage (III), and D) Stage (III) after increasing the inflow rate in Column 2

The occurrence of condensation can be explained by the mechanism that CH_4 was removed. The vertical profiles of Column 1 for the entire duration of Stage (I) and Column 2 for the entire duration of Stage (II) and Stage (III) show that all the CH_4 was removed from the entire profile of these columns while the CO_2 concentration remained constant indicating CO_2 production rate of almost 0 $g.m^2.d^{-1}$. This can indicate that the CH_4 removal was mainly caused by adsorption and not by methanotrophs when applied to ¼" gravel and compost mixture with 1:1 ratio as well as ½" gravel and compost mixture with 1:3 and 1:7 ratios under inflow of 12 $ml.min^{-1}$; therefore, no heat and water were produced. Moreover, the gravel type is limestone, and the adsorption potential of limestone for CH_4 has been reported in depleted carbonate reservoirs (Eliebid et al., 2017). La et al., (2018) also reported partial removal of CH_4 in the mixture of compost and biochar (1:1 and 1:3) through adsorption by biochar. On the other hand, on day 19 of Stage (I), when CH_4 removal in Column 2 was at the maximum level, the CO_2 production rate was 1,929 $g.m^2.d^{-1}$. According to the stoichiometry, oxidation of one mole of CH_4 produces one mole of CO_2; however, the obtained value exceeded the CO_2 production rate of 1,175 $g.m^2.d^{-1}$ and can be attributed to the CH_4 oxidation. On the last days of Stage (II) and (III), CO_2 production in Column 1 was 1,233 $g.m^2.d^{-1}$ and 1,507 $g.m^2.d^{-1}$, respectively, both exceeding the CO_2 production rate due to CH_4 oxidation by 2 times and 2.5 times, respectively. Similar observations occurred after increasing the CH_4 flow

rate in Column 2 at the end of Stage (III) when methanotrophs started to be active (Figure 5-3D). The excess CO_2 production can be attributed to heterotrophic activity in the corresponding columns that have methanotrophic activity. In the previous batch incubation studies on the current compost, low biological oxygen demand was recorded at the room temperature while it dramatically increased while being incubated at 45℃ (See Chapter 3: Berenjkar et al., 2021). It can be possible that, in these columns, the temperature raised due to the heat generated via CH_4 oxidation by methanotrophs that increased the activity of heterotrophs, while in columns with CH_4 adsorption, no heterotrophic activity was found at the room temperature (22℃). The temperature rises from 22℃ to 26-27℃ due to methanotrophic activity was observed by La et al. (2018) in the column walls using a laser thermometer.

5.3.1.5. The variation in the MC at the end of each stage

The initial MC in the compost was 47% and it was adjusted to 15% in the gravel. After mixing compost and gravel to a 1:1 ratio, the MC of the mixture was 24%. Figure 5-4 illustrates MC of the packing material throughout the entire profile of the columns after dismantling them at each stage. During Stage (I) in Column 1, the MC of the compost and gravel mixture did not change significantly; however, it slightly decreased in the top compost layer due to being exposed to the air flow. This further confirms that at this stage the whole reduction was due to CH_4 adsorption to the fine gravel. On the other hand, at the same stage in Column 2, the final MC was increased by 10% in the compost to gravel mixture and decreased approximately 10% in the top compost layer. The increase in the MC can be attributed to the methanotrophic activity in the entire depth of the column while the decrease in the MC of the top layer can be due to the exposure to the air flow.

In the vertical profile of columns in all stages, a low CH_4 removal was observed in the top compost layer compared to the mixture of compost and gravel due to the low MC in this layer being exposed to the air. However, in the control column, MC was secured using a humidifier at the top of the column that sustained CH_4 oxidation in this layer.

In Stage (II), after addition of fresh compost to the gravel to compost mixture, the average MC increased to 38% in column 1 and 43% in column 2. After dismantling the columns, the MC in compost and gravel mixture in Column 2 did not have a significant increase. Again, this confirms that CH_4 removal occurred by adsorption in Column 2. However, in Column 1, the MC increased by 10% in the gravel and compost mixture and decreased by approximately 10% in the top compost

layer. The final MC in the Column 1 shows that it was in the range of optimum MC for this compost (See Chapter 4), which did not restrict mass transfer of CH_4 in the biofilm.

In Stage (III), the initial MC in Column 1 and 2 did not change significantly by addition of fresh compost (MC of 47%) to the gravel and compost mixtures as their MC values were very close. After dismantling the columns, the average MC in Column 1 was 53%, which was slightly more that the initial MC. This increase in the MC confirmed the methanotrophic activity in Column 1. However, in column 2, MC did not change in the mixture of gravel and compost although CH_4 oxidation by methanotrophs was observed from condensation after day 94. As the average removal efficiency was 55%, according to the previous stages, a significant change in the MC was not expected. It is hypothesized that discharge of excessive water from the column outlet and drainage of water by coarse gravel modulated the MC.

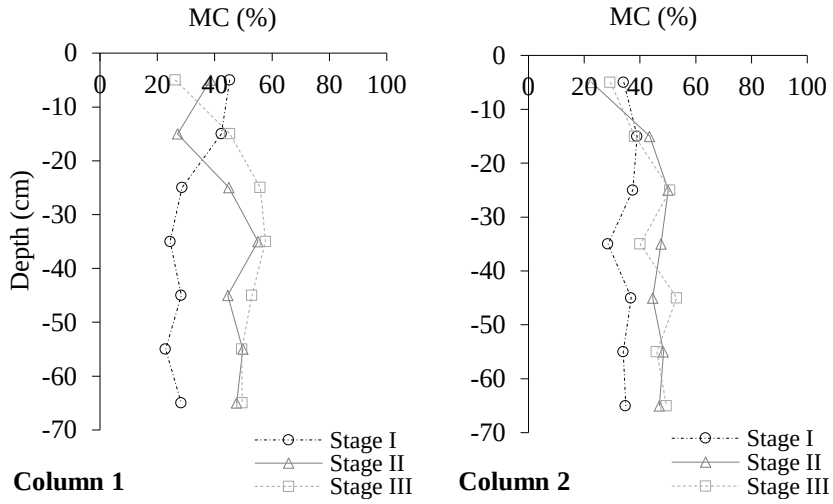


Figure 5-4. MC of the packing materials in the vertical profile of the columns after dismantling at each stage

5.3.1.6. Average CH_4 removal rates and the kinetic parameters for CH_4 oxidation

According to Table 5-1, the average CH_4 removal efficiencies in column 1 and column 2 were higher than the control column that was entirely packed by compost (Niemczyk, 2018). Addition of more compost to Column 1 in Stage (III) than Stage (II) increased the CH_4 removal rate by 1.3 times due to availability of more nutrients and methanotrophs.

The average CH_4 removal rates in the current column designs are higher than or within the range of other studies that have used mixture of compost with granular materials. Scheutz et al. (2009b) studied 1:1 and 1:5 per weight mixture of compost and sand and reported maximum CH_4 oxidation rate of 116 $g.m^2.d^{-1}$ (R.R.: 48%) and 142 $g.m^2.d^{-1}$ (R.R.: 60%), respectively. Ronatco and Cabral (2012) studied 5:1 compost and sand mixture resulting in maximum CH_4 removal rate of 115 $g.m^2.d^{-1}$ and 83% CH_4 removal efficiency at steady-state phase. Rose et al. (2012) used compost and soil mixture of 1:3 and 1:1 and obtained maximum CH_4 removal rate of 420 $g.m^2.d^{-1}$ (R.R.: 90%) and 600 $g.m^2.d^{-1}$ (R.R.: 93%). Frasi et al. (2020) used 5:1 volumetric mixture of compost and sand and found an optimal removal rate of 160 $g.m^2.d^{-1}$ (R.R.: 80%) at 30% MC in the packing material.

Table 5-1. The average CH_4 removal efficiency and removal rate in the columns during Stage (I), (II), and (III) and the control column

Stage	Column 1		Column 2		Control (Niemczyk, 2018)	
	R.E. (%)	R.R. ($g.m^2.d^{-1}$)	R.E. (%)	R.R. ($g.m^2.d^{-1}$)	R.E. (%)	R.R. ($g.m^2.d^{-1}$)
(I)	100	374	50	230		
(II)	49	189	100	377	40	188
(III)	65	248	100/55	374/211		

The removal of CH_4 by adsorption and methanotrophs is not fully ascertained and it depends on the proportion of the mixtures. However, coarse gravel (½") has a higher adsorption effect when used in low ratios (1:3 and 1:7) while the same effect for fine gravel (¼") occurs at a higher ratio (1:1) in the mixture. In addition, after an increase in the CH_4 inflow in Column 2 at the end of Stage (III), it was understood that methanotrophs can be stimulated with high CH_4 flow rates and CH_4 removal by adsorption is replaced by methanotrophic activity. However, it is not clear if CH_4 removal would return to adsorption in the long term. Therefore, prolonged experiment of the column needs to be conducted.

Table 5-2 represents CH_4 oxidation kinetic parameters. At the end of each stage, batch incubations were conducted at various CH_4 concentrations in air headspaces to determine the V_{max} and K_m. The higher V_{max} value attributes to higher capacity to oxidize CH_4, whereas the lower value of K_m corresponds to higher affinity to CH_4.

In Column 1, from Stage (I) to Stage (III), there was an increase in the value of V_{max} while in Column 2, the value of V_{max} decreased in Stage (II) and increased in Stage (III). This is comparable

with the trend of corresponding methanotrophic CH_4 oxidation rates in Table 5-1. In Column 1, CH_4 oxidation rate in Stage (III) was 1.3 times higher than that in Stage (II), and in Column 2, it was 1.1 times higher in Stage (I) than Stage (III), coinciding with relative corresponding V_{max} values in Table 5-2. The values obtained for V_{max} are in the range of the maximum reported V_{max} values in soils including 0.38 $mg.g^{-1}.d^{-1}$ (Kightley et al., 1995), 0.61 $mg.g^{-1}.d^{-1}$ (Park et al., 2005), 3.46 $mg.g^{-1}.d^{-1}$ (Wang et al., 2011), and 1.57 $mg.g^{-1}.d^{-1}$ (Farrokhzadeh et al., 2017).

The values obtained for K_m imply that throughout the three stages of the experiment, methanotrophs were sensitive to a liquid phase CH_4 concentration ranging from 2.43% to 30.4%.

Table 5-2. Kinetic parameters for Column 1 and Column 2 during three stages

Stage	Column 1		Column 2	
	V_{max} ($mg.g^{-1}.d^{-1}$)	K_m (%)	V_{max} ($mg.g^{-1}.d^{-1}$)	K_m (%)
(I)	2.07	2.43	3.63	6.44
(II)	3.37	10.88	2.74	5.64
(III)	3.98	30.4	4.00	23.79

The studied compost is a low-cost implementation and is constituted of readily available material in the landfill in the study area while gravel is considered an expensive material that needs to be transferred to the landfill to be implemented in the bio-cover. It can be inferred that ¼" gravel to compost mixing ratio of 1:7 is an optimum packing material with the highest portion of compost, the lowest amount of fine gravel, and the highest value of CH_4 removal efficiency to stimulate CH_4 oxidation by methanotrophs. As the compost material was renewed at each stage, no clogging was observed for the entire duration of this study, while in the long term, clogging can happen.

5.4. Conclusions and recommendations

To increase the air penetration to the deeper layers of a bio-cover consisting of yard waste and leaf compost (YWLC) and biosolids compost (BSC) mixture (1:4), and to restrict compost clogging due to compaction, the porosity of the compost mixture was increased by addition of limestone gravel in two different sizes of ¼" and ½". Various gravel to compost mixing ratios of 1:1, 1:3, and 1:7 were established in three consecutive stages of flow-through column tests to investigate the optimum gravel to compost mixture. Based on the obtained results, the following conclusions are summarized:

- The CH_4 removal mechanisms in the columns was a combination of adsorption and biological treatment.
- Addition of gravel to the compost resulted in 100% CH_4 removal by adsorption in the mixtures including ¼" gravel to compost ratio (1:1) and ½" gravel to compost ratios (1:3 and 1:7), while in the other mixtures CH_4 was removed by methanotrophs with maximum removal efficiency of 65%.
- A pulsive increase of the inflow rate at the end of experiment, in the column packed with ½" gravel to compost ratio (1:7), stimulated the methanotrophs to oxidize CH_4; however, the average removal efficiency did not exceed 55%.
- Methanotrophic activity produced excess water, and water evaporation from the packing materials was condensed in the columns' headspace wall.
- When CH_4 removal occurred by adsorption, there was no CO_2 production, while in case of CH_4 removal by methanotrophs, the CO_2 production rate was higher than the stoichiometric ratio revealing heterotrophic activity in the columns. It can be hypothesized that the increase in the temperature due to methanotrophs increased the activity of heterotrophs as well.
- CH_4 oxidation in the vertical profile of the columns started from the very bottom layers because there was sufficient air penetration to the depth of the column due to the addition of gravel.
- Excessive biomass development in any of the column setups was not noted due to the application of gravel, addition of fresh compost, and shorter duration of each stage, while it was observed in the control column made entirely with compost.
- Compared to the control column, the air penetration was improved and the CH_4 oxidation efficiency increased. In the current columns, there was low CH_4 oxidation at the top 15 cm due to the low MC in the compost being exposed to the air. However, in the control column CH_4 was mostly oxidized in the upper 15 cm because MC was secured by a humidifier at the top.
- While the column setup emulated the real field-scale bio-cover using a humidifier along with the air flow that could maintain the MC in the upper 15 cm compost, an increase in the CH_4 oxidation in this layer resulted in a higher CH_4 removal efficiency.

- The values of V_{max}, obtained from oxidation kinetics, were in accordance with the CH_4 oxidation rates by methanotrophs, and the maximum value for V_{max} was 3.98.
- The maximum methanotrophic CH_4 removal rate of 248 $g.m^2.d^{-1}$ was obtained for ¼" gravel to compost mixing ratio (1:7). This is a cost-effective and feasible mixture with the lowest portion of gravel.
- As the last stage, Stage (III), was run for 35 days, it is recommended that the optimum mixing ratio be tested for a longer time to investigate the potential clogging and possible peak or drop in the CH_4 oxidation rates.

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Chapter 6: Summary and conclusions

Over two years of sampling from a pilot bio-window composed of biosolids compost (BSC) and yard waste and leaf compost (YWLC) in the landfill in Brady Road Resource Management Facility (BRRMF), Winnipeg, a significant temperature variation was noticed: between 35ºC in summer to -40ºC in winter. Significant seasonal fluctuations in soil moisture content (MC) were also observed, affecting the performance of the bio-window. Furthermore, measuring the temperature within the bio-window revealed that heat was radiating up from the landfill due to methanogenesis and fermentation (temperatures above 45ºC in late summer within the bio-window), stressing the methanotrophs, while a thick, solid winter frost cover affecting gas exchange in addition to low air diffusion into the bio-window were also affecting the efficiency of CH_4 oxidation. Laboratory batch tests on the compost samples collected throughout the year from different depths of the bio-window were performed at mesophilic and thermophilic temperatures to obtain the methanotrophic potential of the compost samples. Biological oxygen demand (BOD) of the compost samples was also assessed, showing that very little O_2 was consumed by heterotrophs. This could confirm that the high temperature observed within the bio-window was not because of soil respiration but because of heat coming from the landfill and the ambient temperature. According to the results, at different times of the year, with variations in the temperature, temperature-appropriate methanotrophic communities were active, but in some cases, they were not in sync with the ambient temperature. It was noticed that there was a late summer transition from mesophilic to thermophilic methanotrophs. Results also showed that methanotrophic activity was negligible when the MC in the compost samples was below 30% (w/w) despite aerobic conditions that generally happened at the top layers at dry season, while they were still active at 65% (w/w) MC.

The next step is to conduct in-depth laboratory-scale studies to improve the bio-window performance, especially around issues of air diffusion, seasonal soil temperature and MC fluctuations, and variations in CH_4 flux.

Based on the *in situ* bio-window findings, the interactive effect of significant environmental factors, including MC, temperature, and initial CH_4 concentration, on CH_4 oxidation rate was studied through batch incubations. To optimize the environmental factors and maximize the CH_4 oxidation rate, Box–Behnken Design (BBD) of Response Surface Methodology (RSM) was

employed, and a statistical model was developed based on the experimental results of batch incubations that were later validated by supplementary batch incubations. Results showed that temperature and MC were significant factors affecting CH_4 oxidation. The interactive effect of environmental factors was insignificant on CH_4 oxidation. Effective CH_4 oxidation occurred at a wide range of temperatures and MCs, and a parabolic curve for MC and temperature was observed simultaneously. CH_4 oxidation rate did not significantly vary at CH_4 concentrations above 20%.
To increase the air penetration to the deeper layers of the bio-cover and inhibit compost clogging due to compaction, the porosity of the compost mixture was increased by the addition of gravel in two different sizes of ¼" and ½". According to the column tests, gravel addition to the compost increased the air penetration to the deeper layers of the column. The performance of the bio-cover varied with gravel size and mixing ratio. At the 1:1 ratio of fine gravel and compost mixture and 1:3 and 1:7 ratios of coarse gravel and compost mixtures, the dominant CH_4 removal mechanism was adsorption with 100% efficiency, there was no CO_2 production, and no change in the MC at the end of the stage. However, when CH_4 removal was by methanotrophs, CO_2 production was more than the stoichiometry indicating heterotrophic activity. The highest methanotrophic CH_4 removal efficiency was obtained for the least amount of fine gravel mixed with compost (1:7).
To conclude:

- Implementing bio-windows is a promising approach for CH_4 emission reduction from landfills, and it is easier to design, manipulate, control, and modify the bio-window set-up to enhance its performance than conventional bio-covers. Moreover, due to covering small areas of the landfills, bio-windows are more economically feasible compared to bio-covers covering the entire surface of the landfill.
- For the first time, thermophilic methanotrophs were reported in the landfill environment.
- Mesophilic and thermophilic methanotrophs selectively responded, within their respective temperature ranges. There was an interaction between activity of either group and MC.
- The current mixture is suitable for bio-covers in landfills at the early stages of fermentation and where the bio-cover is subjected to high temperature and high CH_4 flux.
- It can fairly support CH_4 oxidation recovery in the early spring under high MC and low temperature.

- The compost mixture shows the ability to achieve high CH_4 oxidation rate under high MC in summer (T: 45°C)
- Air diffusion issues can be solved by addition of fine gravel in a low ratio to the deeper layers of the bio-window so more CH4 oxidation efficiency is obtained.

Chapter 7: Engineering significance

The field study in this thesis addressed several issues affecting the performance of the pilot bio-window. CH_4 oxidation was affected by high LFG flux, frost formation, seasonal temperature and MC variations in the bio-window, and poor air penetration.

Two years of sampling from the bio-window confirmed the importance of seasonal soil temperature transitions when methanotrophs may be most stressed or changing in species composition. There was considerable CH_4 oxidation when the temperature in the bio-window was >45°C, and the laboratory tests showed high methanotrophic activity in samples incubated at 45°C (thermophilic condition) compared to negligible activity at 22°C (mesophilic condition), revealing the existence of the thermophilic methanotrophs in a landfill set for the first time. This can be more important to be considered in the high-temperature landfills and those at the early stages of the methanogenesis phase. Moreover, the methanotrophic potential in the bio-window during the winter confirmed the importance of adopting appropriate measures to extend the shoulder season, such as modulating the temperature of the bio-window in early spring and late fall using sing mechanical or passive means (e.g., thermosiphons).

There is a high demand of MC for methanotrophs in the compost to remain active even in the presence of high levels of O_2. This is significant when CH_4 oxidation mostly happens at the top layers of the bio-window exposed to dryness due to climatic conditions. Periodic irrigation of the bio-window is recommended. Such engineering design modifications are more appropriate and less costly when using a bio-window concept rather than a full organic bio-cover.

The highest CH_4 oxidation occurred in summer; however, the air penetration to the deep layers was poor. Extra passive or forced aeration (e.g., aeration pipes) in the bio-window can be beneficial to exploit its total capacity and achieve high levels of CH_4 oxidation rate during the most efficient treatment season.

It is also recommended that the *in situ* bio-window is expanded or multiplied, and the carbon credit obtained from reducing the CH_4 emissions is calculated.

On the other hand, there were some technical issues in the field-scale application of the bio-window. The wind speed was a key factor regulating the CH_4 flux to the bio-window and decreasing the CH_4 oxidation rate. The frost formation and freeze-thaw cycles could displace the

gas probes in the bio-window and make errors in the vertical profile gas samplings, so it is important to fix the probes at their levels by attaching them to the gravel in the GDL using long metal bars that can work as a deep foundation for the probes. Ice formation also decreases the overall porosity of the bio-window, hence the O_2 penetration along with the vertical profile. This restricted CH_4 oxidation at deeper layers of the bio-window while not being frozen. Increasing the porosity in the upper layers using coarse materials can conduct excess water to deeper layers which might not be frozen during the winter because of temperature from waste degradation in the landfill.

The materials in the bio-window degrade over time, being washed or blown away. Native grasses and shrubs can be planted on the bio-window because plant roots can hold the bio-window materials in position and prevent them from being blown or washed away. In the case of bio-windows, plants can be vegetated against the dominant wind on the surrounding topsoil and on the slope to prevent bio-window materials from being washed. Alternative controls comprise applying gravel to withstand wind erosion and coarse rock riprap to prevent water erosion.

Optimization of the bio-window design regarding MC, temperature, and CH_4 concentration can significantly enhance its performance. Therefore, laboratory-scale batch and column experiments were conducted. Despite previous studies that only considered the effect of individual environmental factors on CH_4 oxidation rate in the landfill bio-covers, the current research investigates the interactive effect of these factors through statistical modelling by response surface method (RSM). Compost samples are collected from a bio-window located in a high seasonally fluctuating climatic area. The samples are incubated at a wide range of moisture content and temperature, and the optimum values are obtained by the model. While the optimum temperature was in the range of previous studies (30°C), there was still high CH_4 oxidation at 45°C that was only observed in thermal soils before.

The mixture of BSC and YWLC (4:1) selected for a mixture of methanotrophs capable of effective operation at a wide range of temperatures and MCs. It also proved to be suitable for bio-covers in landfills at the early stages of fermentation and where the bio-cover is subjected to high temperature and high CH_4 flux. The results of this research provide a basis to investigate the existence of the thermophilic methanotrophs in the landfill environment. For future work,

community analyses are recommended to prove the availability of thermophilic methanotrophic populations.

The addition of gravel to the bio-window filling materials increases the air penetration to the deep layers, helps regulate the excess MC within the bio-windows, and affects the CH_4 removal mechanism through the combination of adsorption and microbial oxidation. In the case of CH_4 adsorption, the heterotrophs are inactive.

Appendix A: Photos of the *in situ* bio-window and the sampling procedure

Bio-window construction

Figure A -1. From left to right, digging the hole, the hole with 1.3 m depth, filling the bio-window with compost

Installment of gas sampling probes

Figure A -3. Attaching metal bars to the stainless-steel probes with perforation at the end

Figure A -2. Placement of probes with metal bars fixed in the GDL to make a deep foundation preventing the probe heave and displacement

Flux measurements

Figure A -4. Flux chamber sealed by bentonite and gas sampling for the flux measurement

Vertical profile gas sampling

Figure A -6. Nest of gas probes

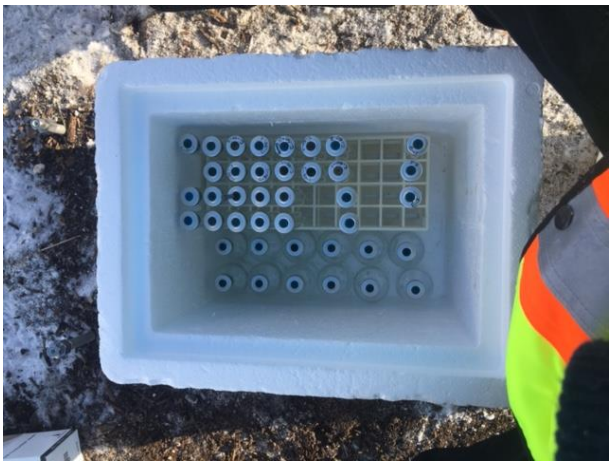

Figure A -5. Serum bottles and tubes for gas samples

Compost sample collection

Figure A -7. Compost sample collection at different months of the year

Figure A -8. The *in situ* bio-window with gas probes installed in winter

Laboratory analyses

Figure A -9. Batch tests with 2 g of compost in 120 ml bottles

Figure A -10. Agilent Gas Chromatographer (GC)

Appendix B: Column test preparation and set-up

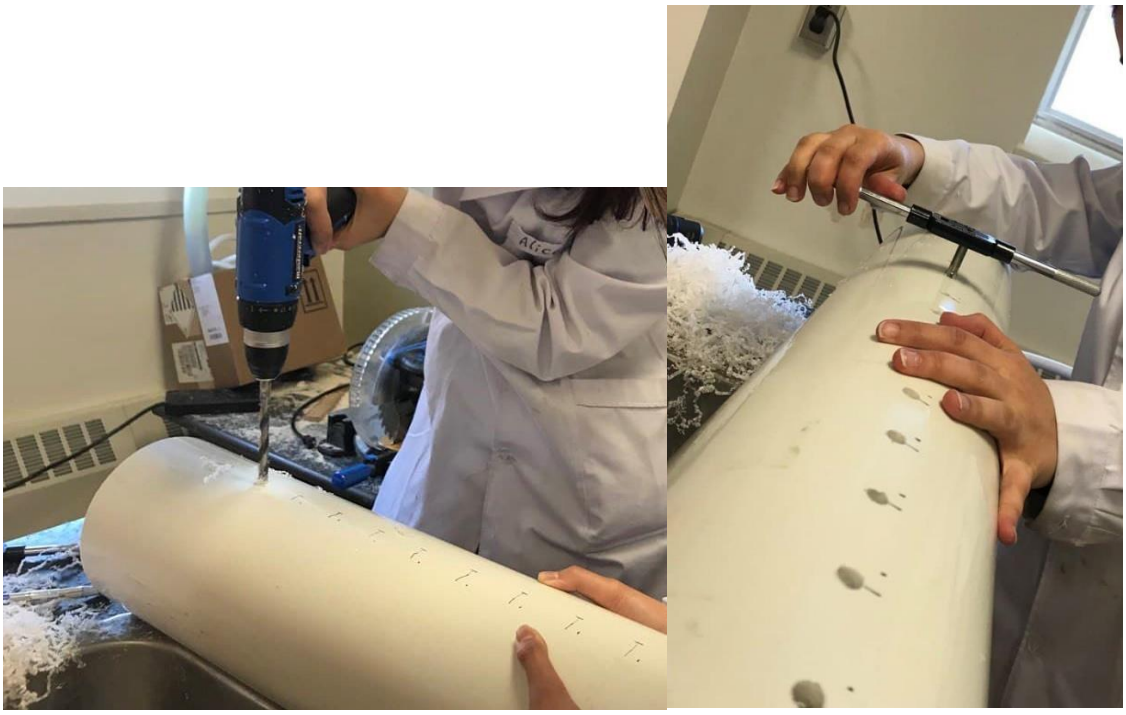

Figure B- 11. Drilling and threading the holes in the PVC pipe for installation of gas sampling ports

Figure B- 12. Hoses, Connectors, and Adaptors

Figure B- 13. Installing the sampling ports equipped with gas tight septa

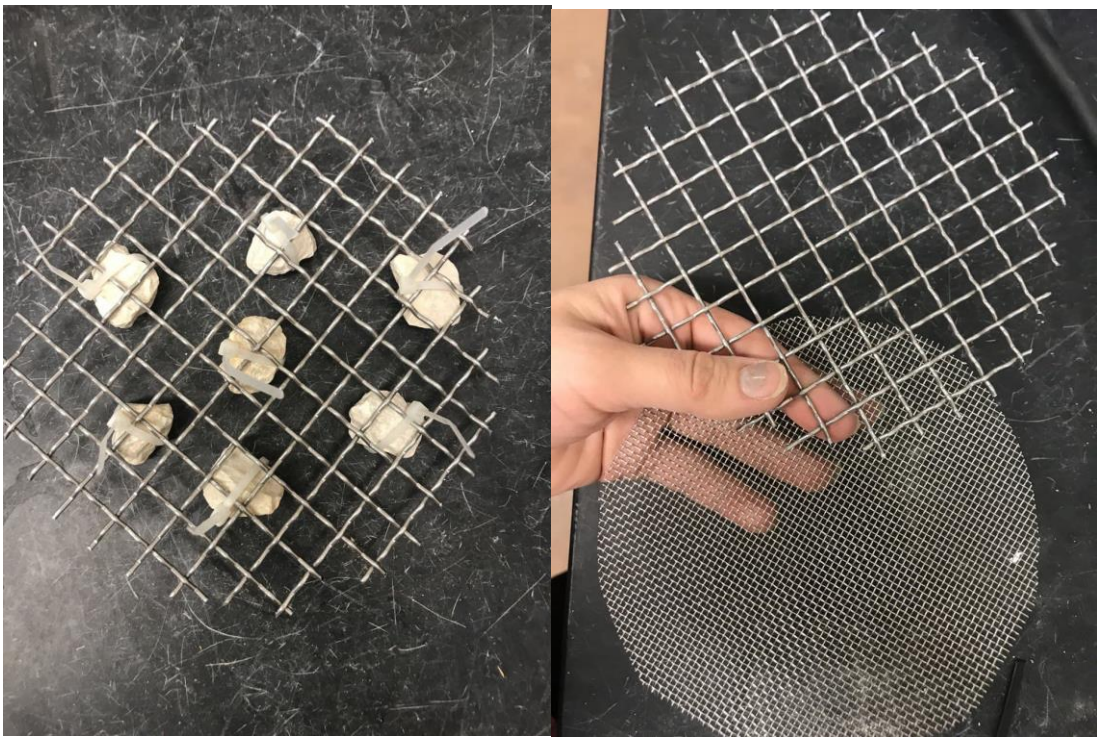

Figure B- 14. Coarse mesh with gravels attached for placement beneath the GDL to distribute the synthetic LFG homogeneously (Left). Fine mesh to place between layers of packing materials (GDL, Compost and gravel, compost) to prevent them mixing (Right, bottom)

Figure B- 15. The packed column with PVC base plate and Flexible PVC Pipe Cap with Stainless Steel Clamps

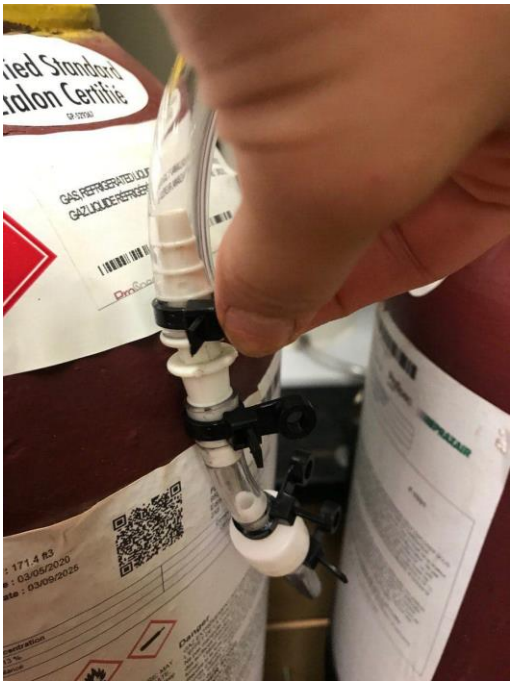

Figure B- 16. Air tightening the connectors

Figure B- 17. The final set-up of the column test with flow meters under the hood and gas tanks with pressure controlling valves and regulators

Figure B- 18. Check valve to make one-way synthetic LFG flow and prevent back flush to the gas tanks

Figure B- 19. Flow meters to measure air injection inflow (Left) and the columns outflow (Right)

Figure B- 20. Outlet port for sampling gas concentrations in the effluent

Appendix C: Supplementary data

Figure C- 1. The BRRMF with composting windrows and the location of the biowindow (Google, n.d.)

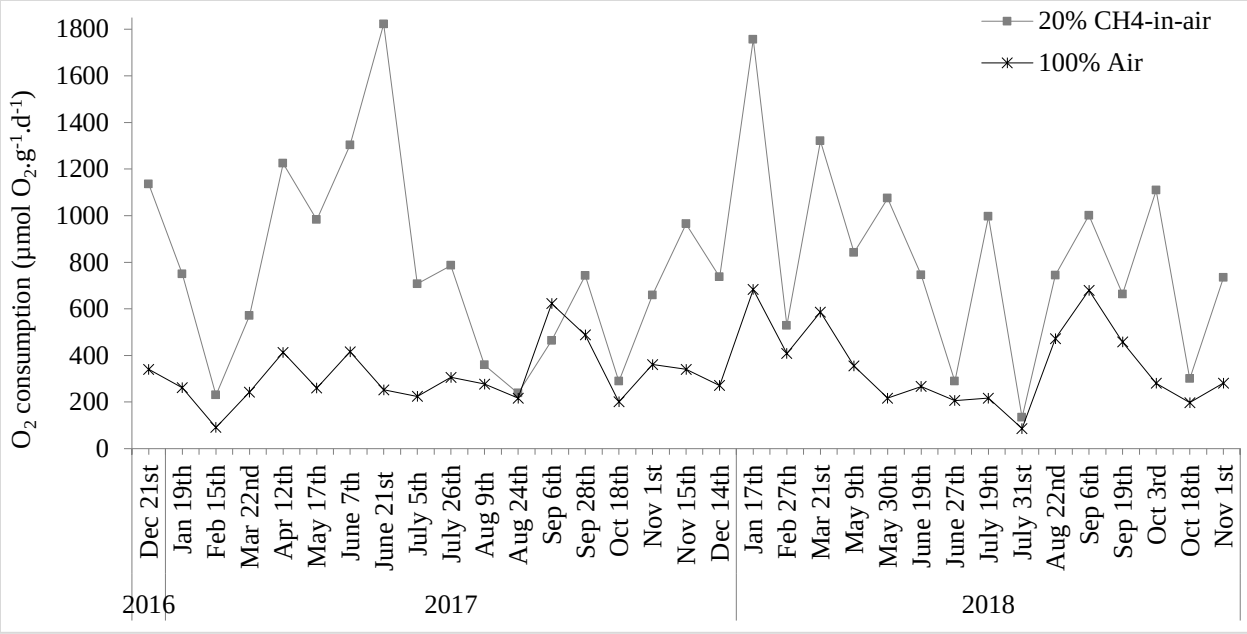

Figure C- 2. Comparison of O_2 consumption by heterotrophic bacteria (100% Air) and MOB and heterotrophic bacteria (20% CH_4-in-air) (Chapter 3)

Table C- 1 CH_4 to CO_2 ratio at various depths of the bio-window throughout the sampling period (Chapter 3)

Year	Date	Depth (cm)							Average CH_4/CO_2 in depth	CH_4/CO_2 in LFG
		10	20	30	40	50	60	70		
2016	Dec 21st	1.92	1.90	1.89	1.87	1.84	1.81	1.82	1.86	2.00
2017	Jan 19th	1.78	1.74	1.71	1.74	1.70	1.67	1.67	1.72	1.86
	Feb 15th	2.13	2.15			2.04	1.90		2.06	1.67
	March 22nd	0.77	0.67	0.69	1.07	0.96	1.18	1.03	0.91	0.73
	April 12th	0.02	0.03	0.11	1.03	1.13	1.66	1.56	0.79	1.40
	June 7th	1.52	1.66	1.85	1.76	1.77	1.78	1.82	1.74	1.81
	June 21st	1.69	1.74	1.85	1.75	1.74	1.76	1.78	1.76	1.85
	July 5th	1.58	1.73	1.79	1.72	1.62	1.74		1.70	1.82
	July 26th	1.55	1.73	1.87	1.75	1.78	1.79	2.13	1.80	1.79
	Aug 9th	1.57	1.70	1.77	1.72	1.73	1.77	1.77	1.72	1.86
	Aug 24th	0.88	1.41	1.53	1.59	1.71	1.65	1.70	1.50	1.76
	Sep 6th	0.70	1.26	1.45	1.61	1.68	1.63	1.73	1.44	1.80
	Sep 28th	1.44	1.67	1.57	1.71	1.74	1.70	1.75	1.65	1.81
	Oct 18th	0.17	0.39	0.14	0.63	1.28		1.40	0.67	1.73
	Nov 1st	0.81	1.38	1.43	1.60	1.44	1.65	1.70	1.43	1.76
	Nov 15th		1.36	1.38	1.56	1.65	1.54	1.68	1.53	1.68
	Dec 14th	1.37	1.48	1.52	1.50	1.52	1.45	1.49	1.48	1.67
2018	Jan 17th	1.27	1.46	1.64	1.64	1.68	1.71	1.70	1.59	1.68
	Feb 27th	1.61	1.69	1.78	1.76	1.80	1.81	1.72	1.74	1.70
	March 21st	1.85	1.84	1.86	1.87	1.83	1.86	1.84	1.85	1.76
	May 9th	1.65	1.70	1.81	1.69	1.75	1.76	1.74	1.73	1.76
	May 30th	1.56	1.64	1.72	1.60	1.64	1.71	1.63	1.64	1.76
	June 19th	1.54	1.60	1.67	1.57	1.59	1.68	1.64	1.61	1.78
	June 27th	1.46	1.53	1.62	1.61	1.54	1.67	1.65	1.58	1.76
	July 19th	1.34	1.76	1.73	1.37	1.60	1.65	1.65	1.58	1.72
	July 31st	1.71	1.69	1.69	1.63	1.62	1.65	1.70	1.67	1.76
	August 22nd	1.67	1.62	1.72	1.59	1.59	1.63	1.67	1.64	1.73
	Sep 6th	1.67	1.67	1.77	1.63	1.65	1.67	1.70	1.68	1.77
	Sep 19th	1.45	1.46	1.58	1.52	1.54	1.64	1.66	1.55	1.75
	Oct 3rd	1.72	1.67	1.72	1.69	1.68	1.72	1.74	1.71	1.75
	Oct 18th	1.74	1.71	1.80	1.68	1.69	1.66	1.87	1.74	1.67
	Nov 1st	1.76	1.60	1.62	1.61	1.64	1.72	1.71	1.66	1.77

Table C- 2 t-Test for means of actual CH_4 oxidation rates and predicted values by BBD (Chapter 4)

	CH_4 oxidation rate ($mg.g^{-1}.d^{-1}$)	
	Actual	Predicted
Mean	1.28	1.28
Variance	0.52	0.46
Observations	17	17
Pearson Correlation	0.94	
Hypothesized Mean Difference	0	
df	16	
t Stat	2.17E-15	
P(T<=t) two-tail	1	
t Critical two-tail	2.12	

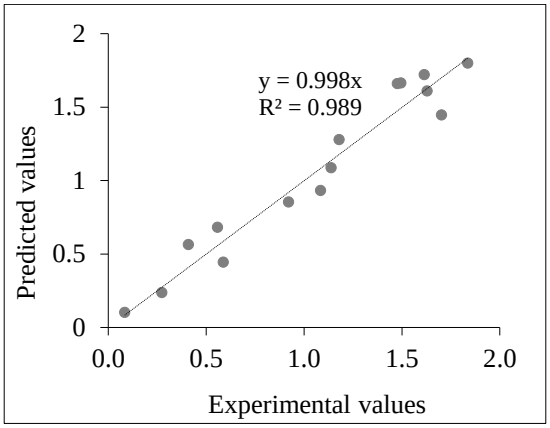

Figure C- 3. The experimental versus predicted values for CH_4 oxidation rate at 22℃ under various MC and initial CH_4 concentrations (Chapter 4)

Table C- 3 t-Test for means of experimental CH_4 oxidation rates and model predictions at 22℃ (Chapter 4)

	CH_4 oxidation rate ($mg.g^{-1}.d^{-1}$)	
	Experimental	Predicted
Mean	1.067	1.069
Variance	0.32	0.33
Observations	15	15
Pearson Correlation	0.97	
Hypothesized Mean Difference	0	
df	14	
t Stat	-0.057	
P(T<=t) two-tail	0.95	
t Critical two-tail	2.15	