OPTIMIZATION OF PARAMETERS FOR METHANE OXIDATION IN LANDFILL COVER COMPOST MATERIALS

by

Monika Joanna Niemczyk

A Thesis submitted to the Faculty of Graduate Studies of

the University of Manitoba

in partial fulfilment of the requirements of the degree of

MASTER OF SCIENCE

Department of Civil Engineering
Faculty of Engineering
University of Manitoba
Winnipeg, MB

Abstract

This research evaluated the efficacy of two compost materials, yard and leaf waste compost (YLWC) and biosolids compost (BSC) at oxidizing methane (CH_4) in a series of laboratory experiments. Initial batch incubation of the YLWC under a 20% CH_4-in-air headspace yielded higher CH_4 oxidation rates than were observed in the same YLWC tested one year prior (higher raBOD), due to less competition for oxygen with heterotrophic bacteria. Very little CH_4 oxidation was observed in the BSC, with moisture content (MC), heavy metals, and methanotrophic inoculum determined to not be limiting variables. Long-term batch tests (>100 days) indicated the highest CH_4 oxidation rates in 1:1 and 1:4 (YLWC:BSC) mixing ratios (360-380 μmol g(d.w.)$^{-1}$ d^{-1}). Column tests found that a 1:4 mixing ratio at a MC of 40% ww (with addition of a methanotroph-enriched compost extract) has the potential to remove a significant portion of the CH_4 flowing through a landfill biocover.

Acknowledgements

I would like to express my utmost gratitude to my advisor, Dr. Qiuyan Yuan, and co-advisor, Dr. Jan Oleszkiewicz, for their guidance and support throughout my M.Sc. work. I would also like to sincerely thank my committee members, Dr. Richard Sparling, for the near-daily advice and inspiration as well as the use of his laboratory to complete the research, and Dr. Stan Lozecznik, for the technical insight and unique perspectives. Also, thank you to J. Bert Smith, Rob Sinclair, and Tony Kuluk of KGS Group for their technical expertise throughout the project.

The work presented in this thesis was built on previous work completed by Nicole Wilkinson under the supervision of Drs. Sparling and Lozecznik, and is gratefully acknowledged. This work also would not have been possible without the collaboration and in-kind contribution of compost materials from the City of Winnipeg Brady Road Resource Management Facility and the City of Edmonton Biosolids Composting Facility.

This work was funded by the Province of Manitoba through a Waste Reduction and Pollution Prevention (WRAPP) grant and Mitacs Canada through an Accelerate grant.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCTION

1.1 OVERVIEW

1.1.1 Landfill CH_4 Emissions and CH_4 Oxidation in Landfill Covers

The disposal of waste to land has been the primary means of disposal throughout the evolution of mankind, and remains as the most widely used end-of-life waste management practice in Europe and North America (Hester & Harrison, 2002). Although advancements in landfill design and operations have significantly reduced the environmental impacts and health concerns associated with landfilling, they continue to be an area of public and environmental concern. One of the main environmental impacts of landfills, and specifically landfills with a high level of organics, concerns the generation and emission of landfill gas (LFG). In municipal solid waste (MSW) landfills, the anaerobic decomposition of organic wastes involves a series of complex, microbiologically-driven, biochemical processes that produce LFG consisting of 55-60% v/v methane (CH_4) and 40-45% v/v carbon dioxide (CO_2) (Scheutz et al., 2009a). Although originating deep within the waste mass (i.e., in the anaerobic zone), both CH_4 and CO_2 readily migrate to the surface and enter the atmosphere as fugitive emissions. Furthermore, the biochemical reactions that generate LFG continue long after landfill closure, and therefore require consideration for several decades after landfill capping.

Specifically, CH_4 is a potent greenhouse gas (GHG) with an estimated 100-year global warming potential (GWP_{100}) that is 28 times that of CO_2 (IPCC, 2013). Since pre-industrial times, the concentration of CH_4 in the atmosphere has increased by a factor of approximately 2.5 – from

722 ppb in 1750 to 1,803 ppb in 2011 (IPCC, 2013). There is sufficient evidence to conclude that this increase is due in large part to contributions from anthropogenic activities. Globally, landfilling and other waste management activities account for 22.7% (1.7-2.3 Gt CO_2-eq. yr^{-1}) of total anthropogenic CH_4 emissions and are the third largest source of anthropogenic CH_4, following releases from the fossil fuel industry (29.0%) and ruminant livestock (animal husbandry) (26.9%) (IPCC, 2013). In Canada, emissions from landfills account for a similar percentage, 20% (20 Mt CO_2-eq. yr^{-1}), of national CH_4 emissions (Environment & Climate Change Canada, 2014).

Total CH_4 emissions from landfills continue to increase despite efforts to divert organics away from landfill (IPCC, 2013), which necessitates that effective and practical technologies be developed to reduce or control these emissions. Presently, many modern sanitary landfills are designed or retrofitted with engineered LFG extraction systems, consisting of vertical wells and horizontal collector pipes installed within the refuse. Captured LFG can be burned in a high temperature flare or used for energy recovery. LFG collection systems can serve as a major control for emissions, although such systems (i) are costly, which precludes their installation at smaller and/or older landfill sites, (ii) vary in effectiveness, with some collection efficiencies reported as low as 40-50% for landfills with a permeable intermediate cover and limited gas well coverage (Barlaz et al., 2009), (iii) are prone to operational disruptions, which further reduce efficiency, and (iv) are not considered practical to continue to operate once LFG production falls below a certain threshold.

Landfill final covers are the final layer of clay and/or soil (or other material) placed over the waste once a landfill cell has been filled to capacity to minimize leachate generation and control

the migration of gases. There is potential for CH_4 to be oxidized in the upper layers of a landfill's final cover soil using O_2 that penetrates/diffuses into the cover from the atmosphere. Unlike a conventional landfill soil cover, a biological cover, or "biocover", is one of several engineered landfill cover systems that has been designed to enhance the growth of CH_4 oxidizing microorganisms known as methanotrophs. Methanotrophs are bacteria that have the unique ability to oxidize CH_4 as their only source of carbon and energy; for this reason, they are considered to be globally-important regulators of CH_4 flux from the biosphere (Hanson & Hanson, 1996). Specifically, a landfill biocover is defined as consisting of a gas distribution layer (GDL) that is highly permeable to evenly distribute the LFG flux and an overlying oxidation layer composed of suitable materials and amendments that support methanotrophic populations (Scheutz et al., 2009a).

1.1.2 Application of Biological Cover Systems to Landfills in Winnipeg and Manitoba, Canada

1.1.2.1 Brady Road Resource Management Facility (BRRMF)

The landfill at Brady Road Resource Management Facility (BRRMF), also known as Brady Road Landfill, is a Class 1 Waste Disposal Ground (WDG) that has been serving the City of Winnipeg and surrounding areas since its opening in 1973. The site consists of 100 ha of existing landfill within 790 ha of total land available for solid waste management, and is estimated to have approximately 100 years of remaining capacity based on current waste diversion practices (Stantec, 2011). Currently, Brady Road Landfill is Manitoba's second-largest point source of GHGs, emitting an estimated 394,296 t CO_2-eq. of GHGs in 2015 (Environment and Climate

Change Canada, 2015). As Winnipeg's only active landfill that is owned and operated by the City of Winnipeg, it receives approximately 400,000 t of residential and commercial waste each year (Stantec, 2011).

In 2013, a landfill gas collection system was commissioned within a closed, northeast portion of the landfill, covering an area of approximately 20 ha that was in-service from 1979-2009. The landfill gas collection system was a requirement under The Climate Change and Emissions Reductions Act, and came at a total cost of $7M, including a more than $2.5M contribution from the Province of Manitoba (City of Winnipeg, 2014). A final clay cap (or cover) was placed over this waste mass prior to it being retrofitted with gas collection wells, to contain the landfill gas and minimize the infiltration of precipitation. Currently, landfill gas collected by the system is burned in an enclosed flare to reduce its GHG impact; however, the collection efficiency of this system is limited, such that there are still fugitive LFG emissions that could benefit from an oxidative cap. Moreover, there remains a significant area of Brady Road Landfill that currently has no controls for GHGs.

In October 2013, the City of Winnipeg started operating a large-scale composting pad, of approximate 9 ha area, at BRRMF, that processes the yard and leaf waste from its curbside collection program (City of Winnipeg, 2017). The City of Winnipeg is also currently examining several alternatives to manage the biosolids generated by its three wastewater treatment plants to the year 2037. As part of its Biosolids Master Plan, the City has completed construction of a pilot biosolids composting facility, also at BRRMF, for up to 20% of its generated dewatered biosolids (10,400 t) (City of Winnipeg, 2015). Start-up of this pilot began in May 2015. The remaining biosolids continue to be disposed of by landfilling at BRRMF.

Currently, the biosolids compost is used as cover on the current landfill cells, as per Condition 75 of Environment Act License No. 3081R for BRRMF which states that, "The Licensee shall utilize all biosolids compost products as landfill cover or as approved by the Director within the Facility for the duration of the pilot study." The long-term practical use for the finished compost from both facilities remains to be determined.

1.1.2.2 **Other Landfills**

There are also a number of closed landfills in Winnipeg, Manitoba that could benefit from a low-cost, low-maintenance technology for reducing fugitive emissions. The City of Winnipeg is responsible for the perpetual care of a total of 33 closed landfills (City of Winnipeg, 2018), which are largely unmanaged for GHGs. The largest of the closed landfills are the Summit Road Landfill and Kilcona Landfill. Summit Road Landfill, located in the northwest part of the city (south of Saskatchewan Avenue and east of Empress Street), consists of 108 ha of closed landfill and was operated from 1964-1998 (City of Winnipeg, 2018). Summit Road Landfill is ranked as the province's fifth-largest GHG emitter (101,541 t CO_2-eq.; 2015 value) (Environment and Climate Change Canada, 2015), despite having not accepted waste for nearly two decades. Likewise, Kilcona Landfill also produces significant emissions (59,094 t CO_2-eq.; 2015 value) (Environment and Climate Change Canada, 2015).

1.2 SUMMARY OF PREVIOUS RESEARCH

The research presented in this thesis is part of a larger study being conducted by Kontzamanis Graumann Smith Macmillan Inc. (KGS Group) in collaboration with the University of Manitoba

with funding by the Province of Manitoba through a Waste Reduction and Pollution Prevention (WRAPP) fund grant. The overall aim of this study is to determine the feasibility of using yard and leaf waste compost (YLWC) and biosolids compost (BSC) from BRRMF within a biologically-active landfill cover (e.g., a biocover) for mitigating CH_4 emissions. Specifically, the present research builds on previous bench-scale work that was conducted in 2014-2015 by Nicole Wilkinson and Dr. Richard Sparling (University of Manitoba) and Dr. Stan Lozecznik (KGS Group), which at the time experimented only with yard and leaf waste compost from BRRMF. The primary conclusions of this phase (Phase 1) of the work are summarized below.

Preliminary batch incubations of the YLWC under a 20% CH_4-in-air headspace confirmed that it is able to support native methanotrophic populations without the need for additional moisture or nutrients. There was, however, a high degree of competition in the compost between methanotrophs and other oxygen-consuming microorganisms (heterotrophs), implying that the YLWC requires further stabilization beyond the compost maturity standard at BRRMF prior to being used as a landfill biocover. CH_4 oxidation capacity was able to be maximized by enriching the YLWC with a methanotroph-enriched compost extract (a 'compost tea') derived from the YLWC. Moreover, it was hypothesized that by irrigating the YLWC with compost tea, any lag time required for methanotrophs to recover from freeze/thaw conditions (in the spring time, for example) could be reduced.

2 LITERATURE REVIEW

2.1 CH_4 OXIDATION IN LANDFILL COVER SOILS

2.1.1 Description of Mechanism

The aerobic oxidation of CH_4 within a landfill's final cover soil has been identified as an important process for mitigating fugitive CH_4 emissions from landfills to the atmosphere. The consumption of CH_4 occurs in the upper layers of the soil profile, where oxygenated conditions promote the growth of methane-oxidizing bacteria known as methanotrophs. The oxidation of CH_4 in landfill cover soil proceeds as illustrated in Figure 2-1; CH_4 generated from the biodegradation of organic wastes within a landfill migrates upwards into the soil cover where it is biochemically oxidized by methanotrophs to CO_2 and water via the overall reaction equation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. Overall, CH_4 oxidation by methanotrophs is an exothermic process with $\Delta G° = -780$ kJ mol^{-1} CH_4 (Scheutz et al., 2009a).

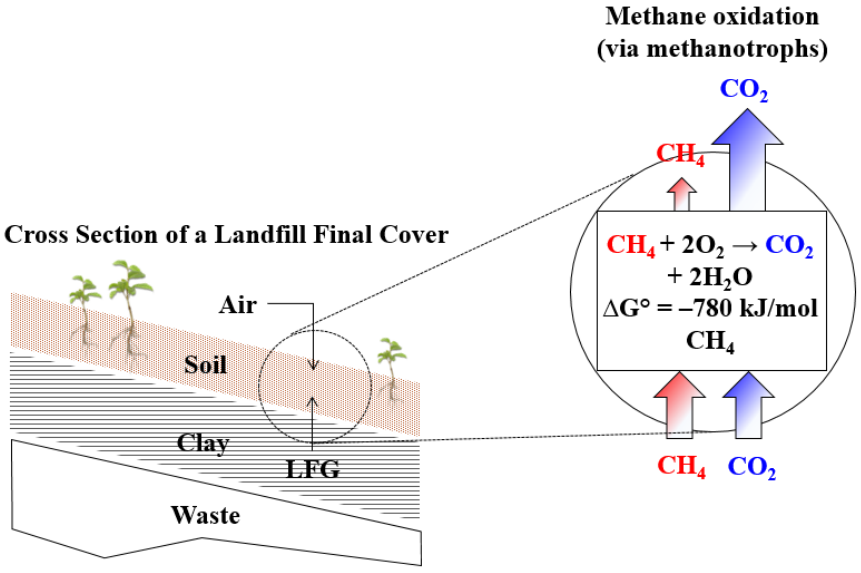


Figure 2-1: CH_4 oxidation in landfill covers

The majority of CH_4 oxidation in landfill soil covers is accomplished by methanotrophs (Hanson & Hanson, 1996). IPCC (2013) estimates that methanotrophic bacteria are responsible for the removal of 9 to 47 Tg CH_4 $year^{-1}$ from the biosphere (from soils).

2.1.2 Methanotrophic Bacteria

Methanotrophic bacteria (or methanotrophs) are a subset of methylotrophic bacteria that are unique in their ability to utilize CH_4 as their only source of carbon and energy. A defining characteristic for methanotrophs is their use of methane monooxygenase (MMO) enzymes to catalyze the oxidation of CH_4 to methanol (CH_3OH) (Hanson & Hanson, 1996).

Methanotrophs are present in the atmosphere and in many soils and sediments where CH_4 and O_2 are readily available (Hanson & Hanson, 1996). Methanotrophs that have been isolated from landfill soils can be divided into two groups based on their cell morphology and metabolic pathways used for assimilation of formaldehyde (CH_2O), the major source of cell carbon. In 1970, classification by Whittenbury et al. labelled methanotrophs as either Type I or Type II (Scheutz et al., 2009a).

The oxidation of CH_4 by methanotrophs is initiated by MMO enzymes, which are classical monooxygenases that use two reducing equivalents to break the O-O bond in dioxygen. One of the oxygen atoms is reduced to create water, and the other is incorporated during the formation of methanol (Scheutz et al., 2009a). Two forms of the MMO enzyme have been isolated in methanotrophs, a particulate (pMMO) and a soluble (sMMO) MMO. While all forms of methanotrophs are believed to be capable of expressing a particulate (i.e., membrane-

bound) MMO when copper is present, only some Type II and one Type I methanotroph are capable of forming sMMO. The ability of some methanotrophs to synthesize sMMO can be interpreted as a survival mechanism that allows those forms to persist in environments where copper is limited (Hanson & Hanson, 1996).

The two pathways that are used by methanotrophs to assimilate formaldehyde for the synthesis of carbon compounds (biomass) are the ribulose-monophosphate (RuMP) pathway and the serine pathway. The RuMP pathway is the more efficient of the two because it requires 3 mol of formaldehyde to form a three-carbon metabolic intermediate (i.e., all cellular carbon is assimilated), whereas the serine pathway utilizes 2 mol of formaldehyde and 1 mol of CO_2 to form the same three-carbon intermediate (Hanson & Hanson, 1996).

Other functional differences between Type I and Type II methanotrophs include the following: (i) Type I methanotrophs have a high CH_4 infinity, while Type II methanotrophs have a low CH_4 affinity; (ii) Type I methanotrophs favour low CH_4/high O_2 environments and are therefore most often found in the top layers of a soil cover, while Type II methanotrophs favour high CH_4/low O_2 environments and are therefore found in the bottom layers of a soil cover; and (iii) Type I methanotrophs are not able to fix atmospheric nitrogen (N_2), while Type II methanotrophs are (Reddy et al., 2014).

2.1.3 Reaction Kinetics of CH_4 Oxidation

The kinetics of CH_4 oxidation in a landfill cover soil can be modelled using the Michaelis-Menten equation, shown below, which is often used to describe single substrate enzyme kinetics:

$$r = \frac{V_{max}[CH_4]}{K_m + [CH_4]}$$

$where: r = CH_4\ oxidation\ rate$

$V_{max} = maximum\ CH_4\ oxidation\ rate$

$[CH_4] = CH_4\ concentration$

$K_m = Michaelis\text{-}Menten\ (half\text{-}saturation)\ constant$

The parameter, K_m, is an affinity constant and is taken as the CH_4 concentration where r is half of V_{max}. K_m has been found to be highly-dependent on the type of methanotroph (i.e., Type I or Type II) that dominates the reaction (Bender & Conrad, 1995; Bogner et al., 1997b). When modelling the kinetics of CH_4 oxidation with the Michaelis-Menten equation, CH_4 is the substrate while MMO is the enzyme. Several assumptions are inherent to the use of the Michaelis-Menten equation, namely that (1) the oxidation of CH_4 to CO_2 is in equilibrium, which suggests that the products, once formed, are not converted back to the substrate; (2) the reaction is at steady-state; and (3) the maximum rate of CH_4 oxidation is obtained when all available catalytic sites on the MMO enzyme are saturated (Segel, 1993). Moreover, the equation assumes that CH_4 oxidation rate is dependent on the initial concentration of CH_4, which has been verified in several studies related to methanotrophic CH_4 oxidation in landfill cover systems (Whalen et al., 1990; Abichou et al., 2011; Chanton et al., 2011; Bajar et al., 2017; Xing et al., 2017).

2.1.4 Factors Affecting CH_4 Oxidation

The CH_4 oxidation rate in landfill covers is influenced by a number of environmental factors, including but not limited to: temperature, soil moisture content, O_2 supply, pH, inorganic nitrogen, and formation of exopolymeric substances.

2.1.4.1 Temperature

Temperature is of the utmost relevance to all biological processes, including the ability of methanotrophs to utilize CH_4. Most methanotrophs are mesophiles (Hanson & Hanson, 1996) with an optimum temperature of 25-35°C in soil environments (Whalen et al., 1990; Dunfield et al., 1993; Bender & Conrad, 1995; Scheutz & Kjeldsen, 2004). When enriched from a mesophilic environment, CH_4 oxidation rates have been found to decline at 40°C and drop to virtually zero by 50°C (Zeiss, 2006). Nevertheless, methanotrophy has been observed up to 55°C from thermophilic compost (Jäckel et al., 2005) and 80°C in geothermal environments (Sharp et al., 2014).

Moreover, the utilization of CH_4 by methanotrophs has also been recorded at far lower temperatures than the previously-stated optimum, suggesting that biological landfill covers can be a viable option even in cold climates. The first psychrophilic methanotroph (optimum temperature of 3.5-10°C; minimal growth at 20°C) was isolated by Omelchenko et al. (1993) from tundra soil (Ural Region, Russia). Since then, methanotrophic activity has been observed at even lower temperatures of 1-2°C (Dunfield et al., 1993; Christophersen et al., 2000; Scheutz & Kjeldsen, 2004; Einola et al., 2007). All CH_4 oxidizing activity at lower temperatures has been

attributed to Type I methanotrophs (Borjesson et al., 2004), which implies that temperature is a selecting variable that determines which methanotroph variety dominates in a given environment. It is also known that Type I methanotrophs have a lower optimum temperature than Type II methanotrophs (Borjesson et al., 2004).

2.1.4.2 **Moisture Content**

The effect of soil moisture on CH_4 oxidation typically follows a parabolic curve, with lower rates being observed under both high and low water contents (Czepiel et al., 1996; Christophersen et al., 2000; Park et al., 2005; Wang et al., 2011). Moisture in soil is essential for sustaining microbial activity, including the activity of methanotrophs, because it serves as a medium for the transport of nutrients and removal of metabolic waste products; however, too much moisture in soil will reduce CH_4 oxidation rates by slowing down CH_4 and O_2 transport, as gaseous diffusion is in the order of 10^4 slower in water than in air (Whalen et al., 1990; Cabral et al., 2004; Sadasivam & Reddy, 2014). In a series of laboratory diffusion tests, Cabral et al. (2004) found that O_2 diffusion drops considerably at a degree of saturation of 80-84% (in de-inking residue), as the air-filled voids are no longer connected, such that gas transport relies exclusively on diffusion in the liquid phase. Alternatively, CH_4 oxidation efficiency is also significantly reduced at low moisture levels (below 5%) that stress microbial activity by dehydration (Stein & Hettiaratchi, 2001; De Visscher et al., 2007; Wang et al., 2011).

Another issue of concern involves the formation of cracks or fissures in a landfill's final cover, which can result in high spatial variations or "hot spots" in LFG emissions. Clay-based caps are particularly susceptible to saturation during periods of heavy rainfall and desiccation during

dry periods, wherein both conditions may result in preferential gas flows that lead to increased emissions (Scheutz et al., 2009a). Czepiel et al. (1996) found that approximately 5% of the cover area of a landfill in New Hampshire resulted in 50% of total CH_4 emissions, while Bergamaschi et al. (1998) concluded that 70% of CH_4 emissions from landfills in Germany and the Netherlands were released from soil cracks.

2.1.4.3 **Oxygen Supply**

The majority of methanotrophic bacteria are obligate methanotrophs and strict aerobes (Scheutz et al., 2009a; He et al., 2011) that can complete CH_4 oxidation reactions even at very low O_2 concentrations. The minimum threshold mixing ratio that can support methanotrophic activity has been reported in literature to range from 1-3% O_2 (Czepiel et al., 1996). Analysis of methanotrophs in pure cultures by Wilshusen et al. (2004a) found that O_2 concentrations ranging from 0.45-20% can sustain maximum CH_4 oxidation rates, both in Type I and Type II methanotrophs. In landfill covers, the depth to which O_2 can penetrate the soil is often the limiting factor for CH_4 oxidation, which implies that soil composition, particle size distribution, and porosity are important parameters that govern the fate of CH_4 emissions.

2.1.4.4 **pH**

The optimum pH for CH_4 oxidation by methanotrophs in soil environments is between 5.5 and 8.5 (Dunfield et al., 1993; Bender & Conrad, 1995; Scheutz & Kjeldsen, 2004), which is consistent with optimum pH values for methanotrophs in pure cultures (between 6.6 and 6.8) (Whittenbury et al., 1970; Hanson & Hanson, 1996). The pH of a landfill cover is largely

dependent on soil type and depth; there is a trend towards more acidic conditions at the top due to dissolution of CO_2 generated by soil respiration and CH_4 oxidation; however, because methanotrophs are capable of successfully adapting to changes in pH (hence their fairly wide operational pH range), pH limitation is unlikely to occur in natural cover soils (Scheutz et al., 2009a).

However, there is evidence of a certain degree of acid-tolerance in methane-oxidizers; Wolf & Hanson (1980) and Saha & Sen (1989) isolated methanotrophic *yeasts* tolerant to pH 4.4 and 3.8, respectively, and Sharp et al. (2014) found methanotrophs of the phylum Verrucomicrobia in conditions of pH 1.8-5.0.

2.1.4.5 **Inorganic Nitrogen**

The influence of inorganic nitrogen on CH_4 oxidation is very complex and may be stimulatory or inhibitory depending on the species of N and its concentration, CH_4 concentration, pH, and the type of methanotrophs present. Determination of the effects of nitrogen on CH_4 oxidation rates in landfill cover soils has recently become an issue of practical importance because of growing interest in the use of compost-amended materials, which contain high inorganic N concentrations, as landfill cover materials.

Several research-based studies have concluded that NH_4^+-based fertilization has a tendency to inhibit CH_4 oxidation in landfill covers because NH_4^+ acts as an inhibitor to the MMO enzyme. Boeckx & Van Cleemput (1996) observed a linear decrease in the CH_4 oxidation rate of a landfill cover soil amended with 25 mg-N kg^{-1}, which they reasoned was due to competitive interaction

on the basis that CH_4 and NH_4^+ are similar in size and shape. Hutsch (1998) found that application of 40 mg-N kg^{-1} to cover soil as NH_4Cl and $(NH_4)_2SO_4$ caused a nearly instantaneous negative decline of 96% in CH_4 oxidation. Similar conclusions were obtained by Scheutz & Kjeldsen (2004), although oxidation rates were found to be unaltered up to 14 mg-N kg^{-1} in NH_4^+-amended soil, which implies that there exists a threshold concentration for inorganic N in landfill covers. Chiemchaisri et al. (2001) reported that addition of NH_4^+ and NO_3^- in excess of 30 µg g^{-1} dry soil had inhibitory effects on CH_4 oxidation rate.

Further studies into the matter of nitrogen as a regulatory factor in CH_4 oxidation have concluded that NH_4^+ in many cases stimulates the growth and activity of CH_4 oxidizers (De Visscher et al., 1999, 2001; De Visscher & Van Cleemput, 2003). Methanotrophs have a relatively high demand for N (0.25 mole of N required for every mole of carbon assimilated) (Anthony, 1982); therefore, long-term unavailability of N interrupts CH_4 consumption by reducing the ability of CH_4 oxidizing bacteria to synthesize proteins needed for metabolic function. In some cases, uptake of N by landfill vegetation has been found to intensify N-limitation and inhibit the growth of methanotrophs (Scheutz et al., 2009a). N-limitation has the potential to be overcome by N_2 fixation from the atmosphere by Type II methanotrophs, although this process is an energetically less favorable option and therefore cannot be solely relied upon to maintain the growth of methanotrophs and therefore CH_4 oxidation (Scheutz et al., 2009a).

Investigations by De Visscher et al. (1999) and De Visscher et al. (2001) found that addition of NH_4^+ stimulated CH_4 oxidation in soils that were only briefly exposed (about 1 week) to high CH_4 concentrations, while NH_4^+ inhibited CH_4 oxidation in soils that had longer exposure (> 1

month) to high CH_4 concentrations. The influence of CH_4 mixing ratio has also been investigated by De Visscher & Van Cleemput (2003) on soils amended with NH_4Cl and $(NH_4)_2SO_4$. At CH_4 mixing ratios greater than 1%, there was a peak in methanotroph activity of the Type I variety, followed by depletion of soil inorganic N which led to a few weeks of N-starved steady-state conditions, and concluding with a second, broader peak of methanotrophic activity most likely dominated by N_2-fixing Type II methanotrophs.

NO_3^- is inhibitory to CH_4 oxidation through osmotic effects, but only at high concentrations not typically found in MSW landfills, for example if there exists a large population of ammonia oxidizing bacteria in the landfill cover soil (Bodelier & Laanbroek, 2004).

2.1.4.6 **Exopolymeric Substances**

Long-term laboratory column experiments aimed at quantifying CH_4 oxidation rates under simulated landfill cover conditions have often exhibited a peak in CH_4 uptake followed by a gradual decline in biotic CH_4 oxidation to a lower steady state value (De Visscher et al., 1999; Wilshusen et al., 2004b; and Scheutz et al., 2009b. The accumulation of exopolymeric substances (EPS) following prolonged exposure to landfill gases has been suggested as a possible contributing factor to the decline in CH_4 oxidation efficiency due to clogging of the soil pores, which impedes the transfer of substrates into bacterial cells, therefore causing short-circuiting of LFG through the cover material (De Visscher et al., 1999; Wilshusen et al., 2004b; and Scheutz et al., 2009b).

The mechanisms that lead to EPS formation in methanotrophic microorganisms are not well understood, although it is hypothesized that EPS is produced to prevent formaldehyde accumulation in cases of carbon excess or lack of nutrients, and hence is linked to nitrogen or oxygen deprivation (Linton et al., 1986). Wilshusen et al. (2004) aimed to quantify the effects of oxygen on the formation of EPS, and found that more stable CH_4 oxidation activity could be achieved at an O_2 concentration of 1.5% compared to 10.5%, and that EPS production at high O_2 concentrations was 2.5 times that of production at low oxygen concentrations. The authors hypothesized that EPS serves as a carbon cycling mechanism for Type I methanotrophs in the event of inorganic nitrogen limitation. Moreover, the shift from Type I to Type II methanotroph dominance that was observed over the 6-month experimental duration could be the result of accumulation of EPS creating microaerophilic conditions that favored the growth of Type II methanotrophs that are able to fix nitrogen directly from the atmosphere when O_2 concentrations are low.

2.2 ENGINEERED LANDFILL COVER SYSTEMS

Following observations that high CH_4 oxidation capacities were often associated with materials that were porous/permeable, coarse, and rich in organic matter, the potential to exploit the process using suitable cover materials and amendments was quickly realized. Laboratory investigations of microbial CH_4 oxidation shifted towards using low-cost materials such as sewage sludge, yard and leaf waste, kitchen waste, and municipal solid waste, either alone or as amendments to the cover soil, to induce favorable conditions for the growth of methanotrophs. Such cover systems have been termed “biological”, “bio-based”, or “engineered” cover systems, and can be used either alone or in conjunction with a gas extraction system to mediate fugitive

CH_4 emissions from landfills. The various types of biological cover systems are summarized herein and are illustrated in Figure 2-2.

Biocovers

As with all types of engineered cover systems, biocovers include a basal 'gas distribution layer' (GDL) that is highly permeable to homogenize LFG fluxes, and an overlying 'oxidation layer' to provide a growth matrix that supports methanotrophic populations. Biocovers are typically spread over the entire area of a landfill, and therefore cost is a critical factor that determines the selection of material (Scheutz et al., 2009a).

Biowindows

Biowindows are integrated into a landfill cover system in discrete, excavated sections and therefore only treat specific areas of a landfill site. Biowindows are more feasible than a full-expanse landfill biocover because they require a considerably lower amount of cover material. LFG is naturally routed to the oxidative layer of the biowindows via the GDL, and so this technique is most practical for landfills that do not have a gas collection system (Huber-Humer et al., 2008).

Biofilters

Biofilters for landfill CH_4 oxidation applications are described as "self-contained, fixed-bed reactors" (Huber-Humer et al., 2008) that contain a suitable packing material for sustaining methanotrophic growth. When integrated into a landfill's existing final cover, biofilters require

an external support structure to contain the filter material, and an active or passive LFG collection system to feed to the filter (Huber-Humer et al., 2008; Sadasivam & Reddy, 2014). Biofilters can also be applied in the field as stand-alone reactors, as was done by Powelsen et al. (2006). Biofilters in literature have been tested using varying configurations (i.e., open- or closed-bed) and flow regimes (i.e., up- or down-flow). Closed-bed systems, although more efficient because they are isolated from the negative impacts of climatic variations, are oftentimes deemed economically infeasible because of high capital and operating costs (Huber-Humer et al., 2008).

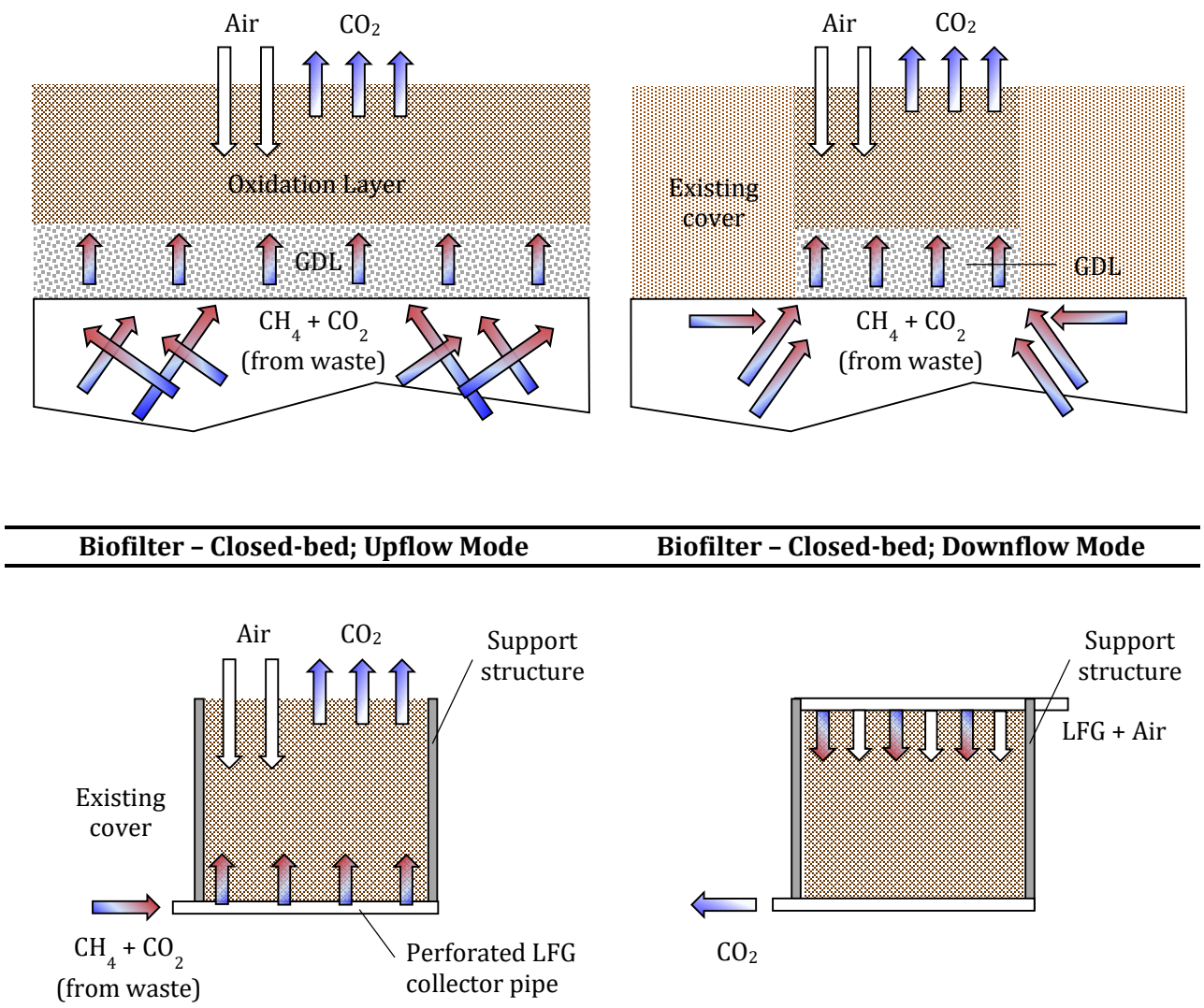


Figure 2-2: Types of biological landfill cover systems

Biotarps

A biotarp is a removal geotextile support at least 15 cm thick that is inoculated with methanotrophic bacteria. While biocovers, biofilters, and biowindows are final covers on a landfill, biotarps are implemented as a daily cover system for mitigating CH_4 emissions from

recently-placed wastes during the active life of a landfill. The support materials that compose the biotarp must have good moisture retention qualities and be non-biodegradable and light enough to transport from one landfill cell/site to another (Sadasivam & Reddy, 2014).

2.3 PRACTICAL APPLICATIONS AND DESIGN OF BIOCOVERS

Composts and other soil amendments are oftentimes so heterogeneous in composition, that short-term batch tests cannot provide conclusive results about the nature of CH_4 oxidation in the field. Continuously-charged column tests can be operated for longer durations and with a higher soil mass and more representative soil particle size to reveal long-term changes that can occur, such as EPS formation or toxic inhibition (Scheutz et al., 2009a).

Laboratory investigations of CH_4 oxidation in simulated landfill conditions have assessed several growth matrices for use in biocovers, including but not limited to MSW and sewage sludge compost garden/leaf/wood waste compost and sand/woodchips (Scheutz et al., 2009b; Roncato & Cabral, 2012; Rose et al., 2012); compost mixed with perlite (Melse & Van der Werf, 2005); mechanically-biological treated (MBT) waste residuals (Einola et al., 2008); and soils amended with biochar (Reddy et al., 2014; Xie et al., 2014; Yargicoglu & Reddy, 2017); and aged refuse (Mei et al., 2016).

The highest rates of CH_4 utilization are typically observed in mature (well-decomposed) composts that were fairly uniform and coarsely structured with low C/N ratios and low ammonium concentrations (Scheutz et al., 2009a). Compost maturity minimizes competition for O_2 with non-methanotrophic heterotrophs to ensure that methanotrophic communities

within the cover are not outperformed (Felske, 2003; Huber-Humer, 2004; Scheutz et al., 2011). Other important influencing factors noted in literature, for example temperature and moisture content, can be regulated using composts because they have a high water retention capacity and high specific surface area (Scheutz et al., 2009a).

The most widely used and recognized approach to the design of landfill biocovers involves four steps (Huber-Humer et al., 2009):

1. Site investigation – To determine the CH_4 loading that the cover system must accommodate.
2. Laboratory investigation – To aid in the selection of an appropriate cover material by evaluating CH_4 oxidation rates associated with potential organic materials under simulated landfill conditions.
3. Baseline study – At the test site, to determine the presence of any hot spots to decide the optimal placement of the cover.
4. Construction and post-installation monitoring – To obtain critical information about the effectiveness of the in-place cover system at mitigating landfill CH_4 emissions.

2.4 SUMMARY OF PREVIOUS LABORATORY STUDIES

The following section provides a summary of the technical findings from the most recent and relevant laboratory research studies involving biologically engineered landfill covers. Tables 2-1 and 2-2 list the design parameters and observed CH_4 oxidation capacities in the selected batch- and column-scale experimental studies involving various cover materials.

Einola et al., 2008 evaluated the CH_4 oxidation capacity of the residual fraction of mechanically-biologically treated (MBT) grey waste collected from the region of Loimi-Häme (Forssa, Southwestern Finland). Two MBT residuals, composted for a total of 22 weeks (i.e., MBT residual 22) and 54 weeks (i.e., MBT residual 54), were tested in a column set-up, with batch assays done before and after. Both materials displayed generally similar CH_4 oxidation rates over the range of loading rates tested (30-78 g CH_4 m^{-2} day^{-1}) in the columns. The CH_4 oxidation rate, however, was slightly higher in MBT residual 22 than in MBT residual 54 at low temperatures of 2-10°C. It was concluded that a landfill cover containing MBT residuals could provide year-round reduction of greenhouse gas emissions from landfills located in geographical zones characterized by cold climates; however, the leachability of certain heavy metals from the MBT residuals would have to be addressed, considering that concentrations of zinc, copper, arsenic, nickel, and lead in one or both leachates exceeded boundary values for materials to be used in landfill final covers. Moreover, the formation of nitrous oxide (N_2O), a GHG 265 times more potent than CO_2, from the MBT residuals (<15 μg N_2O kg_{dw}^{-1} d^{-1}) was reported. The worsening effect of N_2O production on the overall GHG reduction potential of the material was found to be negligible, however.

Perdikea et al., 2008 investigated the possibility of using a thin biocover (TBC) (i.e., less than 40 cm in thickness) as an intermediate waste cover, a concept which previously had not been studied in a systematic manner. Unlike a typical landfill cover, a TBC can be used between the active filling stages of a landfill, and therefore is a particularly relevant technology for use on bioreactor landfills. The initial stage (Stage I) of batch incubation experiments, meant to cultivate an appropriate methanotrophic population, involved the testing of 30 different mixtures of leaf and manure compost (CM) to sawdust (SD) at moisture contents (MC) of 20-

79% ww and SD contents of 0-40% w/w. Only eight of the 30 mixtures, those at high MC (40-70% ww) and low SD contents (≤10% w/w), were found to have satisfactory CH_4 oxidation capacities. Specifically, the poor performance of the mixtures with higher SD contents (>20% w/w) was attributed to high rates of aerobic decomposition in the sawdust itself. The second stage (Stage II) of batch incubations involved the testing of 10/0 and 9/1 CM/SD ratios at four different moisture ranges, 37-40, 47-52, 55-60, and 64-70% ww. The mixtures at MC = 47-52% were concluded to be the optimum media for further testing in column-scale. Some mixtures at higher MCs were equally as or more effective at oxidizing CH_4, but were concluded to be more likely to cause waterlogged conditions in the columns. Accordingly, a set of column experiments were performed for 40 days (average CH_4 inlet flow rate of 3.5 mL/min or a flux of 11.3 g m^{-2} day^{-1}) to assess the effect of CM/SD, MC, and biocover thickness (BC) in a flow-through system. The relatively short operation time was chosen on the basis that a TBC as an intermediate landfill cover would only remain in place for a maximum of 30-40 days. The columns containing mixtures of 10/0 and 9/1 CM/SD with a BC of 30 cm reached 100% CH_4 oxidation efficiencies within a short acclimatization period of 2 days (MC = 52% ww) and 4 days (MC = 47% ww). Overall, columns with a BC of 30 cm yielded better results than columns with a BC of only 15 cm, probably due to increased CH_4 residence time and slower desiccation of the active zone. Thereafter, the effect of a gradual step-wise increase in CH_4 inlet flow rate from 1.0 mL/min (1.9 g m^{-2} day^{-1}) to 7.5 mL/min (67.9 g m^{-2} day^{-1}) was determined for the two columns with the best performance (10/0 and 9/1 CM/SD, MC = 52% ww, BC = 30 cm). Both columns were able to oxidize CH_4 completely, with only a small and temporary decrease in oxidation efficiency when the CH_4 inlet flux was increased to the final tested value of 67.9 g m^{-2} day^{-1}.

Pedersen et al., 2011 evaluated several locally-available compost materials to determine their suitability for use in a full-scale biocover application at Fakse Landfill (Denmark). These materials included raw garden waste compost, aged 1, 4, and 8 years (RC1, RC4, and RC8, respectively); sewage sludge compost (SC); and the resulting fractions from screening of the raw compost – fine compost (FC) and screening residue, aged 1 and 3 years (SR1 and SR3, respectively). The following criteria from literature were identified as possible indicators of the suitability of the composts to oxidize CH_4 emissions:

- Organic content >15% DM (dry matter) (Huber-Humer et al., 2009);
- Total organic carbon (TOC) > 7% DM (Huber-Humer et al., 2009);
- Water contents close to the optimum (70-80% and 100% DM) reported by Mor et al. (2006);
- Total Kjeldahl Nitrogen (TKN) within range of 1800-21000 mg kg^{-1} DM (Wilshusen et al., 2004b), and N_{tot} close to 15,400 mg kg^{-1} DM (Mor et al., 2006);
- C/N ratio of approximately 15 (Humer & Lechner, 2001); and
- Sulfate (SO_4^{2-}) > 500 mg kg^{-1} (Huber-Humer et al., 2009).

Based on a scoring matrix that included CH_4 oxidation rate, O_2 demand, structure (porosity and gas permeability), material availability, and price as selection criteria, only five of the seven materials were selected for further testing in column incubations. The SR3 was excluded from further testing on the basis of its high rate of respiration (i.e., O_2 demand), which was the result of its high content of non-degraded twigs and branches. Meanwhile, the RC8 was also excluded on the account that it showed the lowest CH_4 oxidation potential over three consecutive stages of incubation (i.e., flushes) with CH_4.

In the subsequent column studies, the three best-performing materials had fairly similar average CH_4 oxidation rates of 120 g m^{-2} day^{-1} (FC), 112 g m^{-2} day^{-1} (SC), and 108 g m^{-2} day^{-1} (RC4); however, the long-term CH_4 oxidation trends (i.e., towards 'steady state') were most promising for the FC and SC, with CH_4 oxidation rates of 122 g m^{-2} day^{-1} and 107 g m^{-2} day^{-1} at the end of the 111-day experiment, respectively.

Scheutz et al., 2009b assessed the efficacy of four types of compost mixtures, including the commercial product Supermuld, at reducing landfill CH_4 and volatile organic carbon (VOC) emissions, namely CFC-11, HCFC-21, HCFC-31, and HFC-41. In all four columns, peak CH_4 oxidation rates (reached between days 20 and 40) were followed by a decline to a steady-state oxidation rate (approximately 50 days after start-up), possibly due to nutrient limitation or formation of EPS. This trend was also observed by De Visscher et al. (1999) and Wilshusen et al. (2004) in different media. The column filled with compost mixed with wood chips (1:1) showed the highest average steady state CH_4 oxidation rate (161 g m^{-2} d^{-1}), followed by the Supermuld column (110 g m^{-2} d^{-1}). These rates corresponded to CH_4 oxidation efficiencies of 58% and 48%, respectively, for CH_4 fluxes of 229 to 254 g m^{-2} d^{-1}, which are in the mid-to-high range of reported fluxes in the field. The column containing compost mixed with sand (1:1) was found to produce CH_4, and hence the average steady state CH_4 oxidation rate was reported as negative (-31 g m^{-2} d^{-1}). All VOCs were degraded to some extent. CFC-11 was anaerobically degraded (dechlorinated) to HCFC-21 and HCFC-31 (0-85% efficiency); HCFC-21 was removed via anaerobic and aerobic degradation processes (50-55% efficiency); and HCFC-31 and HFC-41, i.e., the less-chlorinated compounds, were oxidized (28-89% and 76-100% efficiencies, respectively.)

Roncato & Cabral (2012) evaluated the performance of two compost-based substrates in laboratory column tests and later under field conditions at the St. Nicéphore Landfill (Quebec, Canada). The tested substrates were compost mixed with sand (5:1) and the same 5:1 compost:sand mixture mixed with gravel (1:1). The compost was produced from municipal sewage sludge and sludge from the pulp of the paper and agri-food industries. The resiliency of the system under continuous increases in CH_4 load was determined. As the CH_4 influx was gradually increased, oxidation efficiencies remained at 100% until a CH_4 influx of 70 g m^{-2} d^{-1}. Increasing the CH_4 load further to 100 g m^{-2} d^{-1} lead to a drop in oxidation efficiency to 83% (5:1 compost:sand) and 95% (1:1 compost/sand:gravel). After this 100 g m^{-2} d^{-1} load was maintained for a few days, oxidation efficiencies returned to 100% for both mixtures, possibly because the methanotrophic populations had adapted to the higher loading. A more abrupt drop in oxidation efficiency at a CH_4 load of 125 g m^{-2} d^{-1} lead the research team to conclude that a threshold loading had been exceeded, and that this threshold value was somewhere in the vicinity of 100 g CH_4 m^{-2} d^{-1}. Maximum CH_4 oxidation rates obtained in the laboratory were reported as 115 and 118 g m^{-2} d^{-1} for the two mixtures, respectively.

Wang et al. (2011) performed a series of extensive batch incubations of waste biocover soil collected from an organic waste landfill bioreactor in a village in Xindeng town (Zhejiang Province, China). The batch experiments aimed to evaluate the effect of biocover soil properties on CH_4 oxidation (particle size, moisture, and pH value), as well as the kinetics of CH_4 oxidation (0.01-30% CH_4 v/v) and other influencing factors (temperature, oxygen concentration, and nitrogen (NH_4^+–N and NO_3^-–N) stress). The influence of the biocover soil properties on CH_4 oxidation was found to follow a parabolic relationship (i.e., with low observed rates at both ends of the tested range). The maximum CH_4 oxidation rate was observed at a soil granularity

of ≤4 mm (3.60 μmol g_{dw}^{-1} h^{-1}). At particle sizes below ≤0.45 mm and above ≤25 mm, CH_4 oxidation rate fell below 0.91 μmol g(d.w.)$^{-1}$ h^{-1} due to a decreased capacity for air diffusion from the atmosphere (≤0.45 mm) or insufficient residence time for CH_4 owing to preferential flow paths (≤25 mm). The CH_4 oxidation potential was nearly zero at a moisture content ≤10% (due to desiccation), and then increased over the moisture range from 10-30%, reaching a maximum between 30-45% (3.66 μmol g(d.w.)$^{-1}$ h^{-1}) before it decreased to 1.43 μmol g(d.w.)$^{-1}$ h^{-1} at a moisture content of 70% (waterlogged conditions limiting diffusion of oxygen). Maximum CH_4 oxidation activity was observed at pH between 6.7 and 7.9. Meanwhile, the Michaelis–Menten model (K_m = 7.95 x 10^5 ppmv; Vmax = 9.03 μmol g_{dw}^{-1} h^{-1}) was found to be a good fit for the kinetics of CH_4 oxidation in the waste biocover soil; the CH_4 oxidation rate was enhanced by increasing CH_4 headspace concentration from 0.01-10% until such a concentration (≥10%) that the substrate became saturated. Ambient conditions such as temperature, oxygen concentration, and nitrogen were confirmed to have a profound effect on the CH_4 oxidation potential of the waste soil. The CH_4 oxidation rate was found to increase exponentially in the temperature range from 4-30°C and then began to decrease rapidly around 45°C and was completely inhibited at 60°C. The CH_4 oxidizing bacteria were found to prefer oxygen concentrations from 5-20% and were largely inactive at microaerophilic (0-1% O_2) conditions. Lastly, the addition of NH_4^+–N and NO_3^-–N up to 600 mg/kg enhanced CH_4 oxidation rate, probably because of the low background concentration of nitrogen in the waste biocover soil.

Rose et al., 2012 investigated the suitability of four different substrates as potential biofilter materials for a tropically-located landfill in the region of Baixada Fluminense (Rio de Janeiro, Brazil). These substrates included a landfill surface soil (red-yellow podzolic); MSW compost;

and two soil:compost mixtures, 1:1 (w/w) (i.e., M11) and 3:1 (w/w) (i.e., M31). In the column-scale tests, CH_4 oxidation in the soil and compost was detected almost immediately (i.e., no lag phase). Meanwhile, the soil:compost mixtures required an approximately 25-day acclimation period, where very little CH_4 oxidation was observed. Ultimately, the addition of compost to the native landfill cover soil was found to be beneficial, as it induced higher average CH_4 oxidation rates (584 g m^{-3} day^{-1} for M11 and 456 g m^{-3} day^{-1} for M31) than what was observed in the landfill soil alone (447 g m^{-3} day^{-1}). The average CH_4 oxidation rate was highest in the MSW compost biofilter (990 g m^{-3} day^{-1}), although the authors ultimately recommended that a soil:compost mixture be used as a result of its operational advantages.

Reddy et al., 2014 conducted laboratory column experiments to evaluate whether landfill cover soil amended with biochar can promote the growth of CH_4 oxidizing bacteria. The addition of high porosity biochar (20% biochar-amended soil; Column 2) was found to improve gas retention and transport through the cover relative to the control cover (soil only; Column 1). In general, CH_4 concentrations in the biochar-amended column were less than that in the soil column within the oxic zone (~0-40 cm depth in Column 2). In batch incubations of soil samples taken from the columns, V_{max} of the biochar-amended column was significantly higher (0.38 and 1.35 nmol s^{-1} g_{dw}^{-1} at 22°C and 35°C, respectively) than the soil column (0.18 and 0.16 nmol s^{-1} g_{dw}^{-1}). Molecular and isotopic evidence appeared to support the conclusion that biochar is a favourable growth medium for methanotrophic bacteria. On the basis of qPCR analysis of DNA extracted from soil samples taken from the columns, a higher number of particulate MMO (pmoA) gene copies were detected in the column with biochar. Moreover, it was found that the column with biochar showed greater (increasingly positive) values for $\delta^{13}C$(‰) (CH_4) than the soil column, from a 40-cm depth ($\delta^{13}C$(‰) = -35.63) to the uppermost

sampling port ($\delta^{13}C(‰) = -22.76$), where $\delta^{13}C(‰)$ is a calculated value that can be used to quantify the extent of isotope fractionation that occurs when CH_4 is oxidized through a landfill cover.

Table 2-1: Summary of biocover batch incubation studies

Reference	Material	Moisture content	Organic matter	Porosity	Dry bulk density	pH	Temp.	Head-space CH_4 conc.	CH_4 oxidation rate		
									I	II	III
		(% dw)	(% w/dw)	(%)	(g cm^{-3})	-	(°C)	(% v/v)	(µg CH_4 g_{dw}^{-1} $hour^{-1}$)		
Perdikea et al. (2008)	Leaf/manure compost	59-67	40	41.5	0.36	8.3	22	5	-	5.0	-
		89-108	40	41.5	0.36	8.3	22	5	-	5.8	-
		122-150	40	41.5	0.36	8.3	22	5	-	6.4	-
		178-233	40	41.5	0.36	11.3	22	5	-	4.7	-
	Leaf/manure compost & sawdust (9:1)	59-67	46	40.8	0.35	-	22	5	-	3.4	-
		89-108	46	40.8	0.35	-	22	5	-	6.6	-
		122-150	46	40.8	0.35	-	22	5	-	6.3	-
		178-233	46	40.8	0.35	-	22	5	-	6.9	-
Einola et al. (2008)	MBT residual (22 weeks)	79	47	49	0.70	7.4	5	9	<0.16	-	-
							25	9	28	-	-
	MBT residual (57 weeks)	104	39	47	0.70	7.3	5	9	<0.16	-	-
							25	9	20	-	-
Pedersen et al. (2011)	Fine compost (2 years)	64	-	-	-	8.4	Room	15	46	44	27
	Raw compost (1 year)	84	-	-	-	8.5	Room	15	11	25	13
	Raw compost (4 years)	72	-	-	-	8.4	Room	15	53	75	161
	Raw compost (8 years)	50	-	-	-	7.7	Room	15	3	7	5
	Sewage sludge compost	89	-	-	-	8.6	Room	15	19	86	142
	Screening residue (1 year)	73	-	-	-	8.4	Room	15	19	11	11
	Screening residue (3 years)	90	-	-	-	8.5	Room	15	12	36	41

Table 2-2: Summary of biocover column incubation studies

Reference	Material	Moisture content	Temp.	Height of substrate layer	CH_4 loading rate	CH_4 oxidation rate		CH_4 oxidation efficiency	Experiment duration	Gas profiles
		(% dw)	(°C)	(m)	(g CH_4 m^{-2} day^{-1})	(g CH_4 m^{-2} day^{-1})	-	(%)	(days)	yes/no
Perdikea et al. (2008)	Leaf/manure compost	89	22	0.30	11.3	11.3	Steady state	100	40	yes
		108	22	0.30	11.3	11.3	Steady state	100	40	no
		108	22	0.15	11.3	8.7	Steady state	77	40	no
	Leaf/manure compost & sawdust (9:1)	89	22	0.30	11.3	11.3	Steady state	100	40	no
		108	22	0.30	11.3	11.3	Steady state	100	40	no
		108	22	0.15	11.3	7.2	Steady state	64	40	no
Einola et al. (2008)	MBT residual (22 weeks)	79	22-25	0.30	30	30	-	100	5-39	yes
			22-25	0.30	60-78	53-82	-	88-100	39-52	yes
			22-25	0.30	78	64-74	-	82-95	52-77	yes
			9-12	0.30	78	56	-	72	77-87	yes
			2-10	0.30	78	39	-	50	87-124	yes
	MBT residual (57 weeks)	104	22-25	0.30	30	30	-	100	5-39	yes
			22-25	0.30	60-78	53-82	-	88-100	39-52	yes
			22-25	0.30	78	72-79	-	92-100	52-77	yes
			9-12	0.30	78	61	-	78	77-87	yes
			2-10	0.30	78	22	-	28	87-124	yes
Scheutz et al. (2009b)	Compost & woodchips (1:1)	35	22	0.70	229-254	247, 161	Maximum, steady state	100, 58	255	no
	Compost & sand (1:1)	30	22	0.70	229-254	116, -31	Maximum, steady state	48, -10	255	yes
	Compost & sand (1:5)	12	22	0.70	229-254	60, 29	Maximum, steady state	60, 12	255	no
	Supermuld	10	22	0.70	229-254	84, 110	Maximum, steady state	84, 48	255	no

3 RESEARCH OBJECTIVES

The overall objective of the research was to assess the efficacy of two compost materials, yard and leaf waste compost (YLWC) and biosolids compost (BSC), at oxidizing CH_4, in a series of laboratory batch and column experiments under several conditions.

The detailed objectives are as follows:

1. Characterize the Biological Potential of the YLWC and BSC for Methanotrophy (Batch-scale) – The suitability of the YLWC and BSC for CH_4 oxidation, both as an inoculum and a substratum (growth matrix) for methanotrophic bacteria, was investigated in two concurrent batch incubation experiments. First, the maturity/stability of the YLWC and BSC was determined by quantifying compost respiration as a function of readily available Biological Oxygen Demand (raBOD) and CO_2 production. Second, the Methane Oxidation Potential (MOP) of the YLWC and BSC was assessed at room temperature under a 20% CH_4-in-air headspace. The results of the respiration and MOP tests for the YLWC were compared to the YLWC data obtained in the prior phase of the work, to quantify the effect of an additional one year of compost curing time on CH_4 oxidation. In these experiments, both the YLWC and BSC were tested at their *in-situ* moisture contents of 64% and 36% ww.

2. Evaluate the Effect of Select Parameters on Methanotrophy in Batch Enrichments (Batch-scale) – The effect of the following variables on CH_4 oxidation rate in the composts was determined: compost moisture content, compost mixing ratio (i.e., ratio of YLWC to BSC),

inoculation of the BSC with a methanotroph-enriched compost extract ("compost tea"), and compost heavy metals content.

3. Assessment of the Long-term Stability of CH_4 Oxidation in Batch Enrichments (Batch-scale) – Long-term (>100-day) CH_4 oxidation rates were quantified in the YLWC, BSC, and 1:1 and 1:4 YLWC:BSC w:w mixing ratios in batch incubations to assess the stability of CH_4 oxidation in a stationary phase culture that is nutrient limited but in carbon (CH_4) excess.

4. Assessment of CH_4 Oxidation Rates in a Flow-through System (Column-scale) – The CH_4 oxidation performance in a flow-through system was assessed in a series of column experiments with test variables including compost mix ratio, moisture content, and the addition of compost tea.

4 MATERIALS AND METHODS

4.1 MATERIALS USED

This research evaluated the efficacy of two compost materials, YLWC and BSC, at oxidizing CH_4 within an experimental landfill bio-cover. The first sample of YLWC was collected from BRRMF in June 2014, approximately one year prior to the start of the present thesis. The YLWC was tested for its raBOD and MOP shortly after collection, and then again after having been stored at 4°C for approximately one year. In this thesis, the "initial" YLWC is referred to as "iYLWC", while the latter, "matured" material is referred to as "mYLWC". It is the latter material (i.e., mYLWC) that was investigated in the first half of this thesis, along with BSC that was collected from the Edmonton Composting Facility in Edmonton, Alberta in January 2015.

Once BSC from BRRMF became available, a second sample of YLWC and a sample of BSC were collected from the site, in September 2015. These compost were evaluated in the second half of this thesis.

4.2 EXPERIMENTAL PROCEDURES

4.2.1 Experiments Performed Using Batch Incubations

4.2.1.1 General Procedure

Assessment of the methanotrophic potential of the YLWC and BSC was performed in sealed, 120 mL glass serum bottles (Fisher Scientific; Toronto, ON, Canada) following the general

protocol established by Wilkinson et al. in 2014 (with minor changes), which is described as follows. A fixed amount of compost material was added to the bottles, typically 2 g wet weight, unless otherwise stated. The bottles were sealed with a 20 mm blue chlorobutyl septum stopper (Bellco Glass Inc.; Vineland, NJ, USA), and an aluminum crimp cap (Wheaton Industries; Millville, NJ, USA). The septum stopper enabled gases to be collected from the headspace of the bottles via a gas-tight sample-lock syringe. For experiments involving methane, 30 mL of CH_4 were added to each bottle yielding an initial headspace that is 20% (mol%) CH_4, 16.8% (mol%) O_2, and 63.2% (mol%) N_2. Gas chromatography (GC) analysis was used to measure the concentration of headspace gases with time (see Section 4.3 for method). Once GC indicated that there was no detectable O_2 left in the bottles, the bottles were unsealed and allowed to equilibrate with laboratory air for approximately 40 minutes, then re-sealed and 20% CH_4-in-air headspace re-established. This procedure was termed as "headspace flushing," and was done to restore O_2 and CH_4 levels while eliminating potentially inhibitory effects from the build-up of CO_2; a similar protocol was used by Perdikea et al. (2008). All batch incubations were performed at room temperature (22°C) in minimum triplicate assays. When not being analyzed, bottles were stored in a dark cabinet to prevent the growth of phototrophic microorganisms, which are not native to landfill cover soils.

4.2.1.2 **Experiment-Specific Procedures**

Effect of Moisture Content

To assess the effect of moisture content on methanotrophy, the mYLWC and BSC were first dried in a low temperature (30°C) oven for 72 hours, after which their moisture content was measured to be 4.8% and 3.5% g g^{-1} wet basis, respectively. The dried composts (2 g wet weight) were added to 120 mL serum bottles. Then, the moisture content of the composts was amended by adding a calculated volume of Milli-Q® water to each bottle to achieve the following moisture contents: 5, 20, 35, 50, 65, and 80% g g^{-1} wet basis.

Effect of Compost Mixing Ratio

The following five (5) mixing ratios of mYLWC to BSC were tested: 1:1, 1:2, 2:1, 1:4, and 4:1 w:w. The composts were added to 120 mL serum bottles to achieve a total combined weight of 2 g wet weight. The composts were not amended for moisture (i.e., the compost mixes in the bottles were tested at their *in-situ* moisture content).

Effect of Inoculation with a Methanotroph-Enriched Compost Extract

A methanotroph-enriched compost extract (i.e., a "compost tea") was created from the mYLWC and added to the BSC. The culturing protocol used to create the compost tea was based on a similar protocol used by Wartiainen et al. (2006) in isolating the novel methanotroph *Methylocystis rosea*. To create the tea, mYLWC (6 g wet weight) was added to 30 mL nitrate mineral salts (NMS) medium, a defined medium containing no soluble source of carbon

(Whittenbury et al., 1970), and 0.3 mL of a phosphate buffer solution (pH of 6.8). The mixture was vortexed in a centrifuge tube for 1 minute at maximum speed, and 1 mL of the resulting supernatant was added to 9 mL NMS medium and 90 μL phosphate buffer in a 120 mL serum bottle which was then sealed with a septum stopper and crimp cap. The headspace was adjusted to 20% CH_4-in-air by adding 24 mL CH_4 to each serum bottle using a gas-tight sample-lock syringe. Once gas chromatography indicated that there was no detectable oxygen left in the tubes, 1 mL of culture was passaged into 9 mL of fresh media and 20% CH_4-in-air headspace was re-established. After one successful passage, 1.7 mL of the resulting tea was added to the BSC (2 g wet weight) in a 120 mL serum bottle, increasing the moisture content of the compost to 65% g g^{-1} wet basis.

Effect of Heavy Metals

The biosolids compost from the City of Edmonton contained elevated concentrations of the heavy metals chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn), in comparison to the YLWC (Table 4-1).

Table 4-1: Heavy metals content of the YLWC and BSC

Heavy Metal	Concentration (mg/kg)	
	YLWC	BSC
Chromium	5.1	110.10
Copper	14.0	269.65
Lead	7.0	54.10
Zinc	44.0	393.95

Two large volumes of the mYLWC (1 kg wet weight) were weighed out and spiked with heavy metals to test two concentrations, a 1x and 10x heavy metals concentration (that is, the mYLWC at the heavy metals content of the BSC, referred to as mYLWC-1x, and ten times the heavy metals content of the BSC, referred to as mYLWC-10x). The following chemicals were used, chosen on the basis of their high solubility: chromium (III) sulfate ($Cr_2(SO_4)_3 \bullet 15H_2O$), copper (II) chloride ($CuCl_2$), lead (II) acetate ($Pb(C_2H_3O_2)_2 \bullet 3H_2O$), and zinc sulfate ($ZnSO_4 \bullet 7H_2O$). Once the 1 kg batches of the spiked mYLWC were sufficiently mixed, 2 g wet weight of the compost were added to 120 mL serum bottles. The bottles were sealed with a rubber stopper and crimp cap, and a 20% (mol%) CH_4-in-air headspace was established. Total activity in the bottles was monitored over two headspace flushes. CH_4 oxidation rates were compared to a control (unspiked mYLWC).

4.2.2 Experiments using Flow-through Microcosms (Columns)

4.2.2.1 Column Design and Set-up

The 90 cm-high, engineered soil column used throughout the duration of the column experiments was constructed from Plexiglas® tubing (outer diameter = 6" or 15 cm, thickness = 0.25" or 0.6 cm) (Johnston Industrial Plastics Ltd.; Winnipeg, MB), following similar designs used by Humer & Lechner (1999), Kettunen et al. (2006), Perdikea et al. (2008), Scheutz et al. (2009b), Stein & Hettiaratchi (2010), Gebert et al. (2011), Rachor et al. (2011), and Reddy et al. (2014). The column was sealed at both ends, with the design incorporating a removable top lid fitted with a nitrile rubber O-ring (Kepco Sealing Supplies, Inc.; Winnipeg, MB) to ensure a gas-tight seal. An inlet for synthetic LFG (50/50 v/v CH_4/CO_2) (Praxair Canada Inc.; Mississauga,

ON) was installed at the bottom of the column and an inlet for air and an outlet for effluent gas were installed at the top. The flows of LFG and air to the column were controlled using valved variable area flowmeters (Cole-Parmer Canada Company; Montreal, QC). A flowmeter was also installed at the column outlet to measure the flow of exit gas. Tubing was 3/8" (1 cm) internal diameter plastic hose.

Vertically, a total of thirteen (13) sampling ports fitted with 3/8" (1 cm)-thick silicone septa (Cole-Parmer) were located down the sides of the column to enable the collection of soil pore gas samples via syringe needle. The top-most sampling port (Port No. 13) was located 2 cm under the compost fill-line, with additional sampling ports (Ports No. 12 to 1) located every 5 cm thereafter (alternating between the left and right side of the column). The column was packed with a 16 cm-thick gas distribution layer (GDL) of ¼" (0.5 cm) limestone gravel followed by a 64 cm-thick layer of the compost material to be investigated. The compost was gently compacted by hand in 5-10 cm layers, following the procedure used by Kettunen et al. (2006), with the top of each layer gently scraped off prior to placing the next layer to avoid interface effects. The LFG was supplied to the bottom of the column at Q_{LFG} = 15 mL min^{-1}, which corresponds to a CH_4 flux of 470 g m^{-2} d^{-1}, which is in the higher range of reported landfill gas fluxes in the field (Bogner et al., 1997a). A similar CH_4 flux, or load, was used by Wilshusen et al. (2004b) and Reddy et al. (2014). Air was passed tangentially over the column at Q_{AIR} = 200 mL min^{-1} to simulate a light wind blowing over the cover, promoting the diffusive ingress of oxygen into the cover. A schematic of the design of the column is included in Figure 4-1.

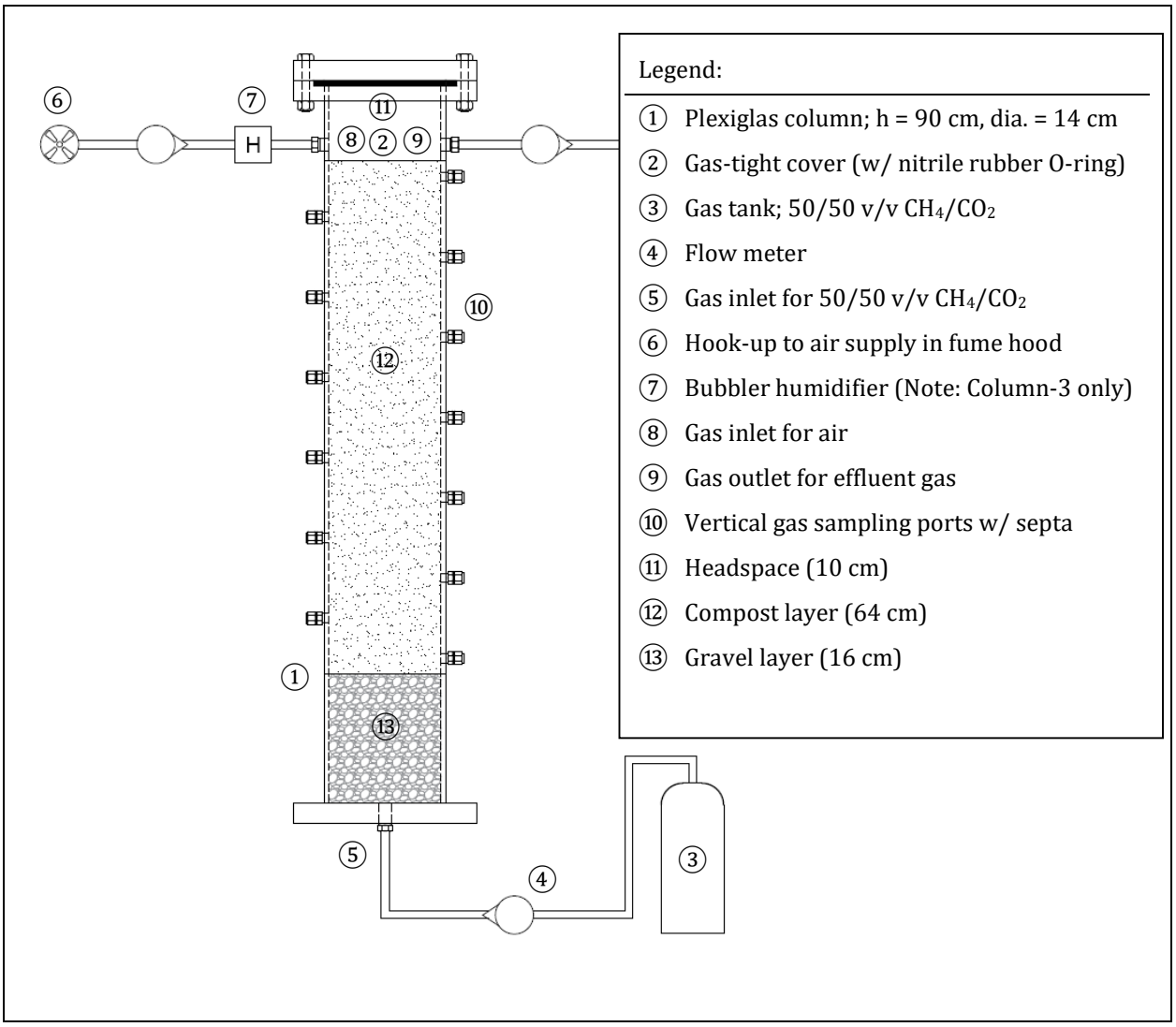


Figure 4-1: Schematic of column set-up

4.2.2.2 **Column Testing Procedure**

At the start of each column experiment, the column was flushed with the synthetic LFG (50/50 v/v CH_4/CO_2) at the design flow rate of 15 mL min^{-1} to remove air from the pore volume of the compost; in this way, the exact starting concentration of gases in the column prior to hooking up the air supply could be known. Once gas samples taken from the side ports confirmed that

the column was fully anaerobic, the 200 mL min^{-1} air flow was turned on. Gas samples were collected regularly from the column outlet and the side sampling ports.

Gas samples were collected from 2" (5 cm) (horizontally) into the column, using a 3" (7.5 cm) gas-tight sample-lock syringe needle, and periodically at the column edge, using a 1" (2.5 cm) syringe needle, to confirm minimal short-circuiting of the gases up the sides of the column. The column was located in a fume hood throughout the duration of the experiments to ensure adequate ventilation so as to minimize the safety hazards associated with working with methane gas in an oxygenated atmosphere. Moreover, the column was covered with aluminum foil to prevent the growth and activity of phototrophic micro-organisms. All column experiments were performed at a standard laboratory temperature of 22°C.

4.2.2.3 **Description of Three Column Trials**

In the first column trial, the column (i.e., Column 1) was packed with a 1:1 mixture of YLWC to BSC with moisture content increased to 60% g g^{-1} wet basis (using Milli-Q® water). The compost mixing ratio and compost moisture content (MC) used in this trial were selected on the basis of results obtained in the prior batch tests, i.e., both the 1:1 YLWC to BSC mixing ratio and MC = 50-65% exhibited the highest CH_4 oxidation potential in separate experiments, and therefore proved to be the logical starting parameters for testing in column-scale.

For the second column trial, the top 15 cm of compost was removed and replaced with a 1:4 YLWC to BSC mixing ratio at an *in-situ* moisture content of 35% g g^{-1} wet basis (i.e., Column 2), under the assumption that the methanotrophic active zone would lie within this top 15 cm.

This column trial used a higher proportion of the woodchip-containing biosolids compost at much lower moisture content, in an attempt to increase the overall porosity and permeability of the compost to gas flow.

The third and final column (i.e., Column 3) experimented with the addition of compost tea, which was mixed into the compost prior to packing it into the column. The compost layer (entire 64 cm) was composed of the same 1:4 YLWC to BSC mixing ratio at a slightly higher moisture content (40% g g^{-1} wet basis) than the previous trial, on account that adding the tea also added moisture. In this trial, the entire contents of the previous column were removed prior to adding the newly-selected compost material. It should also be noted that while previous column trials used ¼" limestone gravel for the gas distribution layer, this column trial used a coarser (½") gravel to facilitate easier diffusion of the CH_4/CO_2 gas. Also, a bubbler humidifier was connected to the air inlet to add moisture to the air flow passing over the column. A summary of the parameters tested in each column trial is provided in Table 4-2. Photographs of the columns used in the three column trials are provided in Figure 4-2.

Table 4-2: Summary of parameters tested in column trials

Column Trial	Compost Mixing Ratio (YLWC to BSC)	Moisture Content (g g^{-1} wet basis)	Addition of Compost Tea (Y/N)	Air Flow Humidification (Y/N)
1	1:1	60	N	N
2	1:4	35	N	N
3	1:4	40	Y	Y

Column-1	Column-2	Column-3

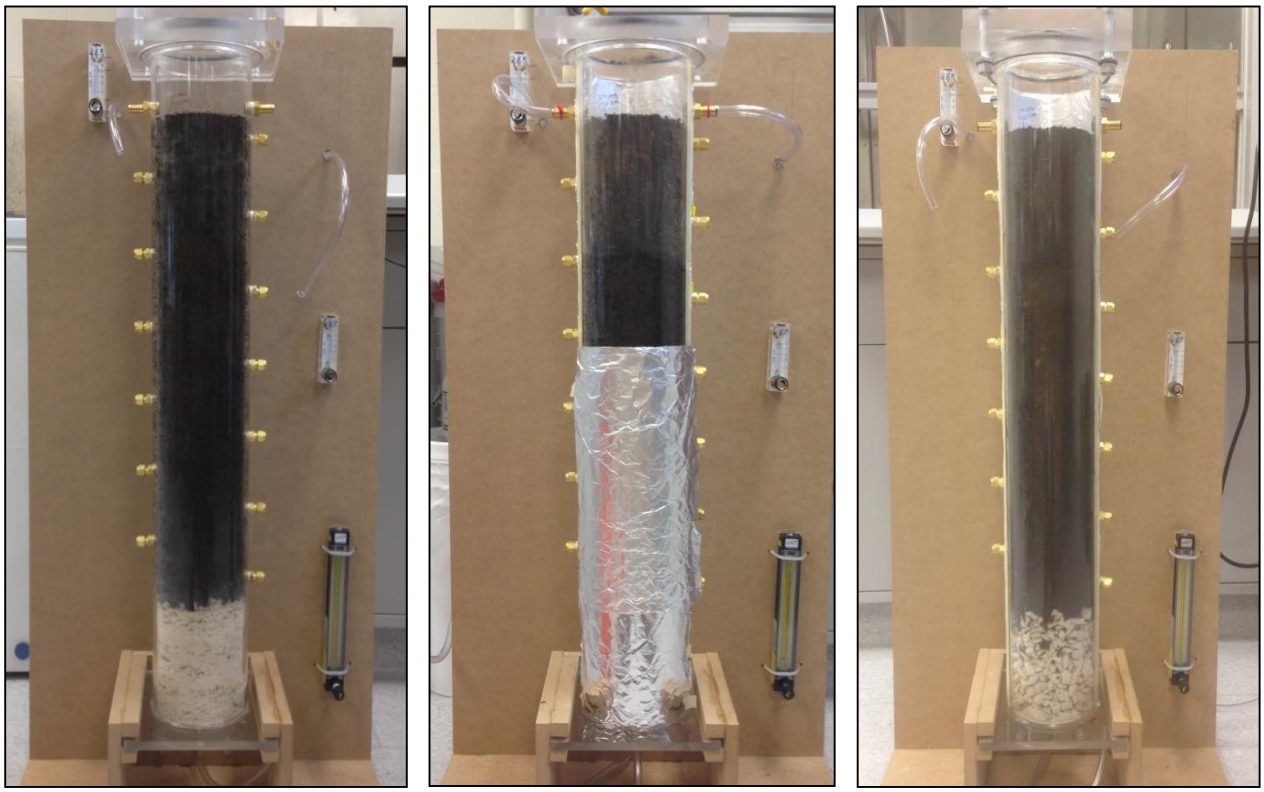


Figure 4-2: Columns from each column trial (Columns 1, 2, and 3)

4.3 GAS CHROMATOGRAPHY ANALYSIS

For all experiments, gas chromatography was performed using a Varian (Agilent) 490 Micro GC with Molesieve-5A and PoraPlot U columns to monitor CH_4 and O_2 consumption and CO_2 production.

4.4 COMPOST PROPERTIES ANALYSIS

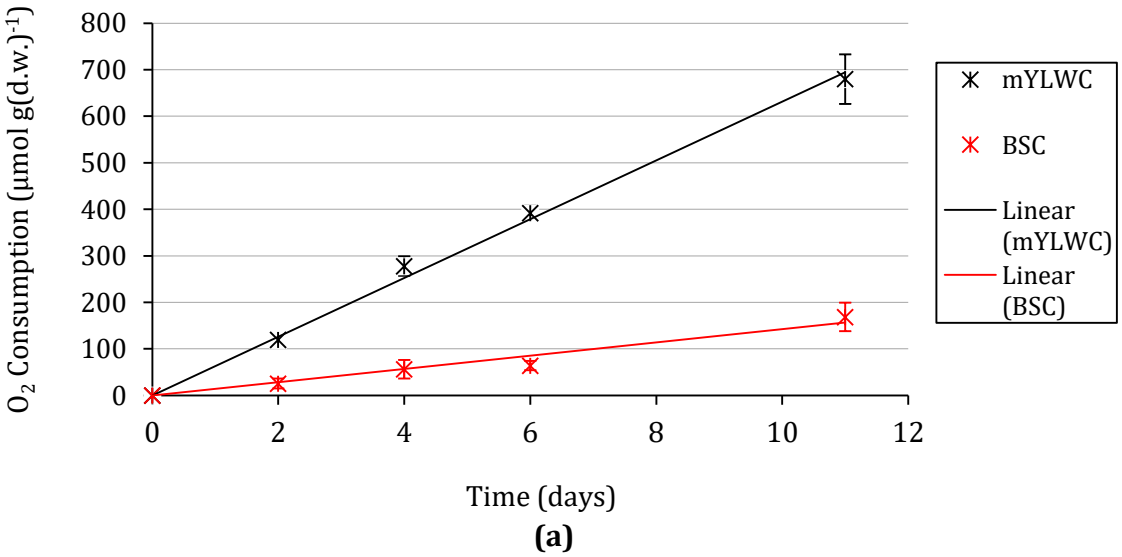
Compost moisture content was analyzed in the laboratory according to Test Method 03.09 Total Solids and Moisture of the Test Methods for the Examination of Composting and Compost (TMECC, 2001) (U.S. Department of Agriculture and U.S. Composting Council).

5 RESULTS AND DISCUSSION

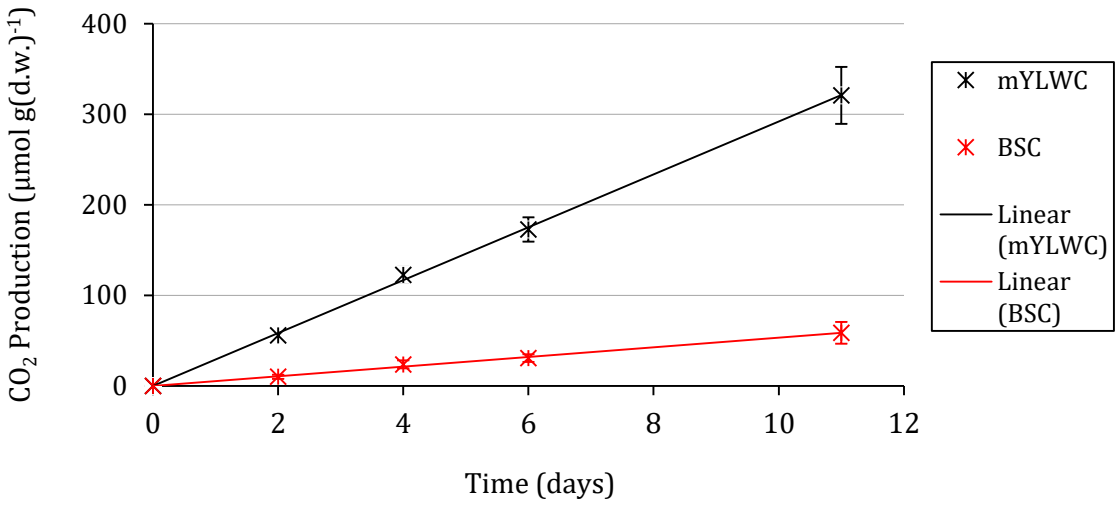
5.1 CHARACTERIZATION OF THE BIOLOGICAL POTENTIAL OF THE YLWC AND BSC FOR METHANOTROPHY (IN BATCH INCUBATIONS)

5.1.1 Evaluation of Compost Respiration

Cumulative O_2 consumption and CO_2 production (in µmol g(d.w.)$^{-1}$) in the mYLWC and BSC incubated under a 100% air headspace are compared in Figure 5-1 (a) and (b), respectively. In both the mYLWC and BSC, the consumption of O_2 and production of CO_2 were found to follow zero-order reaction kinetics ($R^2 > 0.96$) and therefore, the rates of O_2 consumption and CO_2 production (in µmol g(d.w.)$^{-1}$ d^{-1}) were taken as the slope of the respective linear regression lines. Overall, respiration activity was found to be significantly lower in the BSC than in the mYLWC; O_2 consumption rates were calculated to be 63.2 and 14.2 µmol g(d.w.)$^{-1}$ d^{-1} for the mYLWC and BSC, respectively (Figure 5-1 (a)), while CO_2 production rates were found to be 29.2 and 5.3 µmol g(d.w.)$^{-1}$ d^{-1} for the mYLWC and BSC, respectively (Figure 5-1 (b)).



(a)



(b)

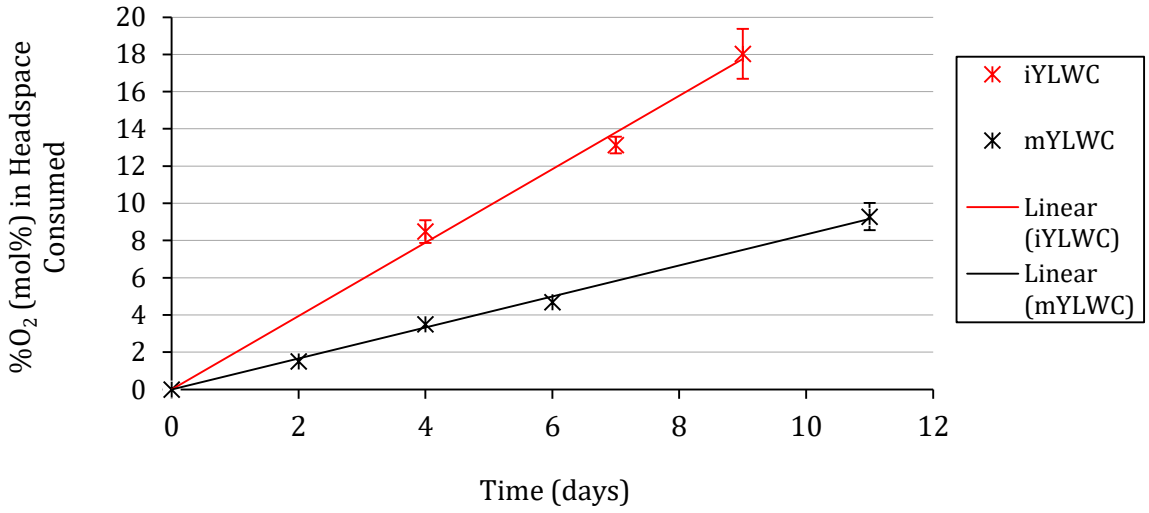
Figure 5-1: Cumulative (a) O_2 consumption and (b) CO_2 production in the mYLWC versus the BSC in the Respiration Test

Humer and Lechner (2001) recommended that O_2 uptake in composts intended for CH_4 oxidation not exceed a rate of 8 mg O_2 g(d.w.)$^{-1}$ 7 d^{-1} (35.7 µmol O_2 g(d.w.)$^{-1}$ d^{-1}). Based on this criteria, only the BSC is sufficiently mature/stable to be utilized within a biocover, while the raBOD of the mYLWC is approximately two-fold the recommended limit.

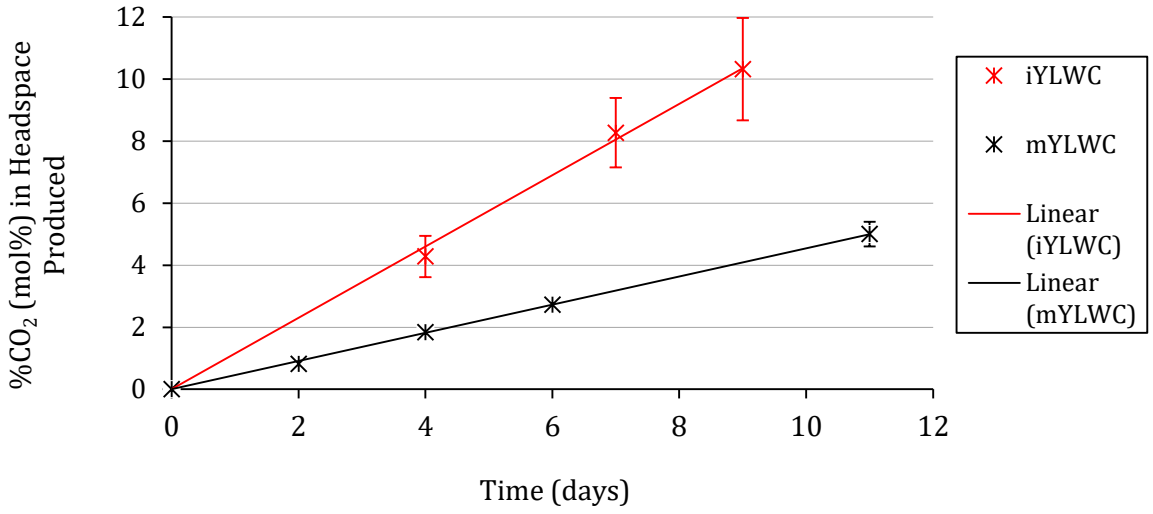
Comparison of Compost Respiration in the mYLWC and iYLWC

Cumulative O_2 consumption and CO_2 production in the iYLWC and mYLWC are compared in Figure 5-2 (a) and (b), respectively. Due to a lack of pressure data taken from the headspace of the test bottles containing the iYLWC (which precluded the calculation of molar rates of O_2 consumption and CO_2 production), these figures display O_2 consumption and CO_2 production in terms of the concentration of O_2 consumed and CO_2 produced (in mol%) in the headspace. In the iYLWC, the starting headspace in the bottles was 19.0% O_2 decreasing to 1.0% O_2 by day 9 (18.0% O_2 consumed, as shown on Figure 5-2 (a)), while in the mYLWC, the starting headspace

was 20.4% O_2 decreasing to 11.1% O_2 by day 11 (9.3% O_2 consumed, as shown on the same figure). In terms of CO_2 production, the starting headspaces contained 0.4% and 1.1% CO_2, increasing to 10.7% and 6.1% CO_2 in the iYLWC and mYLWC, respectively (10.3% and 5.0% CO_2 produced, as shown in Figure 5-2 (b)). Overall the results show lower respiration activity in the mYLWC as a result of further decomposition of the organic fraction of the compost that occurred while the compost was stored at 4°C for approximately one year. It was hypothesized that the use of the more degraded mYLWC would result in a lower degree of competition for O_2 between methanotrophic and heterotrophic bacteria in the compost, and would therefore yield higher initial CH_4 oxidation values than the iYLWC.



(a)



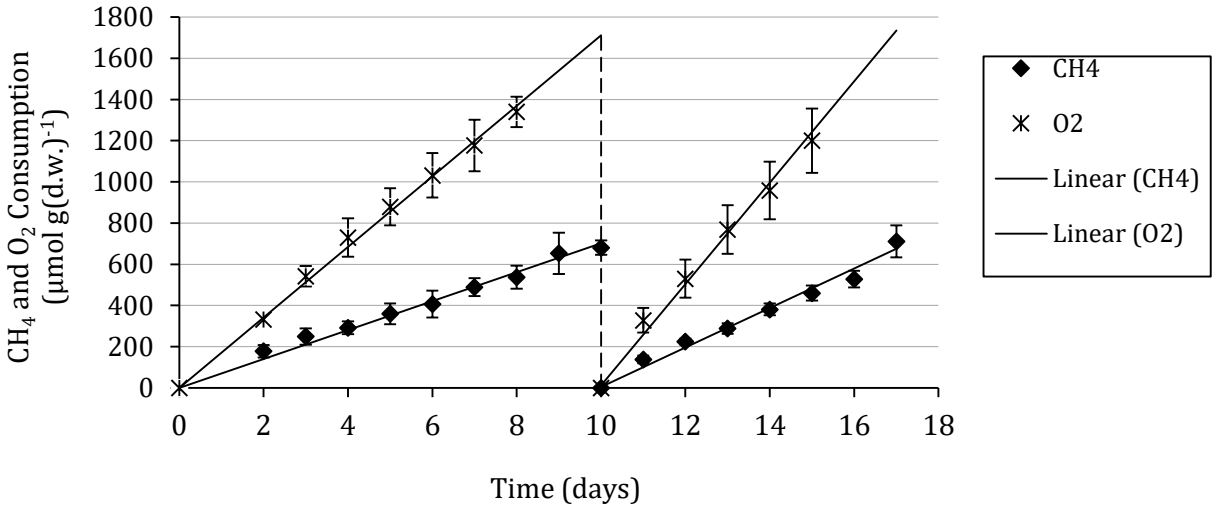
(b)

Figure 5-2: Cumulative (a) O_2 consumption and (b) CO_2 production in the iYLWC versus the mYLWC in the Respiration Tests

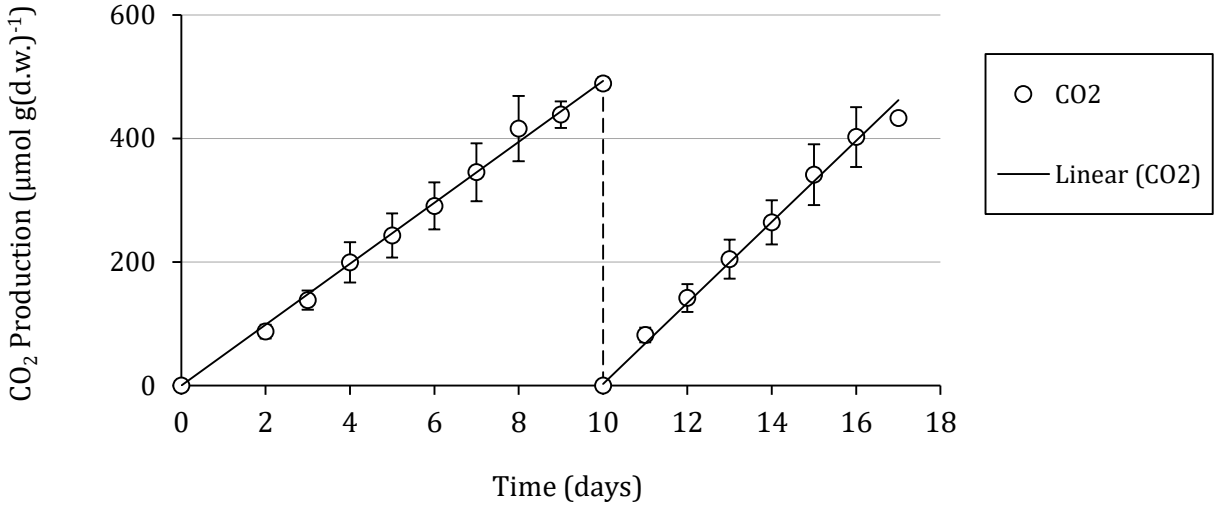
5.1.2 Evaluation of Compost Methane Oxidation Potential (MOP)

Cumulative CH_4 consumption (oxidation) and O_2 consumption (in µmol g(d.w.)$^{-1}$) and cumulative CO_2 production (also in µmol g(d.w.)$^{-1}$) in the mYLWC incubated under a 20% CH_4-in-air headspace are shown in Figure 5-3 (a) and (b), respectively. From Figure 5-3 (a), the initial rates of CH_4 and O_2 consumption in the mYLWC (from days 0 to 10) were calculated to be 70.1 and 171.2 µmol g(d.w.)$^{-1}$ d^{-1}. Following a headspace flush (HF) on day 10, the rates of CH_4 and O_2 consumption were found to increase to 95.9 and 245.9 µmol g(d.w.)$^{-1}$ d^{-1}, respectively (for days 10 to 17), which indicates growth of the inherent population of methanotrophic bacteria in the mYLWC. The ratio of O_2 consumed to CH_4 consumed was calculated to be greater than the theoretical ratio of 2 for methanotrophic activity (2.44 from days 0 to 10 and 2.56 from days 10 to 17), which denotes that a portion of the O_2 was consumed by non-

methanotrophic (i.e., heterotrophic) bacteria in the compost. As shown in Figure 5-3 (b), the rate of CO_2 production in the mYLWC was found to be 49.3 µmol g(d.w.)$^{-1}$ d^{-1} for days 0 to 10, increasing to 66.5 µmol g(d.w.)$^{-1}$ d^{-1} for days 10 to 17. The ratio of CO_2 produced to CH_4 consumed for these values was calculated to be 0.70 and 0.69, which is lower than the theoretical value of 1 for pure methanotrophy. This ratio being less than 1 suggests that some of the carbon may have been converted into bacterial biomass (Perdikea et al., 2008; Gebert et al., 2011), which is consistent with the increase in CH_4 oxidation rate observed in this test. It is also possible that a portion of the CO_2 in the headspace was disassociated to form bicarbonate (HCO_3-), therefore lowering the amount of CO_2 remaining in the gas phase.



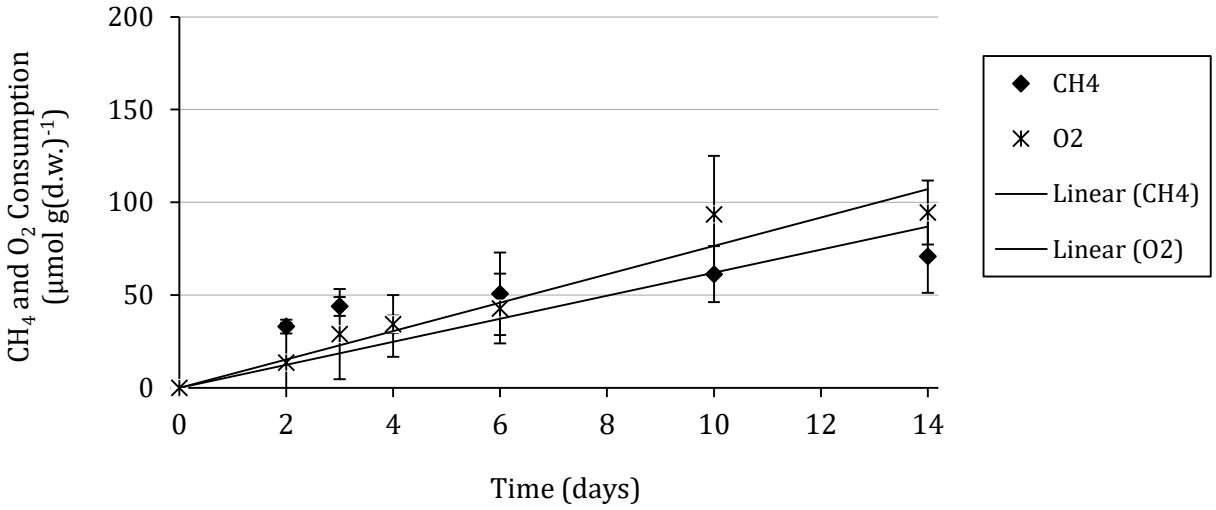
(a)



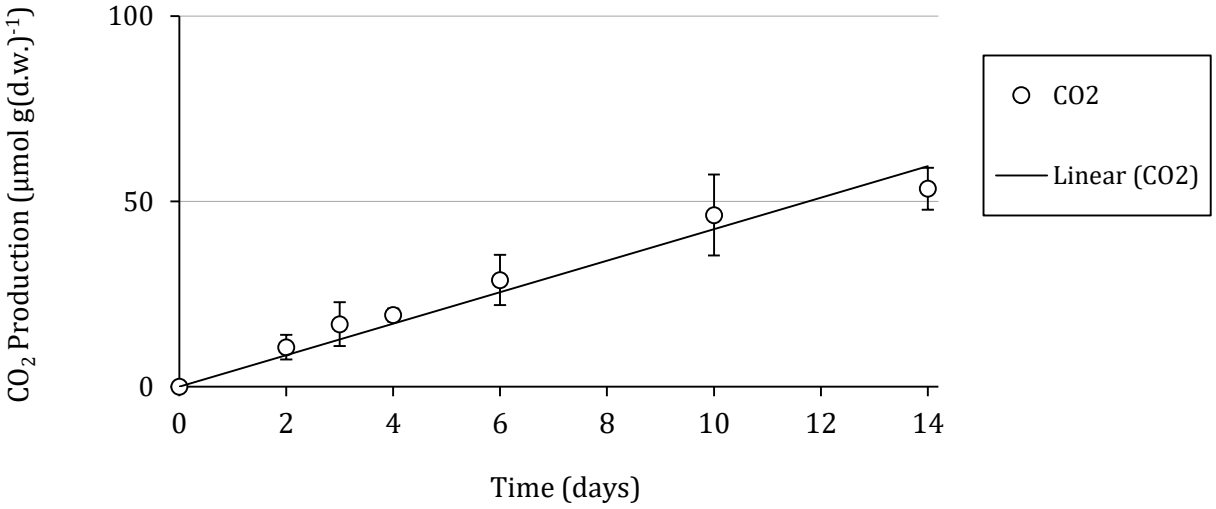
(b)

Figure 5-3: Cumulative (a) CH_4 and O_2 consumption and (b) CO_2 production in the mYLWC

Cumulative CH_4 and O_2 consumption (in µmol g(d.w.)$^{-1}$) and cumulative CO_2 production (also in µmol g(d.w.)$^{-1}$) in the BSC incubated under a 20% CH_4-in-air headspace are shown in Figure 5-4 (a) and (b), respectively. It was initially hypothesized that methanotrophs are present in the BSC because of the fact that the biosolids composting piles at BRRMF are force aerated with air that likely contains low concentrations of CH_4 from the proximal landfill cell areas; however, very little CH_4 removal was detected in the BSC, as shown in Figure 5-4 (a). A clear linear trend in CH_4 consumption was not observed (R^2 = 0.51), probably due to the low CH_4 oxidation rates. Nonetheless, the BSC was found to consume a cumulative 70.9 µmol CH_4 g(d.w.)$^{-1}$ by day 14, which yields an approximate CH_4 oxidation rate of 5.1 µmol g(d.w.)$^{-1}$ d^{-1}. The rate of O_2 consumption (Figure 5-4 (a)) and CO_2 production (Figure 5-4 (b)) in the BSC were found to be 7.7 and 4.2 µmol g(d.w.)$^{-1}$ d^{-1}, respectively.



(a)



(b)

Figure 5-4: Cumulative (a) CH_4 and O_2 consumption and (b) CO_2 production in the BSC

It was hypothesized that the low rates of methanotrophic activity in the BSC may have been due to its lower moisture content (36% ww), due to elevated concentrations of certain heavy metals (Cr, Cu, Pb, and Zn) in the BSC, or due to an insufficient population of methanotrophic bacteria in the BSC. Therefore, the effect of compost moisture content, heavy metal content, and

inoculation on CH_4 oxidation were investigated in subsequent batch incubation experiments (see Sections 5.2.1 to 5.2.4).

Effect of Compost Maturity on CH_4 Oxidation in the YLWC

Cumulative CH_4 consumption (in terms of the concentration of CH_4 consumed (in mol%) in the headspace) in the iYLWC and mYLWC are compared in Figure 5-5 (a) and (b), respectively. As shown, the iYLWC only removed 2.5% of the starting 20% CH_4 in the headspace over 9 days, while the mYLWC removed 5.3% of the starting 20% CH_4 over 10 days, indicating higher CH_4 oxidation activity in the more mature YLWC.

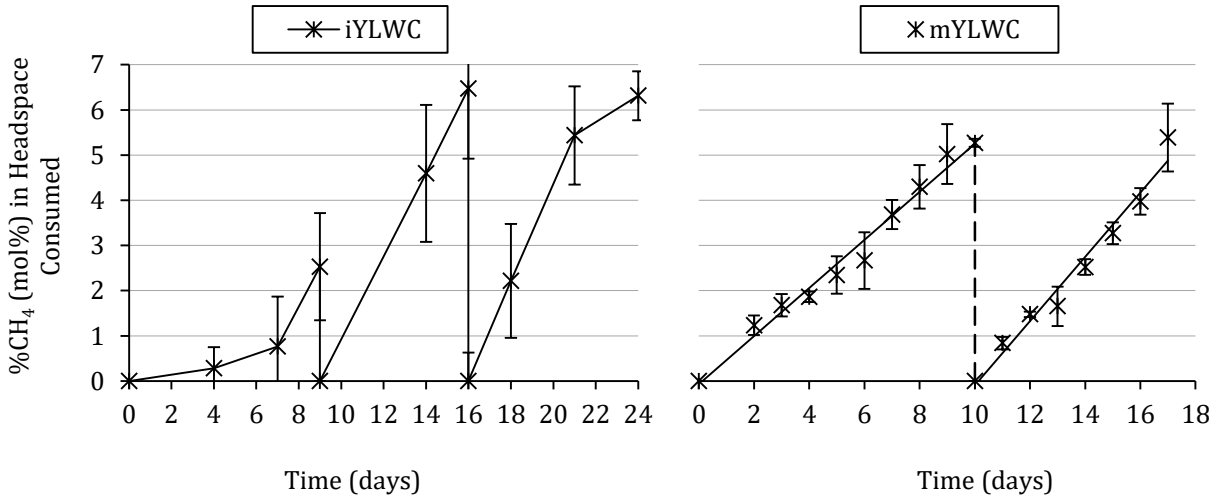
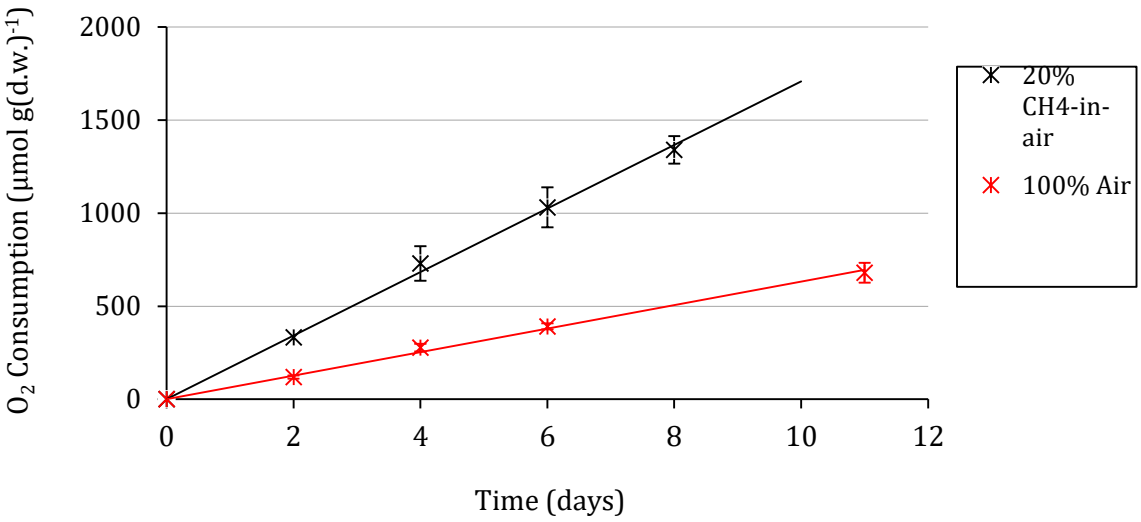
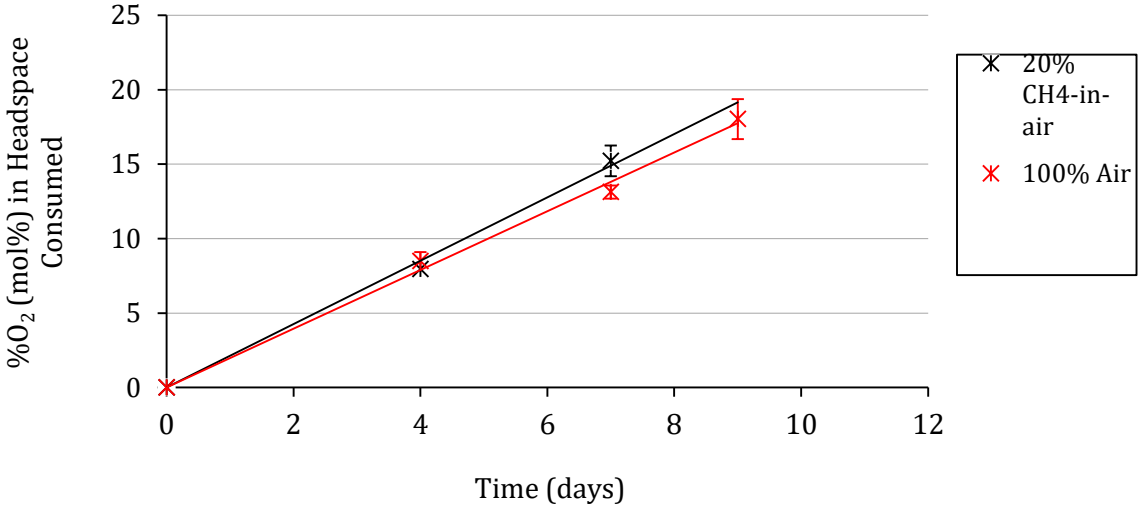


Figure 5-5: Cumulative CH_4 consumption in the (a) iYLWC and (b) mYLWC

Cumulative O_2 consumption in the Respiration Test (headspace was 100% air) and the MOP Test (headspace was 20% CH_4-in-air) are compared in Figure 5-6 (a) and (b) for the mYLWC and the iYLWC, respectively. In these figures, O_2 consumption under the 100% air headspace represents the O_2 demand for heterotrophs, while O_2 consumption under the 20% CH_4-in-air headspace represents the O_2 demand by heterotrophs *and* methanotrophs. From Figure 5-6 (a), it was determined that approximately 37% of the O_2 consumed during CH_4 oxidation in the mYLWC from days 0 to 10 was due to heterotrophs (this value calculated as O_2 consumption in the Respiration Test divided by O_2 consumption in the MOP Test), with the other 63% utilized by methanotrophs to oxidize CH_4. Conversely, from Figure 5-6 (b), approximately 93% of the O_2 consumed during CH_4 oxidation in the iYLWC from days 0 to 9 was due to heterotrophs (i.e., only 7% was available for CH_4 oxidation). These results demonstrate that methanotrophic bacteria were able to better compete for available O_2 in the more mature mYLWC. It was concluded that curing the compost for an additional one year at 4^0C resulted in further reduction of easily bio-degradable organic matter in the compost (observed as a reduction in raBOD and CO_2 production in the Respiration Test), therefore allowing a greater proportion of the available O_2 to be used for CH_4 oxidation rather than for heterotrophic respiration. This result also confirms the prior hypothesis that the initial YLWC required further maturation beyond the compost maturity standard at BRRMF (to reduce the readily available carbon to limit heterotrophic growth) prior to being usable within a biologically-active landfill cover.



(a)



(b)

Figure 5-6: Comparison of O_2 consumption in the Respiration Test and MOP Test in the (a) mYLWC and (b) iYLWC

The importance of using mature/stable compost to limit heterotrophic uptake of O_2 during CH_4 oxidation has been noted in other several studies reported in literature, including Mor et al.

(2006), Gebert et al. (2011), Pedersen et al. (2011), and Scheutz et al. (2011). For example, Pedersen et al. (2011) reported a CH_4 oxidation rate of 79.3 μmol g(d.w.)$^{-1}$ d^{-1} in a 4-year old garden waste compost (raBOD of 2.9 μmol g(d.w.)$^{-1}$ d^{-1}) and a CH_4 oxidation rate of only 16.5 μmol g(d.w.)$^{-1}$ d^{-1} in the same compost aged for only one year (raBOD of 46.5 μmol g(d.w.)$^{-1}$ d^{-1}).

5.2 EVALUATION OF THE EFFECT OF SELECT PARAMETERS ON CH_4 OXIDATION (IN BATCH INCUBATIONS)

5.2.1 Effect of Compost Moisture Content

CH_4 oxidation rates (in μmol g(d.w.)$^{-1}$ d^{-1}) for the range of moisture contents tested (5, 20, 35, 50, 65, and 80% ww) are presented in Figure 5-7 and Figure 5-8 for the YLWC and the BSC, respectively. In the mYLWC, CH_4 consumption was only observed at MCs of 35, 50, 65, and 80% ww; no CH_4 consumption was observed at MCs of 5 and 20% ww. Between days 0 and 7 in the mYLWC, very little difference in CH_4 oxidation rates was observed at MCs of 35, 50, 65, and 80% ww. After day 7 in the mYLWC, the highest CH_4 oxidation rates were generally observed at a MC of 65% ww followed by at MCs of 50, 35, and 80% ww; however, a comparable CH_4 oxidation rate of approximately 175-180 μmol g(d.w.)$^{-1}$ d^{-1} was observed at MCs of 65 and 50% ww on day 12. In the BSC, no CH_4 oxidation was observed over the range of MCs tested.

An optimum MC of approximately 50-65% ww in the mYLWC agrees well with the findings of several other batch-scale studies, including those of Perdikea et al. (2008) and Mor et al. (2006), who reported optimum MCs of 47-60% ww (in a mixture of leaf and manure compost and sawdust) and greater than 52% ww (in a garden waste compost), respectively. In general,

however, an optimum MC of 50-65% ww for CH_4 oxidation is in the higher range of reported optimums (Scheutz et al., 2009; Sadasivam and Reddy, 2014). While the present study found that a MC at and below 20% ww is insufficient for CH_4 oxidation, several other batch-scale studies have reported methanotrophic activity within this range, including optimum MCs as low as 10-20% ww (Whalen et al., 1990; Figueroa, 1993; Boeckx & Van Cleemput, 1996; Christophersen et al., 2000; Park et al., 2009).

Because no CH_4 oxidation was observed in the BSC over the range of MCs tested, it was concluded that MC was not the limiting variable affecting CH_4 oxidation in the previous study.

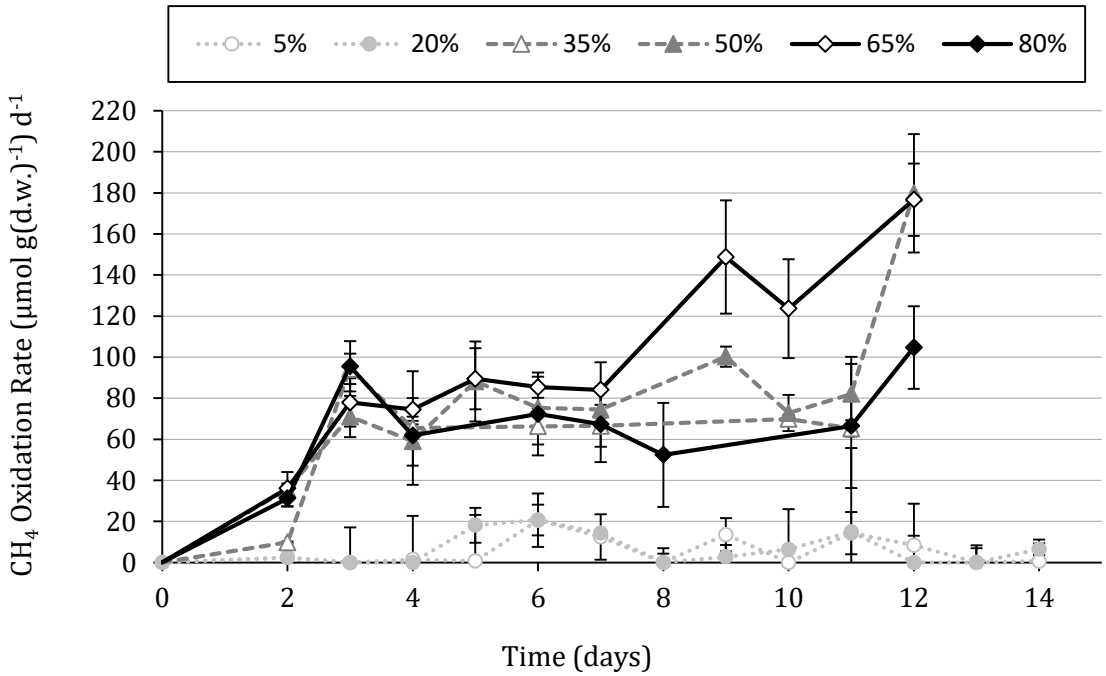


Figure 5-7: CH_4 oxidation rates in the mYLWC at MCs of 5, 20, 35, 50, 65, and 80% ww

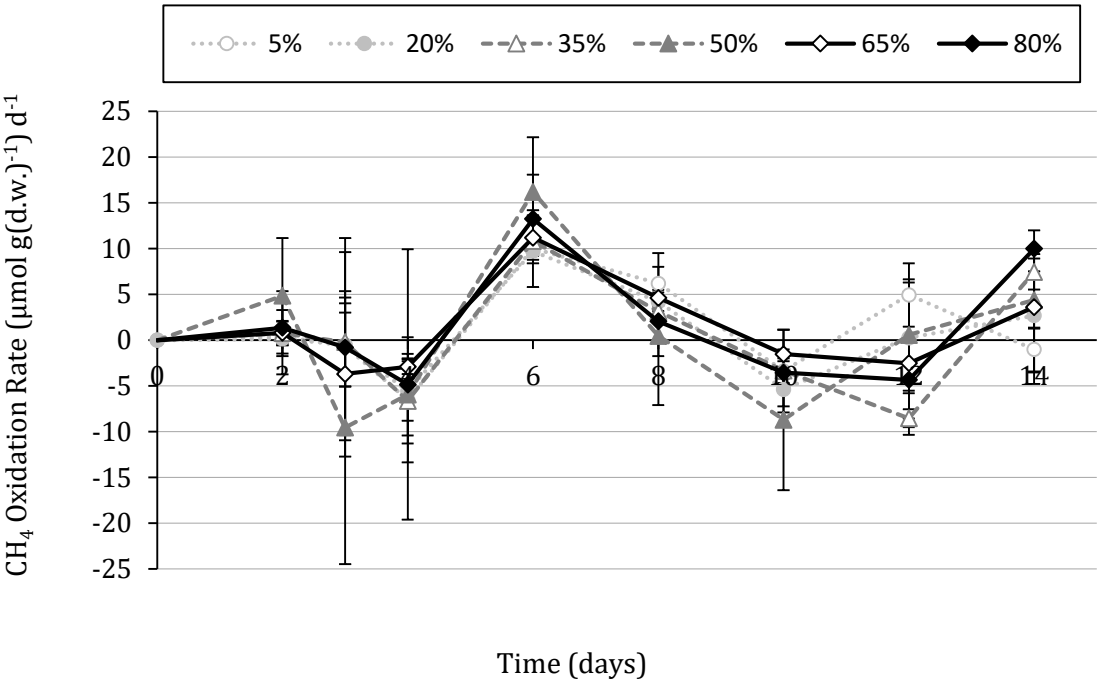


Figure 5-8: CH_4 oxidation rates in the BSC at MCs of 5, 20, 35, 50, 65, and 80% ww

5.2.2 Effect of Compost Mixing Ratio

CH_4 oxidation rates (in µmol $g(d.w.)^{-1}$ d^{-1}) for the five tested mixing ratios (1:1, 1:2, 2:1, 1:4, and 4:1 mYLWC:BSC w:w) as well as the mYLWC and BSC are shown in Figure 5-9. The results are presented and discussed first for the 1:1, 2:1, and 4:1 mixing ratios and then for the 1:2 and 1:4 mixing ratios.

<u>1:1, 2:1, and 4:1 Mixing Ratios</u>

Little CH_4 oxidation activity was observed between days 0 and 2 in the 1:1, 2:1, and 4:1 mixing ratios due to acclimation of the methanotrophic bacteria to CH_4. After this initial lag period, the

sharpest increase in CH_4 oxidation rate was observed in the 4:1 mixing ratio followed by the 2:1 mixing ratio and then the 1:1 mixing ratio. The 4:1 mixing ratio reached a maximum CH_4 oxidation rate of 692.5 ± 30.0 μmol g(d.w.)$^{-1}$ d^{-1} on day 3, while the 2:1 and 1:1 mixing ratios reached maximum CH_4 oxidation rates of 697.8 ± 23.6 and 643.3 ± 19.8 μmol g(d.w.)$^{-1}$ d^{-1}, respectively, on day 5. In all three of these mixing ratios, the initial peaks in CH_4 oxidation rate were followed by a gradual decrease in CH_4 oxidation activity; CH_4 oxidation rates declined to an apparent steady state of approximately 400 μmol g(d.w.)$^{-1}$ d^{-1} and approximately 300-375 μmol g(d.w.)$^{-1}$ d^{-1} in the 2:1 and 4:1 mixing ratios, respectively, and appeared to be declining to a similar steady rate in the 1:1 mixing ratio.

As shown in Figure 5-10, O_2 consumption rates in all three mixing ratios were found to be fairly constant over this period of reduced CH_4 oxidation activity (i.e., a concomitant decrease in O_2 consumption rate was not observed), which suggests increased heterotrophic activity in the composts during this period. It is possible that the increased heterotrophic activity in the composts may have been stimulated by EPS production or methanotrophic cell die-off. A similar trend (i.e., peak CH_4 oxidation rates declining to a lower steady-state oxidation value) was observed by De Visscher et al. (1999), Wilshusen et al. (2004b), and Scheutz et al. (2009b) in different media, and was attributed to nutrient limitation and/or EPS production.

1:2 and 1:4 Mixing Ratios

CH_4 oxidation in the 1:2 and 1:4 mixing ratios followed a different pattern than what was observed in the 1:1, 2:1, and 4:1 mixing ratios. In the 1:2 mixing ratio, CH_4 oxidation rate was found to gradually increase over the entire test period, reaching 496.4 ± 65.5 μmol g(d.w.)$^{-1}$ d^{-1}

on day 15. This rate is comparable with the steady-state CH_4 oxidation rates achieved in the 2:1 and 4:1 mixing ratios. The 1:4 mixing ratio showed a steady, minimal rate of approximately 40 μmol g(d.w.)$^{-1}$ d^{-1} from days 2 to 12 of testing, increasing to 153.7 ± 48.5 μmol g(d.w.)$^{-1}$ d^{-1} on day 16.

It was hypothesized that the 1:2 and 1:4 mixing ratios showed lower initial rates of CH_4 oxidation than the 1:1, 2:1, and 4:1 mixing ratios because they contained a higher proportion of BSC and therefore, perhaps, a smaller population of methanotrophic bacteria, and therefore required more time to build-up an active population of CH_4 oxidizers. It is important to note that all five of the tested mixing ratios, with the exception of the lowest inoculum ratio (i.e., the 1:4 mixing ratio) consumed CH_4 at a much higher rate than what was observed in the YLWC alone. This result confirms that there is a benefit to mixing the two composts; whether that benefit is the result of compost texture, pH, nutrient content, etc. was not clear and was not investigated further.

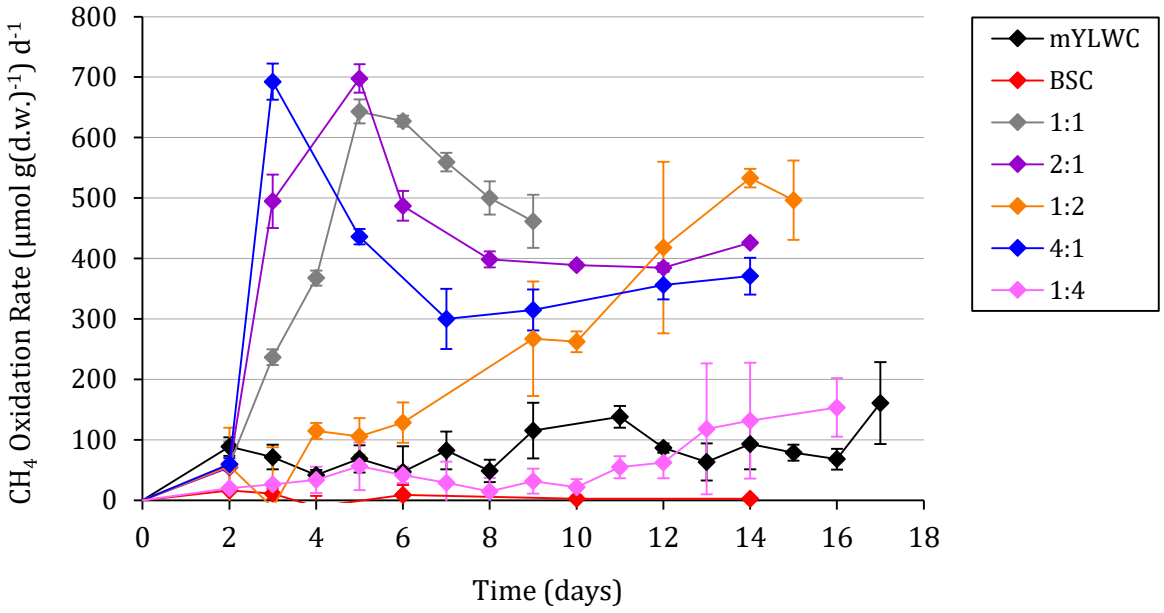


Figure 5-9: CH_4 oxidation rates in the mYLWC, BSC, and 1:1, 2:1, 1:2, 4:1, and 1:4 (YLWC:BSC w:w) mixing ratios

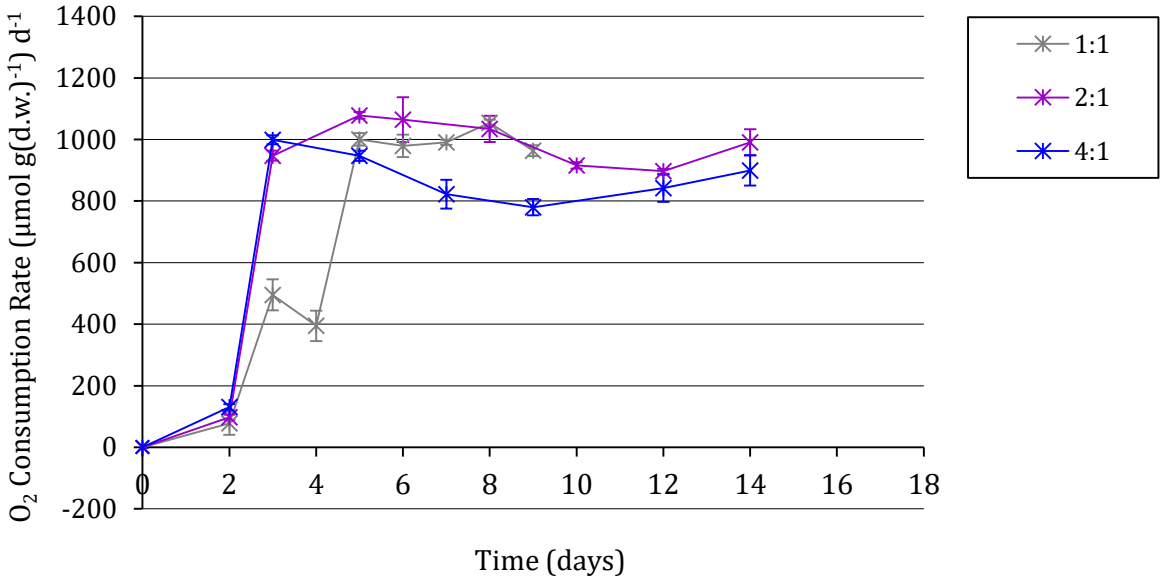


Figure 5-10: O_2 consumption rates in the mYLWC, BSC, and 1:1, 2:1, 1:2, 4:1, and 1:4 (YLWC:BSC w:w) mixing ratios

5.2.3 Effect of Addition of Nutrients and a Methanotroph-Enriched Compost Extract

CH_4 oxidation rates (in μmol g(d.w.)$^{-1}$ d^{-1}) for the BSC inoculated with a methanotroph-enriched compost extract (compost tea) as well as the controls for nutrients (BSC with added NMS medium) and moisture (BSC with added Milli-Q water) are shown in Figure 5-11. Negligible methanotrophic activity was observed in the inoculated BSC and the nutrient and moisture controls (CH_4 oxidation rates found to be less than 10 μmol g(d.w.)$^{-1}$ d^{-1}), which indicates that neither the nutrient content nor the in-situ population of methanotrophic bacteria in the BSC were limiting variables affecting CH_4 oxidation activity in the prior test.

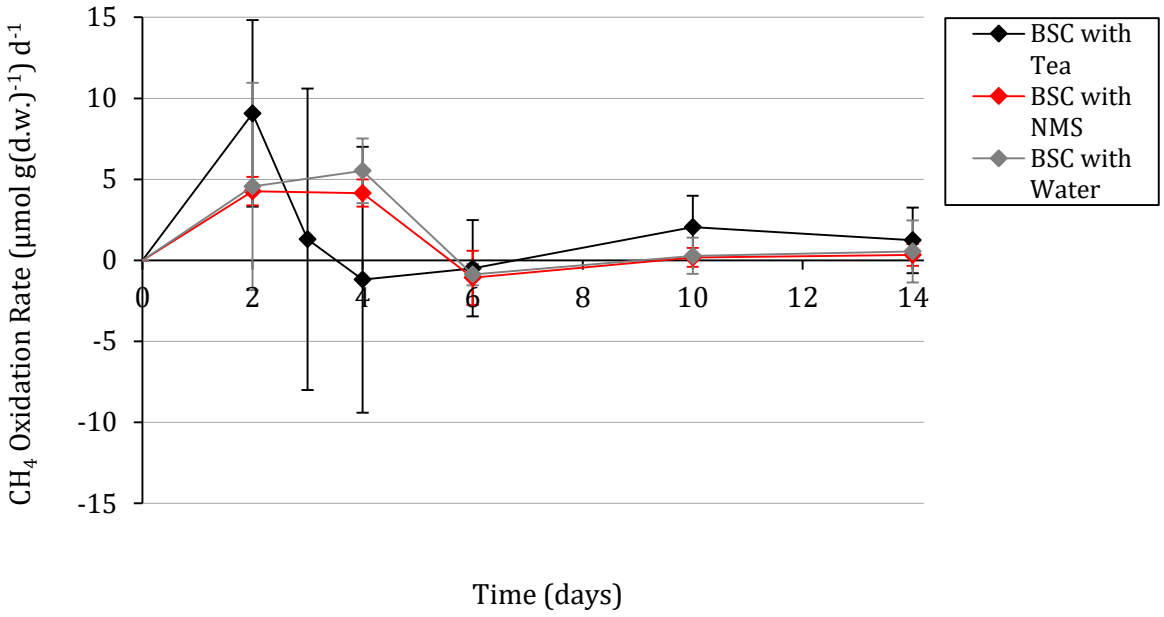


Figure 5-11: CH_4 oxidation rates in the BSC, BSC with NMS medium, and BSC with tea

5.2.4 Effect of Heavy Metals

As shown in Figure 5-12, only minimal differences in CH_4 oxidation rates in the mYLWC-1x, mYLWC-10x, and the control (unamended mYLWC) were observed. Higher CH_4 oxidation rates were observed on Days 9 and 15 in the mYLWC-1x, possibly as a result of higher concentrations of available O_2 in the headspace on these days (headspace flushes were performed on Days 8 and 14, respectively); however, since CH_4 oxidation rates in the mYLWC-1x were not overall higher or lower than in the mYLWC-10x or the control, it was concluded that the addition of Cr, Cu, Pb, and Zn to the mYLWC had no effect on CH_4 oxidation activity in the mYLWC (within the range of heavy metal concentrations tested). Specifically, because no reduction in CH_4 oxidation rates was observed in the YLWC-1x over the control, it was also concluded that the elevated concentrations of the aforementioned heavy metals in the BSC were not the single limiting variable affecting CH_4 oxidation in the previous study.

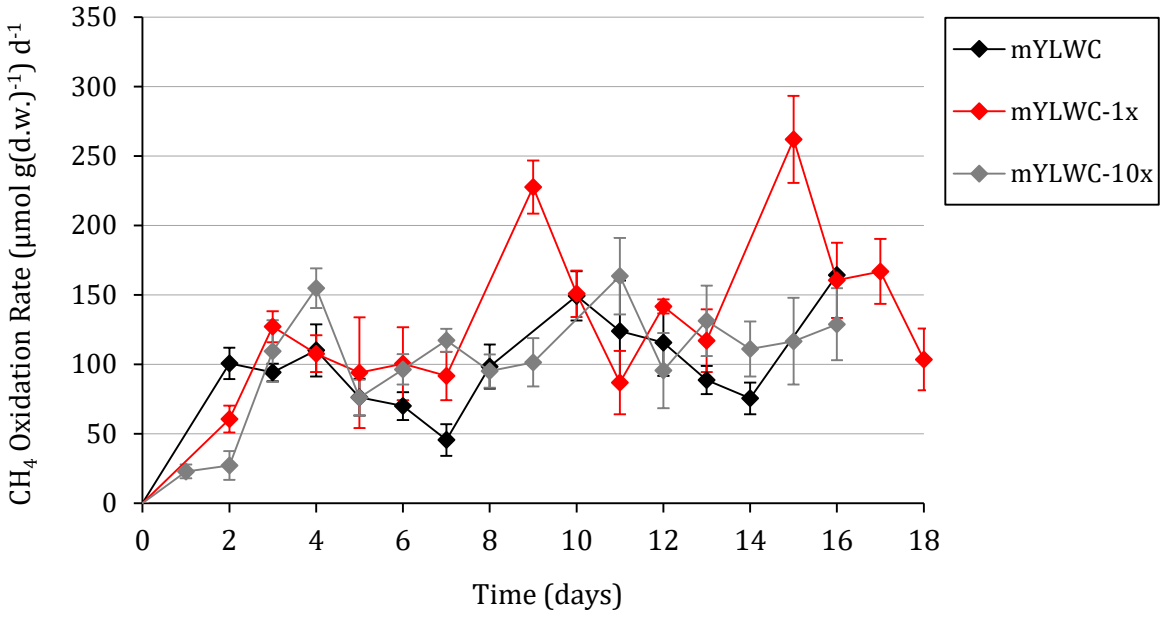


Figure 5-12: CH_4 oxidation rates in the mYLWC amended with heavy metals (mYLWC-1x and mYLWC-10x)

5.3 ASSESSMENT OF THE LONG-TERM STABILITY OF CH_4 OXIDATION IN BATCH ENRICHMENTS

Long-term CH_4 oxidation rates (over a 100-day study period) in the YLWC and BSC collected from BRRMF in September 2015 and in the 1:1 and 1:4 YLWC:BSC w:w mixing ratios are shown in Figure 5-13. It is important to note that the oxidation values in these figures are *minimum* values for CH_4 oxidation, since gas samples from the headspace of the bottles were only collected and tested every 24 hours, and therefore it is likely that total oxygen depletion occurred sometime prior to testing.

As shown in Figure 5-13, there was an initial 3-day lag period in the YLWC and 1:1 and 1:4 mixing ratios, where no CH_4 consumption was observed due to the innate methanotrophs acclimating (adjusting) to the environment in the presence of CH_4. The YLWC reached a maximum CH_4 oxidation rate by approximately day 40 of 130 to 140 μmol g(d.w.)$^{-1}$ d^{-1} and was able to sustain that rate until the end of the test (day 110). The BSC did eventually begin to consume CH_4 around day 60 and reached a maximum CH_4 oxidation rate by day 90 of 160 to 170 μmol g(d.w.)$^{-1}$ d^{-1}. The fact that the BSC was over time able to consume CH_4 pointed to the conclusion that the BSC may have required time to build up its own active methanotroph population. This conclusion, however, does not adequately explain why inoculation of the BSC with an active methanotroph-enriched compost extract (compost tea) was not effective, although it should be mentioned that this inoculation experiment was conducted with BSC from the City of Edmonton; the experiment should perhaps be repeated with BSC from BRRMF prior to making a definite conclusion about the effectiveness of using a compost tea to stimulate methanotrophy from the biosolids matrix.

The 1:4 mixing ratio, though having a longer delay, eventually reached comparable rates of CH_4 oxidation around day 60 to that of the 1:1 bottles. A maximum CH_4 oxidation rate of 360 to 380 μmol g(d.w.)$^{-1}$ d^{-1} was achieved for the 1:1 and 1:4 mixing ratios by day 76 and 79, respectively.

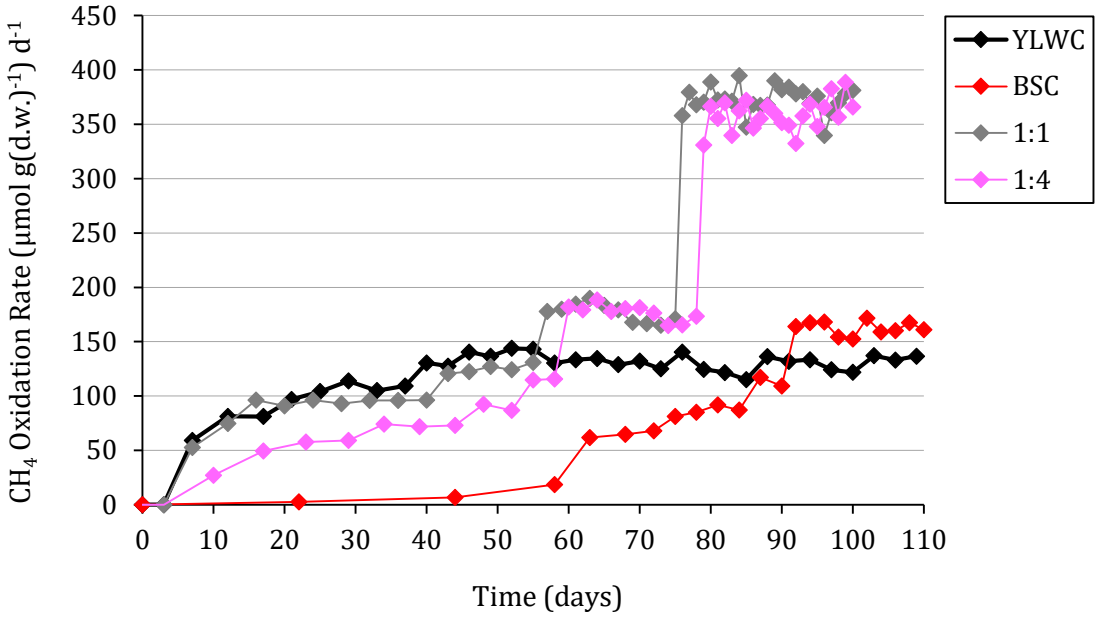


Figure 5-13: Long-term CH_4 oxidation rates in the YLWC, BSC, and 1:1 and 1:4 mixing ratios

5.4 ASSESSMENT OF CH_4 OXIDATION RATES IN A FLOW-THROUGH SYSTEM (COLUMN-SCALE)

5.4.1 Column 1: Testing of Optimum Parameters from Batch Incubation Experiments

The performance of the optimum compost mix ratio (1:1 YLWC:BSC) at an MC within the optimum range determined by the batch incubation experiments was evaluated in the first column trial (Column 1). The depth profiles of the main gas components (O_2, CH_4, CO_2, and N_2) are shown in Figure 5-15 (a) to (c) on select Days 16, 28, and 47 of incubation. Overall, CH_4 oxidation activity was found to be confined to the upper 7 cm of the compost column, where only minimal CH_4 oxidation activity was detected, due to limited diffusion of atmospheric air to the compost column. Nitrogen gas was only found at sampling depths of 2 cm and 7 cm below

the surface of the compost, at concentrations well below atmospheric level (average of 34.9% and 3.0%, respectively, between Days 16, 28, and 47); no N_2 was detected at or below a depth of 12 cm, which indicates no atmospheric air diffusion at or below this depth. From the base of the column up to a depth of 12 cm below the surface, the concentrations of CO_2 and CH_4 were measured to be approximately 50% each (i.e., approximately equal to the concentration of the input LFG; CO_2-CH_4 ratio of approximately 1). Above a depth of 12 cm, however, there was a slightly greater concentration of CO_2 as compared to CH_4 (which suggests methanotrophy) as well as shift towards lower concentrations of these gases due to mixing of the LFG with atmospheric air diffusing into the column. The CO_2-CH_4 ratios within this upper portion of the column are summarized in Table 5-1 and were calculated to only be slightly greater than 1 (average of 1.21 at a depth of 2 cm and 1.06 at a depth of 7 cm), which suggests only minimal conversion of CH_4 to CO_2. The CO_2-CH_4 ratios of the gas emitted from the column, as measured at the column outlet, were calculated to be 1.05, 1.07, and 1.04 on Days 16, 28, and 47, respectively, suggesting that any methanotrophic activity within the compost was insufficient to remove a significant portion of the CH_4 flowing through the column.

In the column, possible EPS production in the form of an orange-brown residue was observed at a depth of approximately 2 cm below the surface of the compost (Figure 5-14), within the zone of apparent CH_4 oxidation activity. A similar observation (bands of discolouration within the oxic portion of bio-columns), also attributed to EPS formation, was also reported by Wilshusen et al. (2004) and Scheutz & Kjeldsen (2005).

Figure 5-14: Possible EPS production in Column 1

It was hypothesized that the poor performance of the tested soil mixture was due to its fine texture (due to the high proportion of fine particles in the YLWC) and the high MC, which limited the air-filled porosity and permeability of the mixture to atmospheric air/O_2. Several other studies have indicated that free air space in compost matrices becomes limiting when MC is greater than 60% ww (Schulze, 1961; Das and Keener, 1997), which is consistent with the present result. With increased moisture, fine-grained composts will also become more plastic and susceptible to compaction, including compaction under their own weight as a result of the increased wet bulk density of the material (Das and Keener, 1997).

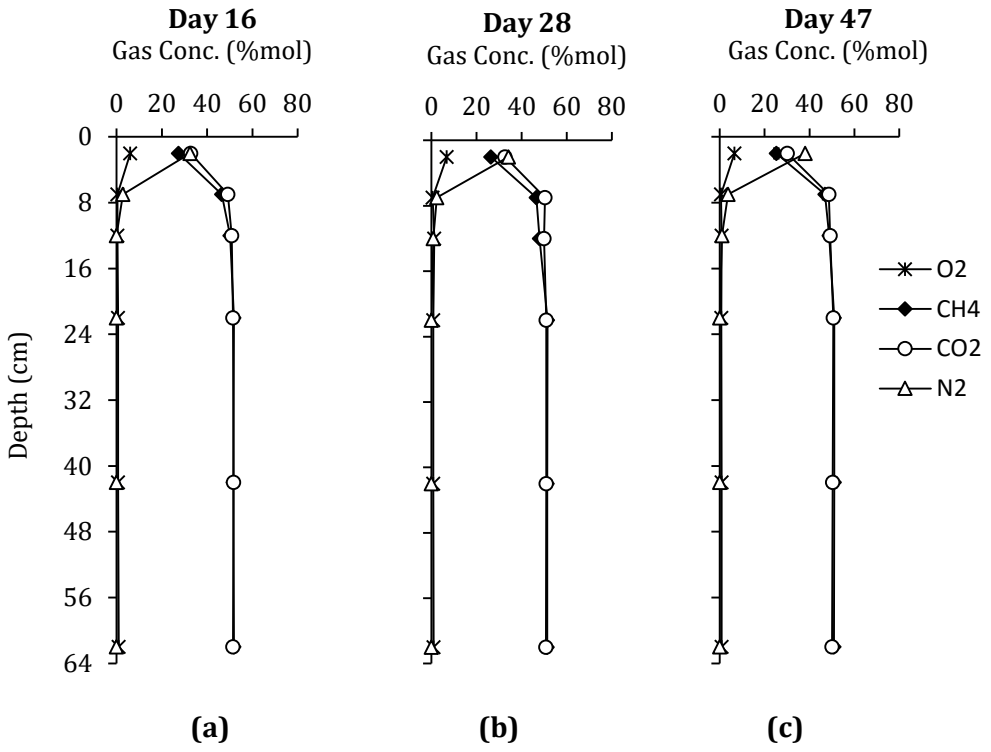


Figure 5-15: Vertical gas concentration profiles in Column 1 on (a) Day 16, (b) Day 28, and (c) Day 47

Table 5-1: CO_2-CH_4 ratios at different depths in Column 1 on Days 16, 28, and 47

Depth (cm)	CO_2-CH_4 Ratio		
	Day 16	Day 28	Day 47
Outlet	1.05	1.07	1.04
2	1.20	1.23	1.19
7	1.06	1.08	1.04
12	1.01	1.04	1.01
22	0.99	0.99	0.99
42	1.00	0.99	0.99
62	0.99	0.99	0.99

5.4.2 Column 2: Testing of a Coarser Mix at Lower Moisture Content

The performance of a more coarsely textured compost mix at a lower in-situ MC was examined in a second column trial (Column 2). In Column 2, the top 15 cm of compost material from Column 1 were removed and replaced with a coarser mixture of 1:4 YLWC:BSC at an MC of 35% ww, with the top 2.5 cm of compost from Column 1 mixed in as an inoculum. Soil gas concentration profiles are shown in Figure 5-16 (a) to (d) for selected Days 4, 6, 54, and 71 of incubation. By Day 4 (when the first gas samples were taken from the column side ports), N_2 was determined to be present down to a depth of 27 cm below the surface of the compost, which indicates a more efficient ingress of atmospheric air into this compost column than what was observed in Column 1 (Figure 5-16 (a)). The corresponding O_2, CH_4, and CO_2 profiles on this day suggest that methanotrophic activity was present throughout this top 27 cm of the compost column. The ratio of CO_2 to CH_4 was calculated to be greater than 1 at and above a depth of 27 cm, with the highest ratios (suggesting the highest rates of CH_4 oxidation) found within the top 7 cm of the compost (2.15 and 2.22 at 2 cm and 7 cm, respectively; Table 5-2). No O_2 was detected at or below a depth of 12 cm, which suggests utilization/depletion of this O_2 by aerobic microorganisms in the compost. By Day 6, a decrease in CO_2-CH_4 ratio (and an increase in O_2 concentration through to Day 14) were observed at sampling depths of 2, 7, and 12 cm, possibly as a result of a decreased rates of heterotrophic respiration in the compost (i.e., removal of raBOD) (Figure 5-16 (b); Table 5-2).

The concentrations of the soil pore gases were fairly constant from this day until Day 54, when a slight decrease in CO_2-CH_4 ratio and N_2 concentrations was observed at depths of 2, 7, 12, and 17 cm (Figure 5-16 (c)). A further slight decrease in these parameters (CO_2-CH_4 ratio and N_2 concentration) at these depths was observed on Day 71 (Figure 5-16 (d)). Similar to Column 1, possible EPS production in the form of an orange-brown residue was observed in the upper

oxygenated portion of the compost column, between a depth of 12 cm and 17 cm (Figure 5-17), which may have resulted in this decline in atmospheric air penetration and CH_4 oxidation activity. It is also possible that further compaction of the compost, under its own weight (as seen in Figure 5-17), contributed these declines.

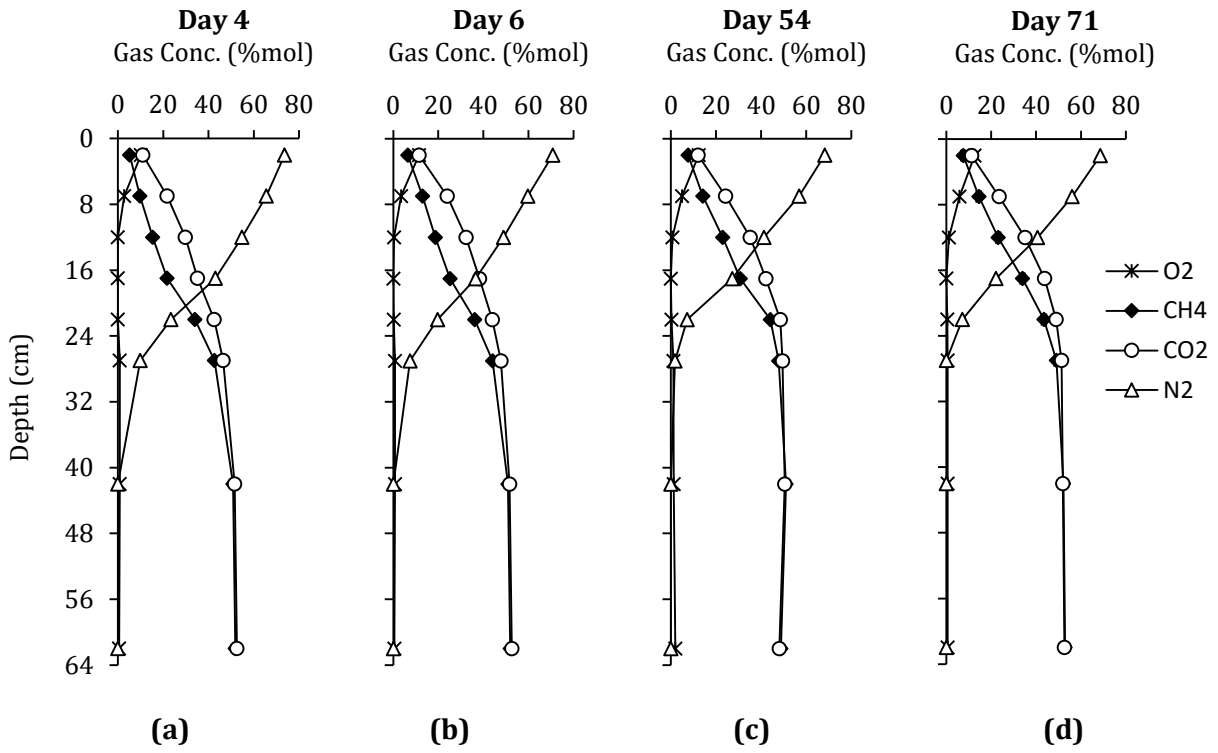


Figure 5-16: Vertical gas concentration profiles in Column 2 on (a) Day 4, (b) Day 6, (c) Day 54, and (d) Day 71

Table 5-2: CO_2-CH_4 ratios at different depths in Column 2 on Days 4, 6, 54, and 71

Depth (cm)	CO_2-CH_4 Ratio			
	Day 4	Day 6	Day 54	Day 71
Outlet	2.45	1.65	1.58	1.35
2	2.15	1.75	1.58	1.47
7	2.22	1.85	1.70	1.63
12	1.93	1.73	1.53	1.51
17	1.62	1.52	1.36	1.29
22	1.25	1.22	1.10	1.12
27	1.09	1.09	1.04	1.05
42	1.01	1.01	0.99	1.00
62	1.01	1.01	0.99	1.00

Figure 5-17: Possible EPS production in Column 2

A wider methanotrophic horizon, essentially 0 cm to at least 27 cm, was concluded to be the direct result of more the efficient transport of atmospheric O_2 to the compost column as a result of the use of a more a coarser mix at a lower moisture content.

5.4.3 Column 3: Testing of Column 2 Mix with the Addition of a Methanotroph-Enriched Compost Extract

The third and final column trial (Column 3) evaluated the performance of a 1:4 YLWC:BSC mixing ratio at a MC of 40% ww with the addition of a methanotroph-enriched compost extract (mixed into the compost prior to packing it into the column). Soil gas concentration profiles are shown in Figure 5-18 (a) to (d) for Days 1, 2, 4, and 9 of incubation. By Day 1 (Figure 5-18 (a)), aerated conditions (and therefore CH_4 oxidation) were detected throughout the entire height of the column. Small concentrations of atmospheric N_2 were present even at the deepest sampling port (located 62 cm below the surface of the compost), where the CO_2-CH_4 ratio was calculated to be 1.06 (Table 5-3). The greatest CH_4 oxidation activity was detected in the upper 32 cm of the compost column, where CO_2-CH_4 ratios ranged between 1.20 and 1.36 (Table 5-3). On Day 2, a shift towards lower concentrations of O_2 and CH_4 and greater concentrations of CO_2 (and therefore greater CO_2-CH_4 ratios) were detected, which indicates an increase in CH_4 oxidation activity in the column. From Days 2 to 4, a slight decrease in CO_2-CH_4 ratio and increase in O_2 was observed at a depth of 2 cm (similar to Column 2), again possibly due to some removal of compost raBOD. From Day 4 to the end of the experiment on Day 9, a further slight reduction in CO_2-CH_4 ratios in the column was observed; however, as the O_2 and N_2 profiles remained fairly constant over this period, it is possible that this result is only the result of insignificant fluctuations in CO_2 and CH_4 concentrations in the column.

On days 1, 2, 4, and 9, the CO_2-CH_4 ratios at the column outlet were calculated to be 1.13, 2.65, 2.28, and 1.86, which strongly indicates removal of a significant portion of the CH_4 flowing through the column.

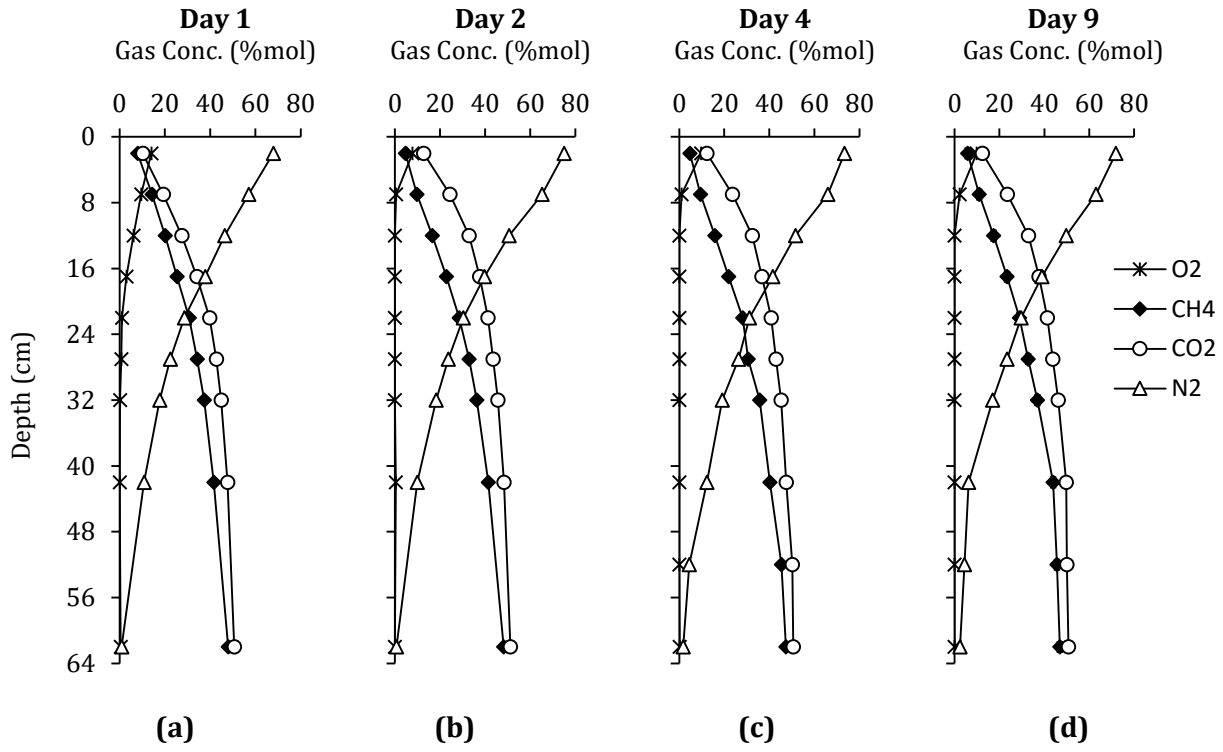


Figure 5-18: Vertical gas concentration profiles in Column 3 on (a) Day 1, (b) Day 2, (c) Day 4, and (d) Day 9

Table 5-3: CO_2-CH_4 ratios at different depths in Column 3 on Days 1, 2, 4, and 9

Depth (cm)	CO_2-CH_4 Ratio			
	Day 1	Day 2	Day 4	Day 9
Outlet	1.13	2.65	2.28	1.86
2	1.28	2.79	2.56	2.13
7	1.35	2.49	2.51	2.14
12	1.36	1.99	2.04	1.89
17	1.35	1.64	1.68	1.61
22	1.29	1.45	1.45	1.43
27	1.25	1.33	1.40	1.33
32	1.20	1.26	1.26	1.25
42	1.14	1.17	1.18	1.13
52	-	-	1.11	1.10
62	1.06	1.06	1.07	1.08

6 CONCLUSIONS

This thesis evaluated the efficacy of two compost materials, YLWC and BSC, at oxidizing CH_4 within a series of laboratory batch and column experiments. The main results and conclusions are summarized herein:

- YLWC that was collected from BRRMF in June 2014 (approximately one year prior to the start of the present thesis) was retested for its raBOD and MOP along with BSC that was collected from the City of Edmonton in January 2015. Overall, respiration activity was found to be significantly lower in the BSC than in the tested YLWC (mYLWC), with O_2 consumption rates calculated to be 63.2 and 14.2 μmol g(d.w.)$^{-1}$ d^{-1} in the mYLWC and the BSC, respectively; however, the mYLWC was found to have a much higher MOP than the BSC, with CH_4 oxidation rates calculated to be 70.1 μmol g(d.w.)$^{-1}$ d^{-1} (days 0-10) increasing to 95.9 μmol g(d.w.)$^{-1}$ d^{-1} (days 0-17) in the mYLWC and only 5.1 μmol g(d.w.)$^{-1}$ d^{-1} (days 0-14) in the BSC.

- Higher CH_4 oxidation activity was observed in the mYLWC than in the YLWC tested one-year prior (iYLWC). It was concluded that curing the compost for an additional one year at 4^0C (storage temperature), resulted in further reduction of easily-biodegradable organic matter in the compost (raBOD), therefore allowing a greater proportion of the available O_2 to be used for CH_4 oxidation rather than for heterotrophic respiration. This result confirmed the prior hypothesis that the iYLWC required further maturation beyond the compost maturity standard at BRRMF prior to being usable with a landfill biocover for oxidation of CH_4.

- Further experiments were conducted to test several hypotheses regarding the underlying cause of the lack of observed methanotrophic activity in the BSC. Neither the low moisture content nor the high concentration of heavy metals in the BSC were found to be the single limiting variable affecting CH_4 oxidation. It was determined, however, through testing several mixing ratios of YLWC to BSC, that inoculating the BSC with YLWC was effective. Several of the mixes (1:1, 1:2, 2:1, and 4:1 YLWC:BSC w:w) were found to consume CH_4 at a much faster rate than what was observed in the YLWC alone, confirming that there is a benefit to mixing the two composts. Whether this benefit is the result of compost texture, pH, nutrient content, etc., was not determined, but could be the subject of further laboratory batch tests. Another type of inoculation of the BSC from the City of Edmonton with a highly-active methanotroph-enriched compost extract (compost tea) was attempted, but was not successful. This inoculation experiment should be repeated with BSC from BRRMF prior to making a definite conclusion about the effectiveness of using a compost tea to stimulate methanotrophy from the biosolids matrix.

- Long-term CH_4 oxidation rates (over a 100-day study period) were assessed in YLWC and BSC collected from BRRMF in September 2015, and in 1:1 and 1:4 YLWC:BSC w:w mixing ratios of these composts. The YLWC reached a CH_4 oxidation rate by approximately day 40 of 130 to 140 μmol $g(d.w.)^{-1}$ d^{-1} and was able to sustain that rate until the end of the test (day 110). The BSC did eventually begin to consume CH_4 around day 60, and reached a maximum CH_4 oxidation rate by day 90 of 160 to 170 μmol $g(d.w.)^{-1}$ d^{-1}. The 1:1 and 1:4 mixing ratios reached a maximum rate of 360 to 380 μmol

g(d.w.)$^{-1}$ d^{-1} by days 76 and 79, respectively, though the 1:4 had a longer delay on account of having a lower innate population of methanotrophs.

- Variables including compost mix ratio, MC, and the addition of a methanotroph-enriched compost extract were tested using flow-through columns. Overall, CH_4 oxidation activity was found to be confined to the upper 7 cm of the compost in Column 1 (1:1 mixing ratio at MC = 60% ww), where only minimal CH_4 oxidation activity was detected, due to limited diffusion of atmospheric air to the compost column. It was hypothesized that the poor performance of the tested soil mixture was due to its fine texture (due to the high proportion of fine particles in the YLWC) and the high MC, which limited the air-filled porosity and permeability of the mixture to atmospheric air/O_2. In the second column trial (Column 2), the top 15 cm of the previous column was replaced with a more coarsely textured compost mix at a lower in-situ MC (1:4 mixing ratio at MC = 35% ww). A wider methanotrophic horizon, essentially 0 cm to at least 27 cm, was observed and was concluded to be the direct result of more the efficient transport of atmospheric O_2 to the compost. In Column 3, which evaluated a 1:4 mixing ratio at 40% ww (with the addition of a compost tea), aerated conditions (and therefore CH_4 oxidization activity) were detected throughout the entire height of the column, with CO_2-CH_4 ratios strongly indicating that a significant portion of the CH_4 flowing through the column was removed.

7 ENGINEERING SIGNIFICANCE

The laboratory studies presented in this thesis addressed several issues related to the design and operation of an engineered landfill biocover using YLWC (yard and leaf waste compost) and biosolids compost (BSC) for the passive treatment of CH_4 emissions.

The experimental results confirmed the importance of compost maturity to minimize competition for oxygen between methanotrophs and heterotrophs, which may initially delay methanotrophy. It is recommended that the YLWC be further matured beyond the compost maturity standard at BRRMF to reduce readily available carbon sources in the compost to limit heterotrophic growth and activity permitting a faster start of methanotrophy in the cover.

It is recommended that BSC alone from BRRMF not be used as a biocover, on account that there was no significant consumption of CH_4 observed until approximately day 60 of testing. Mixing the BSC with YLWC, however, did prove to be effective at stimulating methanotrophy from the biosolids matrix. It is possible to use a lower proportion of YLWC (i.e., a 1:4 YLWC:BSC mixing ratio) with only a limited delay in CH_4 oxidation activity over a mix with a higher proportion of YLWC (i.e., a 1:1 YLWC:BSC mixing ratio).

There is a fairly wide range of moisture contents, essentially 35% (fairly dry) to 80% (saturated) ww that proved to be effective for methanotrophy on the basis of the batch experiments; however, it was shown in the column experiments that excessive moisture may limit methanotrophy by creating water-logged conditions that limit the diffusion of O_2 into the compost cover.

The ability of a compost biocover to oxidize methane is largely limited by the extent to which oxygen can penetrate the compost, which was shown in the column experiments to be a function of several variables, including but not limited to compaction, moisture content, and texture/particle size.

The results of this work have provided the general parameters needed to optimize the design and performance of a landfill compost biocover in a field-scale application. Further testing in field scale is required in order to assess the effect of climatic factors such as precipitation, ambient temperature, and atmospheric pressure on the overall performance of the system and to demonstrate that the concept of a biological landfill cover can successfully be applied in geographical areas characterized by cold climates, such as in Manitoba.

8 REFERENCES

Abichou, T., Mahieu, K., Chanton, J., Romdhane, M., & Mansouri, I. (2011). Scaling methane oxidation: From laboratory incubation experiments to landfill cover field conditions. *Waste Management 31(5)*, 978-986.

Anthony, C. (1982). *The Biochemistry of Methylotrophs.* London, England: Academic Press Inc.

Bajar, S., Singh, A., Kaushik, C. P., & Kaushik, A. (2017). Statistical assessment of dumpsite soil suitability to enhance methane bio-oxidation under interactive influence of substrates and temperature. *Waste Management 63*, 188-195.

Barlaz, M. A., Chanton, J. P., & Green, R. B. (2009). Controls on landfill gas collection efficiency: Instantaneous and lifetime performance. *Journal of the Air & Waste Management Association 59(12)*, 1399-1404.

Bender, M., & Conrad, R. (1995). Effect of CH4 concentrations and soil conditions on the induction of CH4 oxidation activity. *Soil Biology and Biochemistry 27(12)*, 1517-1527.

Bergamaschi, P., Lubina, C., Koenigstedt, R., Fischer, H., Veltkamp, A. C., & Zwaagstra, O. (1998). Stable isotropic signatures (delta C-13, delta D) of methane from European landfill sites. *Journal of Geophysical Research: Atmospheres 103(D7)*, 8251-8265.

Bodelier, P. L., & Laanbroek, H. J. (2004). Nitrogen as a regulatory factor of methane oxidation in soils and sediments. *FEMS Microbiology Ecology 47*, 265-277.

Boeckx, P., & Van Cleemput, O. (1996). Methane oxidation in a neutral landfill cover soil: Influence of moisture content, temperature, and nitrogen-turnover. *Journal of Environmental Quality 25(1)*, 178-183.

Bogner, J., Meadows, M., & Czepiel, P. (1997a). Fluxes of methane between landfills and the atmosphere: Natural and engineered controls. *Soil Use and Management 13(4)*, 268-277.

Bogner, J., Spokas, K., & Burton, E. (1997b). Kinetics of methane oxidation in a landfill cover soil: Temporal variations, a whole-landfill oxidation experiment, and modeling of net CH4 emissions. *Environmental Science & Technology 31(9)*, 2504-2514.

Borjesson, G., Sundh, I., & Svensson, B. (2004). Microbial oxidation of CH4 at different temperatures in landfill cover soils. *FEMS Microbiology Ecology 48(3)*, 305-312.

Cabral, A. R., Tremblay, P., & Lefebvre, G. (2004). Determination of the diffusion coefficient of oxygen for a cover system including a pulp and paper by-product. *Geotechnical Testing Journal 27(2)*, 1-14.

Chanton, J., Abichou, T., Langford, C., Spokas, K., Hater, G., Green, R., . . . Barlaz, M. A. (2011). Observations on the methane oxidation capacity of landfill soils. *Waste Management 31(5)*, 914-925.

Chiemchaisri, W., Visvanathan, C., & Wu, J. S. (2001). Biological activities of methane oxidation in tropical landfill cover soils. *Journal of Solid Waste Technology and Management 27(3)*, 129-136.

Christophersen, M., Linderoed, L., Jensen, P. E., & Kjeldsen, P. (2000). Methane oxidation at low temperatures in soil exposed to landfill gas. *Journal of Environmental Quality 29(6)*, 1989-1997.

City of Winnipeg. (2014, February 26). *Brady Road Resource Management Facility - Methane Gas Collection System*. Retrieved from City of Winnipeg Water and Waste Department: http://www.winnipeg.ca/waterandwaste/garbage/bradyMethane.stm

City of Winnipeg. (2015). *City of Winnipeg Biosolids Master Plan Annual Progress Report.* Winnipeg: City of Winnipeg.

City of Winnipeg. (2017, April 24). *Community and Environmental Improvements*. Retrieved from City of Winnipeg Water and Waste Department: http://www.winnipeg.ca/waterandwaste/garbage/brady/programs.stm

City of Winnipeg. (2018, June 29). *Landfill Monitoring*. Retrieved from https://www.winnipeg.ca/waterandwaste/garbage/landfillMonitoring.stm

Czepiel, P. M., Mosher, B., Crill, P. M., & Harriss, R. C. (1996). Quantifying the effect of oxidation on landfill methane emissions. *Journal of Geophysical Research: Atmospheres 101(D11)*, 16721-16729.

Das, K., & Keener, H. M. (1997). Moisture effect on compaction and permeability in composts. *Journal of Environmental Engineering 123(3)*, 275-281.

De Visscher, A., & Van Cleemput, O. (2003). Induction of enhanced CH4 oxidation in soils: NH4+ inhibition patterns. *Soil Biology and Biochemistry 35(7)*, 907-913.

De Visscher, A., Boeckx, P., & Van Cleemput, O. (2007). Artificial methane sinks. In *Greenhouse Gas Sinks* (pp. 184-200). Wokingham: CABI Publishing.

De Visscher, A., Schippers, M., & Van Cleemput, O. (2001). Short-term kinetic response of enhanced methane oxidation to environmental factors. *Biology and Fertility of Soils 33*, 231-237.

De Visscher, A., Thomas, D., Boeckx, P., & Van Cleemput, O. (1999). Methane oxidation in simulated landfill cover soil environments. *Environmental Science & Technology 33(11)*, 1854-1859.

Dunfield, P., Knowles, R., Dumont, R., & Moore, T. R. (1993). Methane production and consumption in temperate and subarctic peat soils: Response to temperature and pH. *Soil Biology and Biochemistry 25(3)*, 321-326.

Einola, J.-K. M., Karhu, A. E., & Rintala, J. A. (2008). Mechanically-biologically treated municipal solid waste as a support medium for microbial methane oxidation to mitigate landfill greenhouse emissions. *Waste Management 28(1)*, 97-111.

Einola, J.-K. M., Kettunen, R., & Rintala, J. A. (2007). Responses of methane oxidation to temperature and water content in cover soil of a boreal landfill. *Soil Biology and Biochemistry 39(5)*, 1156-1164.

Environment and Climate Change Canada. (2014, July 25). *Municipal Solid Waste and Greenhouse Gases*. Retrieved from Environment and Climate Change Canada: http://www.ec.gc.ca/gdd-mw/default.asp?lang=En&n=6f92e701-1

Environment and Climate Change Canada. (2015, October 15). *Environment and Climate Change Canada - Greenhouse Gas Emissions Reporting Program Online Data Search - Results of GHG Facility Data Search*. Retrieved from http://www.ec.gc.ca/ges-ghg/donnees-data/index.cfm?do=results&lang=en&year=2013&gas=all&fac_name=&prov=MB&city=&naics=all&submit=Submit.

Felske, C. (2003). Minimization of residual emissions from municipal solid waste landfills by methane oxidation in landfill covers. *University Duisburg-Essen, Fachbereich Bauwesen, Schriftenreihe Forum Siedlungswasserwirtschaft und Abfallwirtschaft Universitat Essen, Heft*.

Figueroa, R. A. (1993). Methane oxidation in a landfill top soil. *Fourth International Landfill Symposium* (pp. 701-716). Cagliari, Italy: Proceedings Sardinia '93.

Gebert, J., Rower, I. U., Scharff, H., Roncato, C. D., & Cabral, A. (2011). Can soil gas profiles be used to assess microbial CH4 oxidation in landfill covers? *Waste Management*, 987-994.

Hanson, R. S., & Hanson, T. E. (1996). Methanotrophic bacteria. *Microbiological reviews 60(2)*, 439-471.

He, P., Yang, N., Fang, W., Lu, F., & Shao, L. (2011). Interaction and independence on methane oxidization of landfill cover soil among three impact factors: water, oxygen and ammonium. *Frontiers of Environmental Science & Engineering in China 5(2)*, 175-185.

Hester, R. E., & Harrison, R. M. (2002). *Environmental and Health Impact of Solid Waste Management Activities.* Cambridge: The Royal Society of Chemistry.

Huber-Humer, M. (2004). Abatement of Landfill Methane Emissions by Microbial Oxidation in Biocovers Made of Compost. *University of Natural Resources and Applied Life Sciences Vienna*.

Huber-Humer, M., Gebert, J., & Hilger, H. (2008). Biotic systems to mitigate landfill methane emissions. *Waste Management & Research 26(1)*, 33-46.

Huber-Humer, M., Roder, S., & Lechner, P. (2009). Approaches to assess biocover performance on landfills. *Waste Management 29(7)*, 2092-2104.

Humer, M., & Lechner, P. (1999). Alternative approach to the elimination of greenhouse gases from old landfills. *Waste Management & Research 17(6)*, 443-452.

Humer, M., & Lechner, P. (2001). Design of a landfill cover to enhance methane oxidation-results of a two year field investigation. *Eighth International Waste Management and Landfill Symposium*, (pp. 541-550). Cagliari, Italy.

Hutsch, B. W. (1998). Methane oxidation in arable soil as inhibited by ammonium, nitrite, organic manure with respect to soil pH. *Biology and Fertility of Soils 28(1)*, 27-35.

Hutsch, B. W., Webster, C. P., & Powlson, D. S. (1994). Methane oxidation in soil as affected by land use, soil pH and N fertilization. *Soil Biology & Biochemistry 26(12)*, 1613-1622.

IPCC. (2013). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

Jackel, U., Thummes, K., & Kampfer, P. (2005). Thermophilic methane production and oxidation in compost. *FEMS Microbiology Ecology 52(2)*, 175-184.

Kettunen, R., Einola, J.-K., & Rintala, J. (2006). Landfill methane oxidation in engineered soil columns at low temperature. *Water, Air, and Soil Pollution 177(1)*, 313-334.

Linton, J., Watts, P., Austin, R., Haugh, D., & Niekus, H. (1986). The energetics and kinetics of extracellular polysaccharide production from methanol by micro-organisms possessing different pathways of C sub(1) assimilation. *Journal of General Microbiology 132(3)*, 779-788.

Mei, J., Zhen, G., & Zhao, Y. (2016). Bio-oxidation of escape methane from landfill using leachate-modified aged refuse. *Arabian Journal for Science and Engineering 41(7)*, 2493-2500.

Melse, R. W., & Van der Werf, A. (2005). Biofiltration for mitigation of methane emission from animal husbandry. *Environmental Science & Technology 39(14)*, 5460-5468.

Mor, S., De Visscher, A., Ravindra, K., Dahiya, R. P., Chandra, A., & Van Cleemput, O. (2006). Induction of enhanced methane oxidation in compost: Temperature and moisture response. *Waste Management 26(4)*, 381-388.

Omelchenko, M., Vasilyeva, L., & Zavarzin, G. (1993). Psychrophilic methanotroph from tundra soil. *Current Microbiology 27(5)*, 255-259.

Pariatamby, A., Cheah, W. Y., Shrizal, R., Thamlarson, N., Lim, B. T., & Barasarathi, J. (2015). Enhancement of landfill methane oxidation using different types of organic wastes. *Environmental Earth Sciences 73(5)*, 2489-2496.

Park, J. R., Moon, S., Ahn, Y. M., Kim, J. Y., & Nam, K. (2005). Determination of environmental factors influencing methane oxidation in a sandy landfill cover soil. *Environmental Technology 26(1)*, 93-102.

Park, S., Lee, C. H., Ryu, C. R., & Sung, K. J. (2009). Biofiltration for reducing methane emissions from modern sanitary landfills at the low methane generation stage. *Water Air and Soil Pollution 196*, 19-27.

Pedersen, G. B., Scheutz, C., & Kjeldsen, P. (2011). Availability and properties of materials for the Fakse Landfill biocover. *Waste Management 31(5)*, 884-894.

Perdikea, K., Mehrotra, A., & Hettiaratchi, J. P. (2008). Study of thin biocovers (TBC) for oxidizing uncaptured methane emissions in bioreactor landfills. *Waste Management 28(8)*, 1364-1374.

Powelson, D. K., Chanton, J., Abichou, T., & Morales, J. (2006). Methane oxidation in water-spreading and compost biofilters. *Waste Management & Research 24(6)*, 528-536.

Province of Manitoba. (Revised: 2014, April 23). *Environment Act License No. 3081 R - Brady Road Resource Management Facility (BRRMF).*

Rachor, I., Gebert, J., Grongroft, A., & Pfeiffer, E.-M. (2011). Assessment of the methane oxidation capacity of compacted soils intended for use as landfill cover materials. *Waste Management 31(5)*, 833-842.

Reddy, K. R., Yargicoglu, E. N., Yue, D., & Yaghoubi, P. (2014). Enhanced microbial methane oxidation in landfill cover soil amended with biochar. *Journal of Geotechnical and Geoenvironmental Engineering 140(9)*.

Roncato, C., & Cabral, A. (2012). Evaluation of methane oxidation efficiency of two biocovers: Field and laboratory results. *Journal of Environmental Engineering 138(2)*, 164-173.

Rose, J. L., Mahler, C. F., & dos Santos Izzo, R. L. (2012). Comparison of the methane oxidation rate in four media. *Revista Brasileira de Ciência do Solo 36(3)*, 803-812.

Sadasivam, B. Y., & Reddy, K. R. (2014). Landfill methane oxidation in soil and bio-based cover systems: A review. *Reviews in Environmental Science and Bio/Technology 13(1)*, 79-107.

Saha, U., & Sen, M. (1989). Methane oxidation by Candida tropicalis. *National Academy of Science Letters (India) 12*, 373-376.

Scheutz, C., & Kjeldsen, P. (2004). Environmental factors influencing attenuation of methane and hydrochlorofluorocarbons in landfill cover soils. *Journal of Environmental Quality 33(1)*, 72-79.

Scheutz, C., & Kjeldsen, P. (2005). Biodegradation of trace gases in simulated landfill soil. *Journal of the Air & Waste Management Association 55(7)*, 878-885.

Scheutz, C., Kjeldsen, P., Bogner, J. E., De Visscher, A., Gebert, J., Hilger, H. A., . . . Spokas, K. (2009a). Microbial methane oxidation processes and technologies for mitigation of landfill gas emissions. *Waste Management & Research 27(5)*, 409-455.

Scheutz, C., Pedersen, G. B., Costa, G., & Kjeldsen, P. (2009b). Biodegradation of methane and halocarbons in simulated landfill biocover systems containing compost materials. *Journal of Environmental Quality 38(4)*, 1363-1371.

Scheutz, C., Pedicone, A., Pedersen, G. B., & Kjeldsen, P. (2011). Evaluation of respiration in compost landfill biocovers intended for methane oxidation. *Waste Management 31(5)*, 895-902.

Schulze, K. L. (1961). Relationship between moisture content and activity of finished compost. *Compost Sci*.

Segel, I. H. (1993). *Enzyme Kinetics: Behaviour and Analysis of Rapid Equilibrium and Steady-State Enzyme Systems.* Wiley.

Sharp, C. E., Smirnova, A. V., Graham, J. M., Stott, M. B., Khadka, R., Moore, T. R., . . . Dunfield, P. F. (2014). Distribution and diversity of Verrucomicrobia methanotrophs in geothermal and acidic environments. *Environmental Microbiology*, 1867-1878.

Stantec Consulting Ltd. (2011). *Environmental Impact Assessment of Brady Road Landfill and Future Resources Management Facility.* Winnipeg: Stantec Consulting Ltd.

Stein, V. B., & Hettiaratchi, J. (2001). Methane oxidation in three Alberta soils: Influence of soil parameters and methane flux rates. *Environmental Technology 22(1)*, 101-111.

Stein, V. B., & Hettiaratchi, J. P. (2001). Methane oxidation in three Alberta soils: Influence of soil parameters and methane flux rates. *Environmental Technology 22(1)*, 101-111.

Wang, J., Xia, F.-F., Bai, Y., Fang, C.-R., Shen, D.-S., & He, R. (2011). Methane oxidation in landfill waste biocover soil: Kinetics and sensitivity to ambient conditions. *Waste Management 31(5)*, 864-870.

Wartiainen, I., Hestnes, A. G., Mcdonald, I. R., & Svenning, M. M. (2006). Methylocystis rosea sp. nov., a novel methanotrophic bacterium from Arctic wetland soil, Svalbard, Norway (78 degrees N). *International Journal of Systematic and Evolutionary Microbiology 56(3)*, 541-547.

Whalen, S. C., Reeburgh, W. S., & Sandbeck, K. A. (1990). Rapid methane oxidation in a landfill cover soil. *Applied and Environmental Microbiology 56(11)*, 3405-3411.

Whittenbury, R., Phillips, K. C., & Wilkinson, J. F. (1970). Enrichment, isolation and some properties of methane-utilizing bacteria. *Journal of General Microbiology 61(2)*, 205-218.

Wilshusen, J. H., De Visscher, A., Saint-Fort, R., & Hettiaratchi, J. P. (2004a). Methane oxidation and formation of EPS in compost: Effect of oxygen concentration. *Environmental Pollution 129(2)*, 305-314.

Wilshusen, J. H., Hettiaratchi, J., & Stein, V. B. (2004b). Long-term behavior of passively aerated compost methanotrophic biofilter columns. *Waste Management 24(7)*, 643-653.

Wolf, H. J., & Hanson, R. S. (1980). Identification of methane-utilizing yeasts. *FEMS Microbiology Letters 7(2)*, 177-179.

Xie, T., Reddy, K., Wang, C., Yargicoglu, E., & Spokas, K. (2014). Characteristics and Applications of Biochar for Environmental Remediation: A Review. *Critical Reviews in Environmental Science and Technology 45(9)*, 939-969.

Xing, Z. L., Zhao, T. T., Gao, Y. H., Yang, X., Liu, S., & Peng, X. Y. (2017). Methane oxidation in a landfill cover soil reactor: Changing of kinetic parameters and microorganism community structure. *Journal of Environmental Science and Health, Part A, 52(3)*, 254-264.

Yargicoglu, E. N., & Reddy, K. R. (2017). Effects of biochar and wood pellets amendments added to landfill cover soil on microbial methane oxidation: A laboratory column study. *Journal of Environmental Management 193*, 19-31.

Zeiss, C. (2006). Accelerated methane oxidation cover system to reduce greenhouse gas emissions from MSW landfills in cold, semi-arid regions. *Water, Air, and Soil Pollution 176(1)*, 285-306.