

**Methane consumption by a landfill cover soil under variable
soil moisture and temperature conditions**

by

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Author's declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Statement of contributions

Chapter 2 consists of an experiment write-up, and Chapter 3 consists of a co-authored manuscript-format paper, where in both these chapters, I was primarily responsible for the study design, execution, data analysis, and writing. The contributions of the co-authors are as follows for both chapters: I designed the experiments with guidance from Fereidoun Rezanezhad, Stephanie Slowinski, Laura Hug, and Philippe Van Cappellen. I performed the laboratory experiments and data analysis with guidance from Stephanie Slowinski and Fereidoun Rezanezhad. The modeling portions were completed with the assistance of Mehdi Ramezanzadeh. Fereidoun Rezanezhad, Laura Hug, and Phillippe Van Cappellen supervised the project and provided guidance on data interpretation. I performed the data analysis, visualizations, and wrote the chapters. Chapter 3 will be modified for journal submission and reviewed by all co-authors. I am the sole author of all other chapters in this thesis.

Abstract

Methane (CH₄) is a significant greenhouse gas (GHG) that contributes to climate warming when released into the atmosphere, with over 80 times the warming potential of carbon dioxide (CO₂) over a 20-year period. Landfills are one of the largest anthropogenic sources of CH₄, and hot-spots of CH₄ emissions in landfill cover soils represent a large proportion of emissions that are thus a target for mitigation. These hot-spots can enrich microbes that consume CH₄ and produce CO₂ as a less potent GHG, via CH₄ oxidation. CH₄ oxidation rates are modulated by multiple environmental variables including soil moisture and temperature. Therefore, it is important to investigate the interactive effects of these factors on CH₄ oxidation rates, to further understand the response of CH₄ oxidation activity under changing conditions whether via seasonality or climate change.

In Chapter 2, I conducted a closed-headspace batch experiment with cover soil from a hot-spot of a former landfill to measure CH₄ consumption and CO₂ efflux rates associated with variations in soil moisture and temperature simultaneously. Soil samples were incubated under a factorial design of 5 soil moisture contents ranging from 11 to 47% WFPS (water-filled pore space), and 6 temperatures ranging from 1 to 35°C. At each temperature and WFPS combination, CH₄ was spiked into the headspace, and headspace CH₄ and CO₂ concentrations were measured over 2 hours to calculate CH₄ consumption and CO₂ efflux rates. The maximum CO₂ efflux rate was observed at the maximal WFPS and temperature conditions of this experiment ($91.5 \pm 10.3 \text{ nmol h}^{-1} \text{ g DW}^{-1}$ at 47% WFPS and 35°C), while the maximum CH₄ consumption rate was observed at intermediate soil moisture and temperature conditions ($1.86 \pm 0.05 \text{ nmol h}^{-1} \text{ g DW}^{-1}$ at 25% WFPS and 25°C). The results from this experiment showed the preliminary optimal conditions for CH₄ consumption

and associated CO₂ efflux within this range of tested soil moisture and temperature conditions, and served as a baseline for the experimental design of Chapter 3.

In Chapter 3, I conducted a series of closed-headspace batch incubations with cover soil from the same hot-spot site to expand on the findings from Chapter 2. The incubations assessed the CH₄ consumption and CO₂ efflux rates under simultaneous variations of soil moisture and temperature, with modifications including a wider range of soil moistures, and higher concentrations and subsequent injections of CH₄. Soil samples were incubated under a factorial design of 5 soil moisture contents ranging from 20 to 100% WFPS, and 4 temperatures ranging from 1 to 35°C. At each temperature and moisture combination, CH₄ was spiked into the headspace through multiple consecutive injections, and headspace CH₄ and CO₂ concentrations were measured to calculate CH₄ consumption and CO₂ efflux rates. The maximum CH₄ consumption rate was observed at the moderate soil moisture and temperature conditions (330±12.3 nmol h⁻¹ g DW⁻¹ at 60% WFPS and 25°C), while the maximum CO₂ efflux rate was observed at the maximal WFPS and temperature conditions used in the incubations (652±85.0 nmol h⁻¹ g DW⁻¹ at 100% WFPS and 35°C). A diffusion-reaction model was developed to simulate and fit the observed data to represent the effects of temperature and soil moisture on the CH₄ consumption and CO₂ efflux rates, predicting similar optimal conditions to the observed experimental data. Temperature sensitivity analysis (Q_{10}) also supported the CH₄ consumption being via CH₄ oxidation. These results provide insight into how seasonal changes in soil moisture and temperature impact CH₄ oxidation rates, and therefore also net CH₄ emissions, in landfill cover soils and other environments.

Overall, the results from Chapters 2 and 3 together emphasize that the dominant controls on the optimal soil moisture for CH₄ consumption are the interactive effects of moisture limitation of

microbial activity and of gas (CH_4 and O_2) diffusion, whereas for the CO_2 effluxes, the dominant controls are the interactive effects of moisture limitation of gas (O_2) diffusion and solute mobility. The difference in optimal conditions for CH_4 consumption and CO_2 efflux rates also highlight the presence of different microbial groups underlying the various soil processes. These findings can be expanded on for further understanding of CH_4 oxidation activity at hot-spots and for the development of tools for mitigation of CH_4 emissions from landfills.

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List of abbreviations

CH ₄	Methane
GHG	Greenhouse gas
CO ₂	Carbon dioxide
WFPS	Water-filled pore space
DW	Dry weight
O ₂	Oxygen
N ₂ O	Nitrous oxide
H ₂ O	Water
MDL	Method detection limit
HgCl ₂	Mercuric (II) chloride
GC	Gas chromatograph
DOC	Dissolved organic carbon
DIC	Dissolved inorganic carbon
TDN	Total dissolved nitrogen
NH ₄ ⁺	Ammonium
SD	Standard deviation
C ₆ H ₁₂ O ₆	Glucose

List of symbols

Q_{10}	Temperature sensitivity coefficient
θ	Moisture content
ϕ	Porosity
ρ_b	Bulk density
F_{gas}	Calculated gas flux
ΔC_{gas}	Change in gas concentration
V	Volume of headspace
R	Gas constant
T	Temperature
t	Time
V_{soil}	Volume of soil
r	Rate of reaction
$D_{el,i}$	Effective diffusion coefficient (aqueous)
$D_{eg,i}$	Effective diffusion coefficient (gas)
θ_l	Volume fraction of liquid phase
θ_g	Volume fraction of gas phase
c_i	Concentration of the specimen
$c_{G,i}$	Gas phase concentration
$k_{G,i}$	Volatilization rate constant
$\nu_{i,j}$	Stoichiometric coefficient of specimen i
ϕ_e	Effective porosity

$D_{L,i}$	Diffusion coefficient in water
$D_{G,i}$	Diffusion coefficient in air
$D_{0,i}$	Temperature independent pre-exponential constant for substance i
$E_{A,i}$	Activation energy for diffusion
f_{temp}	Function representing the temperature dependency of the reactions
K_{CH_4}	Half saturation constant for methane
K_{O_2}	Half saturation constant for oxygen
C_{CH_4}	Concentration of methane
C_{O_2}	Concentration of oxygen

1 Introduction

1.1 Greenhouse gas, soil, and climate change

Greenhouse gas (GHG) emissions are a major contributing factor to climate change, where carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are the main GHGs that contribute to climate warming by trapping heat in the atmosphere (Filonchyk et al., 2024; Leifeld, 2006; Yusuf et al., 2012). When solar radiation reaches the earth's surface, the energy is re-emitted as heat as infrared radiation, which GHGs can absorb and ultimately trap in the atmosphere (Filonchyk et al., 2024). The major GHGs have different proportions in the atmosphere and have different warming potentials; CH₄ has a global warming potential 28 times greater than CO₂ over a 100-year period, or 84 times greater over a 20-year period (Aghdam et al., 2019; Delgado et al., 2022; Gebert et al., 2022; IPCC, 2013; Scharff et al., 2024). As a result, CH₄ emissions to the atmosphere are an especial concern and target for the mitigation of GHGs and global warming.

Naturally occurring processes in the environment can release GHGs into the atmosphere, and soils play an important role as they can be both sources and sinks of GHGs. CO₂ can be emitted from soils due to the microbial breakdown of organic matter, though this is also balanced by the uptake of CO₂ by primary production (Camarda et al., 2019; Schimel, 1995). Terrestrial emissions of GHGs can also come from wetlands, agriculture, and permafrost soils, where CH₄ emissions can be especially high as these anoxic environments often develop and promote methanogenesis (Blair & Mataraarachchi, 2021; Filonchyk et al., 2024; Leifeld, 2006). Soils are therefore a significant environmental component to consider with respect to GHGs due to their storage and emission capacities, whether natural or anthropogenic.

Anthropogenic activities can alter these soil environments and increase their GHG emissions to the atmosphere. For example, modern agriculture often relies on cleared land which reduces the overall ability of the soil to sequester carbon and GHGs, and raising livestock directly emits CH₄ via enteric fermentation (Lynch et al., 2021). Waste management is another source of anthropogenic GHG emissions, particularly CH₄, in the atmosphere. Globally, the waste management sector (*i.e.*, landfills and wastewater) is the third largest (18%) anthropogenic source of CH₄ emissions, behind fossil fuels and enteric fermentation (Bogner et al., 2008; Gillespie et al., 2024; Scharff et al., 2024; Yusuf et al., 2012). Therefore, waste management is a necessary yet overlooked sector that makes up a large proportion of anthropogenic CH₄ emissions.

1.2 CH₄ emissions from landfills

Landfills in particular are an area of concern, as nearly two-thirds of municipal solid waste is landfilled globally, and the nature of landfilling results in the generation of landfill gas (comprising of CO₂ and CH₄) that is released to the atmosphere (Kaza et al., 2018; Lombardi et al., 2006; Scharff et al., 2024; Themelis & and Ulloa, 2007). Municipal landfills are an important source to consider because they collectively make up a significant portion of CH₄ emissions, and landfilling solid waste has been a widespread approach for waste disposal around the world and historically (Blair & Mataraarachchi, 2021; Mor et al., 2024). In Canada, municipal landfills contribute to over 20% of the country's CH₄ emissions (Environment and Climate Change Canada, 2022).

1.2.1 CH₄ production in landfills

When municipal solid waste is landfilled, landfill gas containing CH₄ is produced as a by-product in the absence of oxygen (O₂) in the deeper waste layer of the landfill (landfill structure as an

example shown in Figure 1-1) (Gebert et al., 2022; Scheutz et al., 2009; Themelis & Ulloa, 2007). Specifically, there is microbial anaerobic decomposition of the organic waste, which ultimately results in the generation of landfill gas, including CH₄ (Abichou et al., 2009; Mor et al., 2024; Themelis & Ulloa, 2007). One way that CH₄ emissions can be reduced from landfills includes the diversion of organic waste from landfills, which would reduce the amount of landfill gas and CH₄ production (Gebert et al., 2022; Scharff et al., 2024). Landfills can also have a gas distribution layer (Figure 1-1), which is important for distributing the CH₄ gas as it diffuses upwards from the waste layer (Gebert et al., 2022). In addition, some landfills have infrastructure in place in this layer where landfill gas and CH₄ can be collected and converted into energy (Lombardi et al., 2006; Mor et al., 2024; Themelis & Ulloa, 2007). The uppermost layer, sometimes referred to as the CH₄ oxidation layer (Figure 1-1) or more generally as the landfill cover soil, is where microbial CH₄ oxidation would take place with O₂ diffusing from the surface into the soil (Chiemchaisri et al., 2012; Gebert et al., 2022). Microbial CH₄ oxidation is increasingly studied as a natural control on CH₄ emissions, where existing methanotrophic microbial communities can consume CH₄ in the presence of O₂ to produce CO₂, which is less potent as a GHG (Gebert et al., 2022; Hilger & Humer, 2003; Meyer-Dombard et al., 2020; Scheutz et al., 2009). Microbial CH₄ oxidation and the factors influencing it are further discussed in section 1.3.

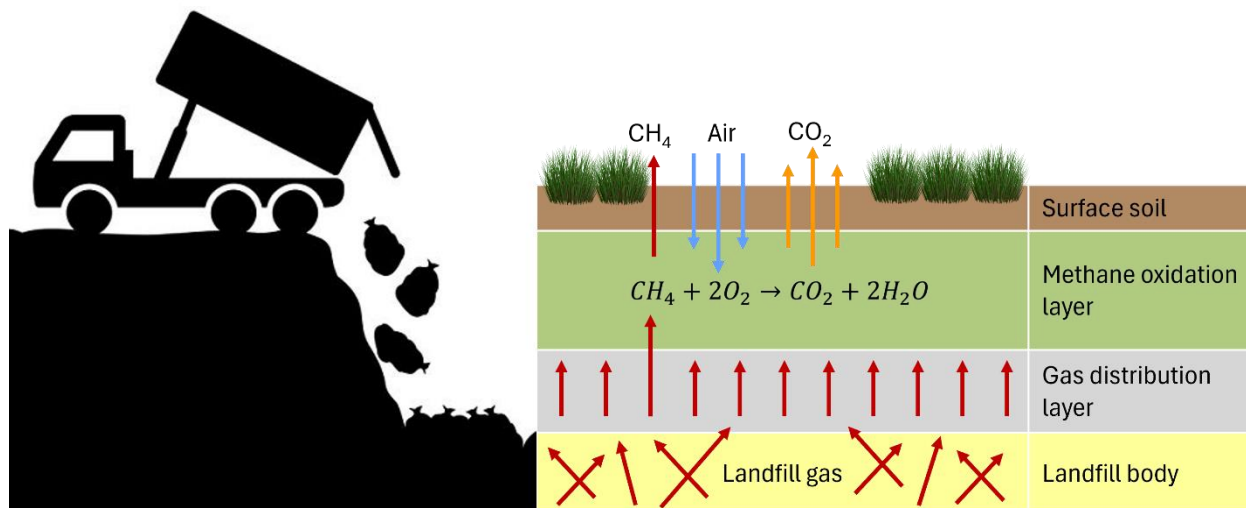


Figure 1-1: Schematic representation of landfill structure, layers, and relevant processes when waste is landfilled (modified from Gebert et al., 2022).

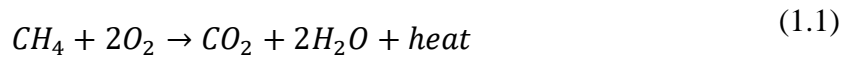
1.2.2 Hot-spots of CH₄ emissions from landfills

Landfill cover soils, where microbial CH₄ oxidation can occur, can exhibit hot-spots of CH₄ emissions. Hot-spots of CH₄ emissions are local areas at the landfill cover surface where there are relatively higher or uncontrolled CH₄ emissions (Delgado et al., 2022; Gebert et al., 2022; Wu et al., 2023). Hot-spots can develop in various manners including cracks in the landfill cover soil, leakage through instrumentation for collecting CH₄ gas, and unequal distribution of gas in deeper layers of the landfill (Gebert et al., 2022; Scheutz et al., 2009; Wu et al., 2023). Therefore, hot-spots of CH₄ emissions are key targets for the reduction of CH₄ emissions as they represent a greater proportion of CH₄ released into the atmosphere that is not quantified. The relatively higher concentrations of CH₄ from hot-spots can also enrich existing methanotrophic microbial communities, which means there may be greater capacity for CH₄ oxidation at a hot-spot (Gebert et al., 2022; Scheutz et al., 2009). This microbial activity is beneficial as a solution for the reduction of CH₄ emissions from municipal landfills and cover soils. Thus, hot-spots of CH₄ emissions from

landfills are a priority target for the reduction of CH₄ emissions (Environment and Climate Change Canada, 2022).

1.3 Factors influencing microbial CH₄ oxidation

CH₄ oxidation is carried out by methanotrophs, where the microbes consume CH₄ and produce CO₂ in the presence of O₂, with the following general chemical reaction (Scheutz et al., 2009):



The oxidation of CH₄ is mediated by the CH₄ monooxygenase enzyme which is present in several aerobic methanotrophic species, such as *Methylobacter* and *Methylocystis* species (Cébron et al., 2007; Hanson & Hanson, 1996; Koo & Rosenzweig, 2021; Meyer-Dombard et al., 2020). Methanotrophs are often active where both CH₄ and O₂ are present, in a variety of environments and climates such as peatlands and rice paddies (Guerrero-Cruz et al., 2021; Hanson & Hanson, 1996; Le Mer & Roger, 2001). Landfill cover soils are also ideal for CH₄ oxidation, where CH₄ is supplied via landfill gas in deeper layers of the landfill and O₂ is supplied from the atmosphere (Cébron et al., 2007; Guerrero-Cruz et al., 2021; Hanson & Hanson, 1996). CH₄ oxidation is influenced by various climatic and environmental factors including temperature, soil moisture, ammonia concentration, and O₂ supply (Boeckx et al., 1996; Park et al., 2005; Scheutz et al., 2009). Soil moisture and temperature will be the main climatic and environmental factors discussed in this thesis.

1.3.1 Soil temperature effect on CH₄ oxidation

Temperature plays a role in CH₄ oxidation as it controls chemical reaction rates and enzymatic activity (Börjesson et al., 2004; Reddy et al., 2019). Most methanotrophs are mesophiles and typically operate optimally at moderate temperatures around 25 to 40°C, where low or high temperatures may inhibit enzyme activity and growth (Hanson & Hanson, 1996; Reddy et al., 2019). This is also approximately the optimal range for CH₄ oxidation activity, which many studies have reported to be around 30 to 36°C (Boeckx & Van Cleemput, 1996; Börjesson et al., 2004; Hilger & Humer, 2003; Park et al., 2005; Scheutz et al., 2009). The temperature sensitivity of reactions can also be described using a Q_{10} temperature coefficient, which is a measure of the increase in reaction rate with a 10°C increase in temperature (Davidson & Janssens, 2006; Winkler et al., 1996). The Q_{10} value for biological reactions is typically around 2 to 3, and for CH₄ oxidation in landfill cover soils, a range of 1.7 to 8.4 has been reported (Boeckx & Van Cleemput, 1996; Börjesson et al., 2004; Einola et al., 2007; Park et al., 2005; Scheutz & Kjeldsen, 2004).

1.3.2 Soil moisture effect on CH₄ oxidation

Soil moisture is another controlling factor on CH₄ oxidation rates, as water is essential for biological activity via the diffusion of substrates and nutrients (Borowik & Wyszowska, 2016; Reddy et al., 2014). The level of soil moisture affects the connectivity of the soil aggregates and pore spaces, which is important for microbes to access dissolved substrates in the water or gases in the air spaces (Borowik & Wyszowska, 2016; Whalen & Reeburgh, 1996). Excess water could limit the air space and supply of gases (*i.e.*, CH₄ and O₂ for CH₄ oxidation), whereas a lack of water could result in water stress and declined microbial activity (Boeckx & Van Cleemput, 1996; Einola et al., 2007; Manzoni et al., 2016; Scheutz et al., 2009). In addition, CH₄ has low solubility in water, and gaseous diffusion is faster than aqueous diffusion, thus moderate soil moisture levels

are ideal for CH₄ oxidation (Einola et al., 2007; Hilger & Humer, 2003; Park et al., 2005; Whalen & Reeburgh, 1996). Low to moderate soil moistures are reported to be optimal for CH₄ oxidation in landfill cover soils, ranging from 10 to 35% (Boeckx & Van Cleemput, 1996; Einola et al., 2007; Park et al., 2005).

1.4 Thesis objectives

The main objective of this thesis is to assess the simultaneous effects of soil moisture and temperature on the rates of CH₄ consumption, and associated CO₂ production, from a landfill cover soil. This overall objective was investigated through laboratory soil incubation experiments coupled with a diffusion-reaction model. The specific objective of Chapter 2 was to develop the method to preliminarily assess the effect of varying soil moisture and temperature in combination on the capacity for CH₄ consumption. The specific objective of Chapter 3 was to expand on the simultaneous variations of soil temperature and moisture and develop a diffusion-reaction model to represent CH₄ consumption processes.

1.5 Thesis outline

This thesis is comprised of four chapters, including the current Chapter 1. Chapter 2 describes the preliminary soil incubation experiment investigating the effects of soil moisture and temperature on the rates of CH₄ consumption. The results from Chapter 2 were used to inform the experimental design of Chapter 3. Chapter 3 is in a manuscript-style format which has been modified for this thesis and will be submitted for publication to the Journal *Science of the Total Environment*. This chapter describes another soil incubation experiment, examining the impact of varying soil moisture and temperature in a factorial-batch manner on CH₄ consumption rates, given multiple

consecutive injections of CH₄. Chapter 4 describes overall conclusions and recommendations for future research. Appendices I and II contain supplementary materials for Chapters 2 and 3 respectively.

2 Effects of soil moisture and temperature on methane consumption in a landfill cover soil: A preliminary experiment

This chapter describes a preliminary experiment that was performed to assess the capacity for methane (CH_4) consumption using soil from a hot-spot of CH_4 emissions identified at a former landfill. Various soil moisture and temperature conditions were tested in this batch experiment in a continuous manner, whereby the same set of soil moistures experienced changes in temperature together. CH_4 consumption was observed at similar optimal conditions to what has been reported, but at a smaller magnitude compared to the carbon dioxide (CO_2) production from this experiment and compared to other CH_4 oxidation rates in literature. Therefore, the results of this preliminary experiment (Chapter 2) were used to inform the design the incubation experiments presented in Chapter 3, where a wider range of moistures was tested, a higher concentration of CH_4 was used, and consecutive injections of CH_4 were tested in attempt to ensure saturation of the pore spaces with CH_4 .

2.1 Introduction and motivation

Landfills are one of the largest anthropogenic sources of CH_4 emissions, with waste generation expected to increase by 70% by 2050 as the global population continues to increase (Gillespie et al., 2024; Kaza et al., 2018; Scharff et al., 2024). Canadian landfills generated 30 megatons of CO_2 equivalents of CH_4 in 2015, 63% of which evaded capture and were emitted to the atmosphere (Environment and Climate Change Canada, 2022). In deeper layers of the landfill when oxygen is depleted, anaerobic decomposition becomes dominant and produces landfill gas, comprising of CH_4 and CO_2 , as a byproduct (Scheutz et al., 2009; Themelis & Ulloa, 2007). Hot-spots of CH_4 emissions from landfills are a key target for mitigating CH_4 emissions as they represent

unmonitored losses in the quantification of CH₄ emissions (Delgado et al., 2022; Environment and Climate Change Canada, 2022; Wu et al., 2023). Hot-spots also enrich methanotrophic microbial communities, which can be used as a natural control on CH₄ emissions by consuming CH₄ and producing CO₂ via CH₄ oxidation (Abichou et al., 2009; Gebert et al., 2022; Scheutz et al., 2009).

Various factors can influence CH₄ oxidation activity, including soil moisture, temperature, and CH₄ concentration (Bender & Conrad, 1995; Boeckx & Van Cleemput, 1996). The effects of these individual factors on CH₄ oxidation rates have generally been well-studied in landfill settings, where soil moisture and soil temperature are the most relevant climatic factors. Soil temperature modulates CH₄ oxidation capacity via its impacts on both the solubility of CH₄ in water and on microbial reaction kinetics (Scheutz et al., 2009; Velasco et al., 2018; Whalen & Reeburgh, 1996). The reported optimal temperatures for CH₄ consumption rates in other studies range from 30 to 36°C (Bender & Conrad, 1995; Boeckx et al., 1996; Spokas & Bogner, 2011). CH₄ oxidation activity is also modulated in part by soil moisture because of its effects on gas diffusivity, dissolved substrate accessibility, and microbial activity (Borowik & Wyszowska, 2016; Einola et al., 2007; Scheutz et al., 2009). Soil moistures of 10 to 35% have been reported as optimal for CH₄ oxidation in landfill cover soils (Bender & Conrad, 1995; Einola et al., 2007; Park et al., 2005). Previous studies have assessed the effects of both soil moisture and temperature on CH₄ oxidation rates in soils, both individually and simultaneously. Park et al. (2005) investigated the individual effects of soil moisture, temperature, and initial CH₄ concentration on CH₄ oxidation rates, whereas Einola et al. (2007) demonstrated the interactive effect of soil moisture and temperature on CH₄ oxidation rates, highlighting the fact that variations in soil moisture and temperature likely cause coupled changes to the biogeochemistry and microbial activity of the system. This chapter addresses these

elements together to better simulate different seasonal conditions and understand their combined effects on CH₄ oxidation rates from a landfill cover soil.

In this chapter, I present the results from a preliminary soil incubation experiment that was conducted to assess the interactive effects of both soil moisture and temperature variations on CH₄ consumption rates in a landfill cover soil. Cover soil from a former landfill was prepared under 5 different moisture conditions ranging from 11 to 47% water-filled pore space (WFPS) and incubated at temperatures ranging from 1 to 35°C, from which headspace gas concentrations were measured after spiking a constant concentration of CH₄ gas. The resulting CH₄ consumption and CO₂ efflux rates were calculated to assess and compare CH₄ consumption and CO₂ efflux rates across different soil moisture and temperature conditions.

2.2 Materials and methods

2.2.1 Soil collection, preparation, and characterization

Landfill cover soil was collected from a CH₄ emission hot-spot site at a former landfill in Kitchener, Ontario, Canada, which is now used as an urban park (known as McLennan Park). Soil was sampled to a depth of approximately 10 cm. The soil was air-dried, gently homogenized, and sieved to less than 4 mm, then placed in an environmental chamber (Percival I-41NL XC9) at 15°C for 5 days as an equilibration period prior to starting the incubation experiment.

Soil aliquots were used to determine initial moisture content (θ), porosity (ϕ), bulk density (ρ_b), and solid-phase chemical composition using standard procedures. The porosity and bulk density of the soil samples were determined gravimetrically from the saturated mass, the oven-dried mass (24 h at 105°C), the original sample volume, and an assumed particle density of 2.65 g cm⁻³, following the methods of Boelter (1972) and Gardner (1986). The bulk density and porosity were

1.23 g cm⁻³ and 0.34, respectively. The soil organic carbon and total nitrogen were measured on a CHNS Carbo Erba analyzer (method detection limit, MDL: 1% by mass) and were determined as 1.35% and <1%, respectively.

2.2.2 Soil incubation

A factorial batch experiment was conducted by incubating soil samples at different imposed moisture contents (11%, 18%, 20%, 40% and 47% WFPS) and at different imposed temperatures increasing from 1 to 35°C (1, 5, 10, 15, 25, 35°C; Phase I) then decreasing from 35 to 1°C in the same intervals (35, 25, 15, 10, 5, 1°C; Phase II) (Figure 2-1). The factorial nature of this experimental design allowed for the examination of the effects of moisture and temperature to better understand the role of these climatic factors on CH₄ oxidation rates.

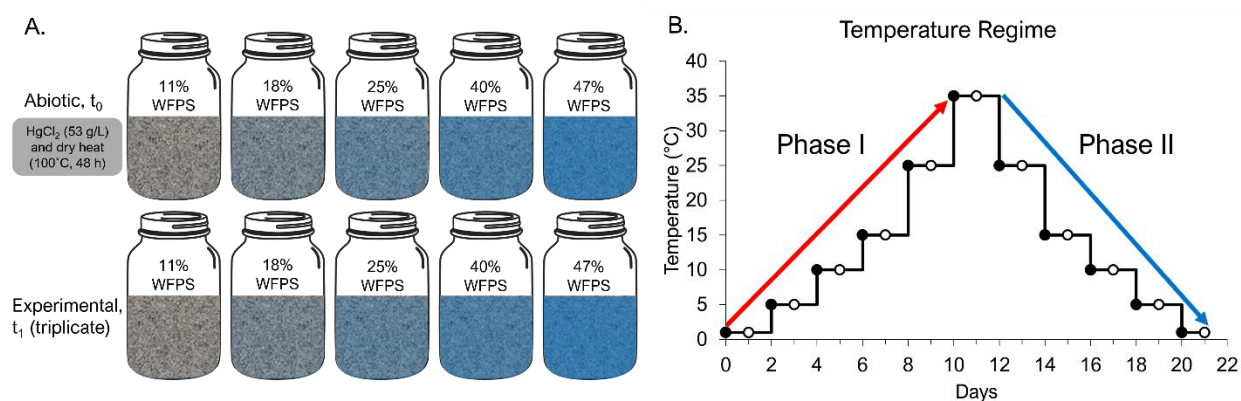


Figure 2-1: Soil incubation experimental design (A) and temperature regime of the experiment (B). Phase I (red arrow) represents the increase in temperature from 1 to 35°C and Phase II (blue arrow) represents the decrease in temperature from 35 to 1°C. Black solid points represent the day 1 of the experimental cycle where jars were open to the atmosphere, and black open points represent day 2 of the experimental cycle where jars were closed, the headspace was spiked with CH₄ (150 ppm), and then sampled for gas.

Aliquots of 120 g of homogenized and air-dried soil were added to 240 mL amber bottles (Fisherbrand Amber Boston Round Glass Bottles) with an open-top cap (Thermo Scientific I-

Chem Open-Top Septa cap) and 22 mm Teflon septa (Chromatographic Specialties), leaving ~120 mL of headspace gas volume in the bottles (hereafter referred to as the experimental jars). Moisture content was adjusted by adding an aqueous solution that closely matched the pH, electrical conductivity, and ionic composition of rainwater in the field site, by dissolving NaCl (4.5 μM), KCl (1.2 μM), $(\text{NH}_4)_2\text{SO}_4$ (23 μM), $\text{Ca}(\text{NO}_3)_2$ (15 μM), and $\text{Mg}(\text{NO}_3)_2$ (5 μM) salts in ultrapure deionized water. This artificial rainwater was intended to minimize disturbances to the native microbial community upon large changes in porewater chemistry that can cause osmotic or pH shocks (Halverson et al., 2000; Killham, 1985). The soil moisture levels were achieved by adding 2.0, 4.4, 6.8, 11.7, or 14.1 mL of the artificial rainwater to sieved soil samples and then mixing gently for about 2 to 3 minutes, corresponding to moisture levels of approximately 11%, 18%, 20%, 40% and 47% WFPS, respectively. The moisture contents as the percentage WFPS were calculated from the soil porosity and the amounts of water added, plus the previously determined residual water remaining in the air-dried soil.

The samples for each moisture were prepared in triplicate yielding 15 jars in total. One additional sample of each of the five moisture contents was prepared and used as an abiotic control (Figure 2-1A). Abiotic control jars contained soil that was dried at 100°C for 48 hours and treated with mercuric chloride (HgCl_2), at a concentration of 53 g L^{-1} and at a rate of 500 mg kg^{-1} soil, as an inhibitor of soil microbial activity (Trevors, 1996). The abiotic control jars were used to get representative t_0 CH_4 and CO_2 concentrations at the beginning of the incubation period for each % WFPS. All jars were incubated following a temperature regime shown in Figure 2-1B, whereby temperatures increased in a stepwise manner from 1 to 35°C (1, 5, 10, 15, 25, 35°C; Phase I) then decreased from 35 to 1°C in the same intervals (35, 25, 15, 10, 5, 1°C; Phase II). The jars were incubated in these conditions for a total period of 21 days.

2.2.3 Gas flux measurements

The jars underwent a 2-day sampling regime; day 1 consisted of a 24-hour acclimation period to the new temperature where the jars were aerobic and open to the atmosphere; day 2 consisted of capping the jars, spiking the headspace with CH₄ (150 ppm) using a 10 mL Luer-Lok™ plastic syringe and 22-gauge needle by piercing the septum of the jar lid, then collecting gas samples in the same way. Gas samples were taken from the jar's headspace after 5 minutes from the abiotic control jars (t_0) and after 2 hours from the experimental jars (t_1) to measure the difference in gas concentrations over the 2-hour incubation, letting the abiotic controls represent t_0 for each t_1 from the experimental jars (to prevent taking too much gas from the experimental jars). This cycle was repeated for every temperature of the temperature regime (Figure 2-1B), resulting in 11 sampling time points.

The CH₄ and CO₂ gas concentrations were measured using a Shimadzu Gas Chromatograph (Model GC-2014) equipped with a flame ionization detector and methanizer. The GC was calibrated each time with standards prior to gas concentration measurements. Gas fluxes (F_{gas} , nmol h⁻¹ g DW⁻¹; grams dry weight) were obtained from the observed changes in gas concentrations after closure and were calculated by:

$$F_{gas} = \frac{\Delta C_{gas} V}{RT \Delta t V_{soil}} \quad (2.1)$$

where ΔC_{gas} is the change in gas concentration (CH₄ or CO₂) over the closed incubation period, determined by subtracting the gas concentration at t_0 (5 minutes) in the abiotic controls from the gas concentration at t_1 (2 hours) in the experimental jars (nmol mol⁻¹), V is the volume of the headspace (L), R is the gas constant (0.082057 L atm k⁻¹ mol⁻¹), T is the temperature (K), Δt is the

time the headspace was closed off (h), and V_{soil} is the volume of the soil sample (cm^3 ; soil dry mass/bulk density). The F_{gas} values calculated using CH_4 and CO_2 concentrations are hereafter defined as the CH_4 consumption rate and CO_2 efflux rate, respectively.

2.2.4 Porewater geochemistry

Porewater was extracted from the initial soil and the experimental samples upon termination of the experiment and analyzed for pH, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total dissolved nitrogen (TDN), major anions, and ammonium (NH_4^+). To extract porewater, ultrapure deionized water was added to the soil of the experimental jars until saturated (100% WFPS), as the moisture contents of the experiment were too dry to extract sufficient porewater for analyses. The wet soil was mixed manually, transferred into a 50 mL Teflon centrifuge tube (Nalgene®), and centrifuged at 4000 rpm for 30 minutes, where the supernatant porewater was filtered through a $0.45 \mu\text{m}$ membrane filter (polypropylene syringe filters, VWR) into 50 mL polypropylene centrifuge tubes. Unfiltered porewater was analyzed for pH using handheld meters (LAQUA Twin meters, model Horiba B-213). Porewater concentrations of DOC, TDN, and DIC were measured in the filtered porewater using a total organic carbon analyzer (Shimadzu TOC-LCPH/CPN; MDL: 4.6, 2.9, and $2.8 \mu\text{mol L}^{-1}$, respectively). The samples for DOC analysis were acidified to $\text{pH} < 3$ with 20 μL of 1 M hydrochloric acid (HCl). 2 mL of filtered porewater were transferred into 5 mL centrifuge tubes for NH_4^+ analysis, which was performed using a Gallery Discrete Analyzer ($\pm 10\%$ error and $\pm 3\%$ precision; MDL: $1.87 \mu\text{g NH}_3\text{-N/L}$). Approximately 1 mL of porewater was further filtered through a $0.2 \mu\text{m}$ pore size membrane filter (Thermo Scientific Polysulfone filter) and frozen at -20°C for later analysis of major anions, including chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) using ion chromatography (IC, Dionex ICS-5000

with a capillary IonPac® AS18 column; MDL: 2.14, 1.32, and 0.81 $\mu\text{mol L}^{-1}$, respectively) and all standards were prepared from certified multi-anion standards (Sigma-Aldrich).

2.3 Results and discussion

2.3.1 *CO₂ efflux rates*

CO₂ effluxes increased with increasing moisture and temperature conditions (Figure 2-2 and AI-1), with the highest flux occurring at the maximal conditions of the experiment (47% WFPS and 35°C) at a rate of $91.5 \pm 10.3 \text{ nmol h}^{-1} \text{ g DW}^{-1}$ (\pm SD; standard deviation). Among all the temperature conditions, the higher moisture contents generally yielded greater CO₂ production. When comparing Phase I and II of the experiment, CO₂ production rates were overall similar, with some incubations showing a greater CO₂ flux in Phase II. There was a clear effect of both soil temperature and moisture on the CO₂ efflux rates (Figure 2-2), which was expected as it has been reported that the methanotrophs grow and respire between 25 to 30°C (Reddy et al., 2019) and CO₂ production from soil is optimal around 55 to 65% WFPS (Byun et al., 2021; Fairbairn et al., 2023; Linn & Doran, 1984). The temperature sensitivity was evident in the CO₂ results, especially once reaching the higher temperatures of the experiment where there was a greater increase in the CO₂ efflux rates from 15 to 35°C.

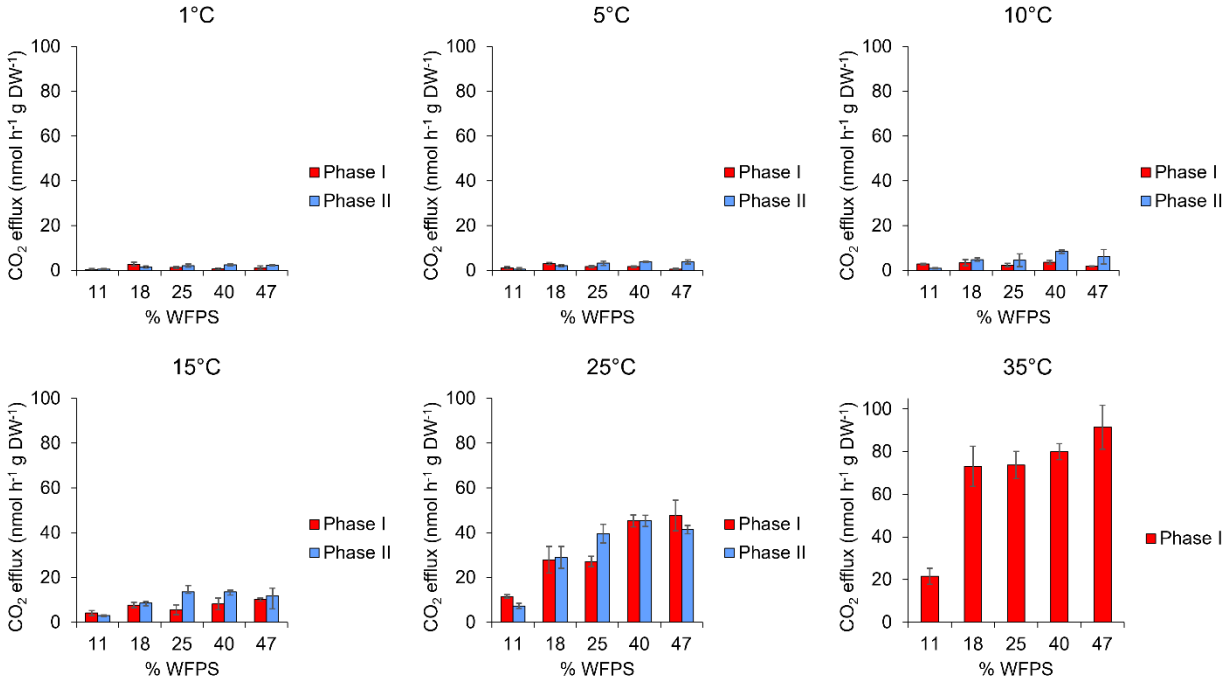


Figure 2-2: CO₂ effluxes at each temperature of the incubation experiment under different soil moisture contents in phases I and II. Error bars are the standard deviation of the triplicate measurements.

2.3.2 CH₄ consumption rates

The maximal CH₄ consumption rate was observed to be 1.86 ± 0.05 nmol h⁻¹ g DW⁻¹ at moderate soil moisture and temperature conditions of the experiment (25% WFPS and 25°C) (Figure 2-3 and AI-2). On the lower end of the temperature range (1 and 10°C), the highest CH₄ consumption rates were typically occurring at the at the higher moisture contents. For the higher temperatures, CH₄ consumption was highest at the lower-intermediate moisture levels between 18 and 25% WFPS. Higher rates of CH₄ consumption were observed in Phase I relative to Phase II for nearly all moisture and temperature conditions. The optimal conditions are in line with other studies in literature, though the lower CH₄ consumption rates should be noted, likely due to the low CH₄ concentration and other aspects of the experimental design.

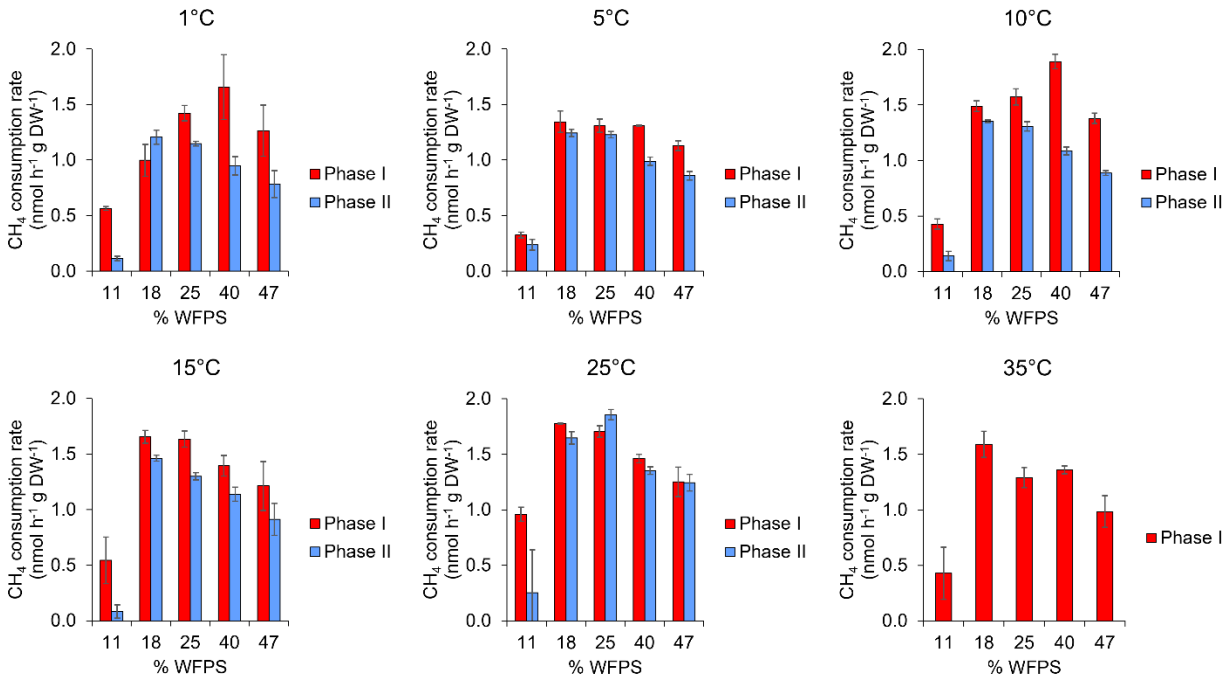


Figure 2-3: CH₄ consumption rates at each temperature of the incubation experiment under different soil moisture contents in phases I and II. Error bars are the standard deviation of the triplicate measurements.

The rates of CH₄ consumption observed in the soil from this site were lower in magnitude compared to similar soil moisture and temperature experiments using landfill cover soil (Park et al., 2005). This may be due to the much lower concentration of CH₄ used in this experiment (150 ppm) compared to other studies (400,000 ppm by Park et al., 2005). The results of Whalen & Reeburgh (1996) also showed reduced rates of CH₄ oxidation in the experimental soils due to the joint effects of varied moisture and temperature conditions. These interactive effects, and the lower concentration of CH₄ supplied in the experiment, may be reasons for the lower rates of CH₄ consumption observed in our results, relative to similar experiments in literature.

2.3.3 Comparison of CH₄ consumption and CO₂ efflux rates

One notable difference in these results is the magnitude between the CO₂ efflux and CH₄ consumption rates (Figures 2-2 and 2-3). In theory, if CH₄ consumption was the dominant reaction producing CO₂ in the soil system, there would be similar rates of CO₂ production as those of CH₄ consumption given that 1 mole of CO₂ is produced per mole of CH₄ oxidized (Scheutz et al., 2009). However, the much larger CO₂ effluxes and the different optimal moisture and temperature conditions indicate that the production of CO₂ is likely from microbial respiration of soil organic matter (Lloyd & Taylor, 1994). The optimum CO₂ efflux rate was observed at these conditions due to the trade-off between dissolved substrate diffusion and O₂ diffusion in the pore spaces, while for CH₄ consumption, the diffusion of CH₄ and O₂ gases is optimized at lower soil moistures.

In addition, to support the rates of CH₄ consumption observed, a supplementary set of abiotic soil samples were prepared in the same manner (treated with mercuric chloride (HgCl₂) and dried at 100°C for 48 hours). The supplementary abiotic jars were incubated at select moisture and temperature conditions, then CH₄ was supplied at the same concentration, and headspace gas samples were taken at multiple time points over the same incubation period (Figure AI-3). CH₄ concentrations for this abiotic soil remained constant over the incubation period (other than an initial loss likely due to diffusion of CH₄ into the pore spaces), suggesting that the decrease in CH₄ in the experimental jars of the main experiment, while small, was due to CH₄ consumption through CH₄ oxidation.

2.4 Conclusions and next steps

This chapter was a preliminary experiment that assessed the capacity for CH₄ consumption, and the combined effects of soil moisture and temperature on CH₄ consumption rates from a landfill

cover soil. The optimal rate for CH₄ consumption was 1.86 nmol h⁻¹ g DW⁻¹ at moderate temperature and moisture conditions (25% WFPS and 25°C). In contrast, the optimal rate for CO₂ efflux was 91.5 nmol h⁻¹ g DW⁻¹ at the maximum temperature and moisture conditions studied (47% WFPS and 35°C). The different responses of CH₄ consumption and CO₂ efflux rates to different soil moistures and temperatures suggest that the microbial groups responsible for the different reaction pathways of CH₄ consumption and CO₂ production via respiration have different optimal temperature and moisture conditions. The true optimal conditions, particularly of soil moisture and CH₄ concentrations, for CH₄ consumption and CO₂ production may not have been captured in the range of conditions from this experiment, thus expanding this range would benefit the experimental design. The experimental design in Chapter 3 takes these results into account, incorporating a wider range of soil moistures, higher CH₄ concentrations, and consecutive injections of CH₄ into the headspace.

Methane consumption by a landfill cover soil under variable soil moisture and temperature conditions

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3 Methane consumption by a landfill cover soil under variable soil moisture and temperature conditions

3.1 Introduction

Waste management makes up ~18% of the global anthropogenic methane (CH₄) emissions (Bogner et al., 2008; Scharff et al., 2024; Scheutz et al., 2009), in which municipal solid waste in landfills represent 60% of waste sector CH₄ emissions (Gillespie et al., 2024; Mor et al., 2024). Landfills can be sources of CH₄ through the anaerobic decomposition of organic waste, which can diffuse through the landfill cover soil surface to the atmosphere (Börjesson & Svensson, 1997; Gebert et al., 2022; Themelis & Ulloa, 2007). As a result, there can be localized sites of concentrated CH₄ emissions, or “hot-spots”, which are important to consider due to their greater relative contribution to CH₄ released into the atmosphere (Delgado et al., 2022; Gebert et al., 2022; Wu et al., 2023). These hot-spots can enrich methanotrophic microbial communities capable of oxidizing CH₄ to carbon dioxide (CO₂), which is less potent as a greenhouse gas (Hanson & Hanson, 1996; Hilger & Humer, 2003; Scheutz et al., 2009). Microbial CH₄ oxidation has been widely studied as a biological approach to reducing CH₄ emissions in landfills, and is known to be affected by soil moisture, temperature, CH₄ concentration, and other factors (Boeckx & Van Cleemput, 1996; Park et al., 2005; Reddy et al., 2019).

Previous studies often examined the impact of soil moisture and temperature on CH₄ oxidation activity independently. Low to moderate soil moisture contents between 10 to 35% (Boeckx & Van Cleemput, 1996; Einola et al., 2007; Park et al., 2005) and temperatures between 30 to 36°C (Boeckx & Van Cleemput, 1996; Hilger & Humer, 2003; Spokas & Bogner, 2011) have been reported as optimal conditions for CH₄ oxidation in landfill cover soils. The temperature sensitivity

of CH₄ oxidation can also be assessed using a Q_{10} value, which is a temperature coefficient that represents the increase in reaction rate given a 10°C increase in temperature (Davidson & Janssens, 2006; Scheutz et al., 2009; Winkler et al., 1996). Biological processes of soils typically have Q_{10} values of approximately 2 to 3 (Byun et al., 2021; Davidson & Janssens, 2006), and studies on temperature sensitivity of CH₄ oxidation in landfill cover soils have reported Q_{10} values from 1.7 to 8.4 (Boeckx & Van Cleemput, 1996; Börjesson et al., 2004; Einola et al., 2007; Park et al., 2005; Scheutz et al., 2009). However, the impact of soil moisture and temperature together on CH₄ oxidation in landfill cover soils has been understudied. Einola et al. (2007) and Whalen and Reeburgh (1996) are a few studies that also assessed the impact of landfill soil moisture and temperature simultaneously, emphasizing that these factors are closely linked and it is necessary to understand their combined effects on CH₄ oxidation.

In this study, the experimental conditions (soil moisture and temperature) were controlled in a series of soil incubations to mimic the variations in soil moisture and temperature that might be observed as a result of seasonal dynamics and intensifying climate change. The consumption rate of CH₄ and the efflux rate of CO₂ were measured in batch experiments under variable soil moisture (20, 40, 60, 80, and 100% WFPS; water-filled pore space) and temperature (1, 15, 25, and 35°C) conditions. We assessed the effects of soil moisture and temperature variations on CH₄ consumption rates using an approach whereby multiple injections of CH₄ were supplied consecutively. The separate injections of CH₄ were meant to progressively saturate the soil and assess the rate of CH₄ consumption with each subsequent injection. Headspace gases were collected following injections of CH₄ to estimate the rate of CH₄ consumption, as well as CO₂ efflux, across each soil moisture and temperature combination. In addition, Q_{10} values were calculated to assess the temperature sensitivity of CH₄ consumption and CO₂ efflux rates, and a

diffusion-reaction model was developed to represent the processes controlling CH₄ consumption and CO₂ production and the influence of temperature and moisture content on these processes. This study is unique given the simultaneous variation of soil moisture and temperature, in combination with the modeling simulations of CH₄ consumption in a landfill soil.

3.2 Materials and methods

3.2.1 Soil collection, preparation, and characterization

Landfill cover soil was collected from the same former landfill hot-spot site and prepared for incubation in the same manner as in Chapter 2 (see section 2.2.1). Following the preparation, the soil was stored at 4°C in an environmental chamber (Percival I-41NL XC9) prior to starting the incubations. Soil aliquots were used to characterize various properties of the soil (as described in section 2.2.1 in Chapter 2). The bulk density and porosity were 0.90 g cm⁻³ and 0.32, respectively. The soil organic carbon and total nitrogen were determined as 8.6% and <1%, respectively.

3.2.2 Soil incubation

A series of incubation experiments were conducted by incubating soils of different imposed moisture contents (20%, 40%, 60%, 80%, and 100% WFPS) at selected temperatures (1, 15, 25, and 35°C). A glass bottle for each of the 5 soil moisture contents was prepared for incubation at the 4 temperatures, for a total of 20 experimental bottles to examine CH₄ consumption rates at each soil moisture and temperature combination (Figure 3-1).

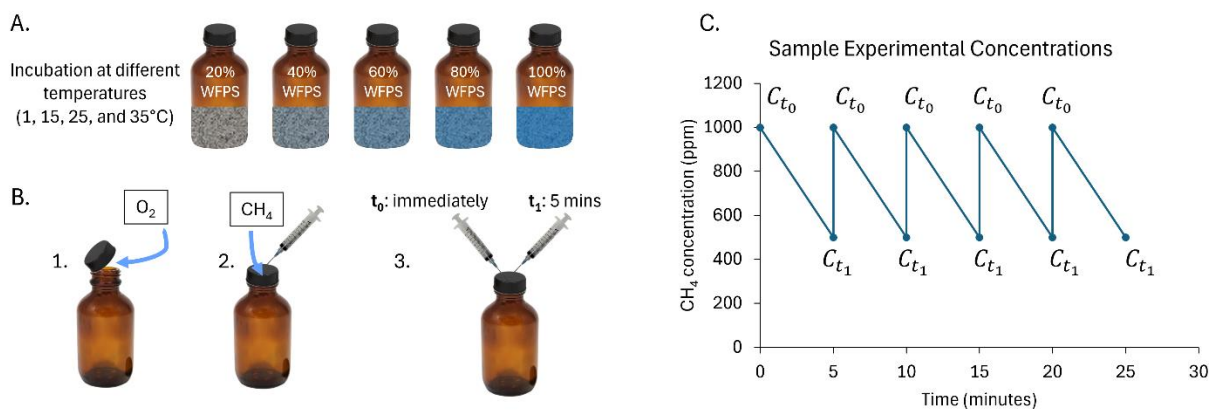


Figure 3-1: Soil incubation experimental design (A), a schematic of the CH₄ injection procedure (B), and a sample graph showing the headspace concentrations of CH₄, indicating consumption of the injected CH₄ during the incubation (C).

Aliquots of 108 g of homogenized and air-dried soil were added to 240 mL amber bottles (Fisherbrand Amber Boston Round Glass Bottles) with an open-top cap (Thermo Scientific I-Chem Open-Top Septa cap) and 22 mm Teflon septa (Chromatographic Specialties), leaving ~120 mL of headspace gas volume in the experimental bottles. Moisture content was adjusted with an aqueous solution prepared as described in section 2.2.2 in Chapter 2. The soil moisture levels were achieved by adding 2.1, 9.6, 17.2, 24.9, and 32.5 mL of the artificial rainwater to the soil and homogenizing the sample. The corresponding moisture levels were approximately 20%, 40%, 60%, 80% and 100% WFPS (Figure 3-1; see section 2.2.2 in Chapter 2). The incubation bottles were placed in an environmental chamber incubator (Percival I-41NL XC9) where the air temperature was controlled at 1, 15, 25, and 35°C.

Two additional samples of each moisture and temperature condition were prepared for use as controls (Figures AII-3 and AII-4). One set of samples was used as a “soil, no CH₄” control, in which the sieved soil was prepared and incubated in the same manner, then received injections of lab air in the same volumes rather than CH₄ (see section 3.2.3). The other set of samples was used

as the “abiotic” control, in which sieved soil was autoclaved three times in five days at 121°C and 15 psi for 1 hour. The autoclaved soil was further oven-dried at 100°C for 2-3 days, prepared and incubated in the same manner, then received injections of CH₄ in the same manner as the experimental bottles (see section 3.2.3). All bottles, solutions, and equipment for the abiotic controls were also autoclaved before use at 121°C and 15 psi for 30 minutes.

At each selected incubation temperature, all bottles were first prepared and left in the environmental chamber incubator approximately 3 days before CH₄ injections and gas flux measurements to allow for equilibration of the soil to the temperature. The bottles were left open for this equilibration period to allow for the input of oxygen into the bottles, then capped prior to the gas sampling. The incubation period of the bottles with the CH₄ (or lab air for the “soil, no CH₄” control) in the closed headspace was 25 minutes.

3.2.3 *CH₄ injections*

Caps were placed on the bottles in order to take gas samples from the headspace and estimate consumption of CH₄ by the soil following CH₄ injections. First, a “rate test” was performed by injecting a known amount of CH₄ into an additional bottle prepared and incubated in the same manner, to assess the rate of CH₄ consumption at that temperature and moisture in 5 minutes. For the rate test, a 30 mL sample of the headspace was taken out of the bottle to account for pressure differences from injecting CH₄ gas and taking gas samples. CH₄ (1250 ppm) was injected into the headspace, and a t_0 gas sample was taken from the headspace immediately following the injection. 5 minutes after the initial injection, a t_1 gas sample was taken (Figure 3-1). The concentration of CH₄ consumed within this 5-minute period was used as the target concentration for the subsequent 4 injections of CH₄ into the same bottle of the “multi-injection test”.

The “multi-injection test” was performed by introducing multiple injections of CH₄ into the same bottle. The multiple injections were conducted to continually saturate the system with CH₄ and observe whether there was a difference in consumption rate with subsequent injections of CH₄, by amending the CH₄ concentration to approximately the same level with each injection (Figure AII-1). For the multi-injection test, the same initial steps were carried out as described above for the rate test. From there, a subsequent injection of the pre-determined amount from the rate test was prepared and injected immediately following the previous t_1 sample, then the next t_0 sample was taken immediately following the injection. The t_1 sample was taken after another 5 minutes, and this cycle was repeated for a total of 5 injections (1 initial and 4 subsequent injections) (Figure 3-1). The rate test and multi-injection test were repeated for all combinations of temperature and moisture conditions.

3.2.4 Gas flux measurements and temperature sensitivity (Q_{10})

The CH₄ and CO₂ gas concentrations of all collected headspace gas samples were measured using a Shimadzu Gas Chromatograph (Model GC-2014) equipped with a flame ionization detector and methanizer. The GC was calibrated each time with standards prior to gas concentration measurements. Gas fluxes (F_{gas} , nmol h⁻¹ g DW⁻¹; grams dry weight) were obtained from the observed changes in gas concentration between the t_0 and t_1 samples of each injection after closure, calculated by:

$$F_{gas} = \frac{\Delta C_{gas} V}{RT \Delta t V_{soil}} \quad (3.1)$$

where ΔC_{gas} is the change in gas concentration (CH₄ or CO₂) over the closed incubation period, determined by subtracting the gas concentration at t_0 (immediately following injection) from the

gas concentration at t_1 (5 minutes) in the experimental bottles (nmol mol^{-1}), V is the volume of the headspace (L), R is the gas constant ($0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1}$), T is the temperature (K), Δt is the time between injections (h), and V_{soil} is the volume of the soil sample (cm^3 ; soil dry mass/bulk density). The F_{gas} values calculated using CH_4 and CO_2 concentrations are hereafter defined as the CH_4 consumption rate and CO_2 efflux rate, respectively.

Q_{10} values were calculated as a measure of temperature sensitivity of the soil samples in the experiment, using the average CH_4 consumption or CO_2 efflux rate up to the optimal temperature at a given moisture (Figure 3-5 and Table 3-4). This was calculated using an exponential rate increase:

$$Q_{10} = \left(\frac{r_2}{r_1}\right)^{\left(\frac{10}{T_2-T_1}\right)} \quad (3.2)$$

where r_2 is the CH_4 consumption or CO_2 efflux rate ($\text{nmol h}^{-1} \text{ g DW}^{-1}$) at the optimal temperature (T_2 in $^{\circ}\text{C}$; see Figure 3-5) and r_1 is the rate at 1°C (T_1).

3.2.5 Porewater geochemistry

Porewater was extracted from the initial soil sample and selected experimental samples (80% WFPS at 25°C and 100% WFPS at 25°C) upon termination of the experiment. These samples were analyzed for pH, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total dissolved nitrogen (TDN), and major anions. The porewater extraction was done in the same manner as described in section 2.2.4 in Chapter 2.

3.2.6 Modeling simulations

To simulate the variations in experiment's measured CH₄ consumption rates as a function of the variations in soil moisture content and temperature, a diffusion-reaction model was developed to represent the processes removing and producing CH₄ in the headspace, as well as the effects of temperature and soil moisture on these processes. The mass conservation equation for CH₄ in a water saturated porous medium with the main controls on CH₄ mass conservation being the CH₄ oxidation chemical reaction kinetics and CH₄ diffusion between the headspace and porewater in one dimension is:

$$\frac{\partial(\theta_l c_i)}{\partial t} + \frac{\partial(\theta_g c_{G,i})}{\partial t} + \nabla \cdot [-(D_{el,i} + D_{eg,i} k_{G,i})] \nabla c_i = \sum_j \nu_{i,j} r_j f_{temp,j} \quad (3.3)$$

with the effective diffusion coefficients in the liquid and gas phases, $D_{el,i}$ and $D_{eg,i}$, respectively, calculated using Eqs. 3.4, 3.5, and 3.6:

$$D_{el,i} = \frac{\theta_l^{\frac{10}{3}}}{\phi_e^2} D_{L,i} \quad (3.4)$$

$$D_{eg,i} = \frac{\theta_g^{\frac{10}{3}}}{\phi_e^2} D_{G,i} \quad (3.5)$$

$$D_{L/G,i} = D_{0,i} \exp\left(-\frac{E_{A,i}}{RT}\right) \quad (3.6)$$

where θ_l and θ_g are the volume fraction of liquid and gas phases, c_i is the concentration [ML⁻³] of the specimen i , $c_{G,i}$ is the gas phase concentration [ML⁻³], $k_{G,i}$ is the volatilization rate constant [-], $D_{el,i}$ and $D_{eg,i}$ are the effective diffusion coefficients [L² T⁻¹] in the aqueous phase and gas phase, respectively, r_j is the rate of j th reaction in a reaction network, and $\nu_{i,j}$ is the stoichiometric coefficient of specimen i in the reaction j . ϕ_e is effective porosity, and $D_{L,i}$ and $D_{G,i}$ are the

diffusion coefficients [$L^2 T^{-1}$] in water and air, respectively. In Eq. 3.6, $D_{0,i}$ is the temperature independent pre-exponential constant for substance i , $E_{A,i}$ is the activation energy for diffusion, and R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). f_{temp} is a function representing the temperature dependency of the reactions as follows (Jin & Kirk, 2018; Rosso et al., 1993):

$$f_{temp} = \frac{(T - T_{max})(T - T_{min})^2}{(T_{opt} - T_{min})[(T_{opt} - T_{min})(T - T_{opt}) - (T_{opt} - T_{max})(T_{opt} + T_{min} - 2T)]} \quad (3.7)$$

where T_{min} , T_{max} , and T_{opt} ($^{\circ}\text{C}$) are the minimum, maximum, and optimum temperature values for the reaction.

To investigate the impact of soil moisture and temperature on CH_4 consumption rates in a landfill cover soil, the CH_4 consumption was represented by assuming that CH_4 oxidation was the dominant reaction controlling CH_4 production and consumption kinetics. The following reaction rate expression was used to represent the rate of CH_4 oxidation (*i.e.*, consumption):

$$r_{\text{CH}_4} = -r_{max,\text{CH}_4} \frac{C_{\text{CH}_4}}{K_{\text{CH}_4} + C_{\text{CH}_4}} \frac{C_{\text{O}_2}}{K_{\text{O}_2} + C_{\text{O}_2}} \quad (3.8)$$

where r_{max,CH_4} is the rate constant for CH_4 oxidation [$\frac{\text{mol}}{\text{m}^3 \text{ sec}}$], C_{CH_4} is the concentration of CH_4 [$\frac{\text{mol}}{\text{m}^3}$], K_{CH_4} and K_{O_2} are the half saturation constant for CH_4 and O_2 [$\frac{\text{mol}}{\text{m}^3}$], and C_{O_2} is the concentration of O_2 [$\frac{\text{mol}}{\text{m}^3}$]. In the modeling simulations performed in this study, the transport and biodegradation processes in the soil domain were evaluated by solving Eq. 3.3 and the rate of CH_4 consumption was evaluated by Eq. 3.8. These sets of equations were solved using the COMSOL Multiphysics[®] software (version 5.6).

To investigate the impact of temperature and moisture on biodegradation processes and CH₄ consumption, a microbial reaction network of 3 microbially-catalyzed chemical reactions was implemented in the numerical simulations. The list of reactions in the reaction network and their reaction rate constants fitted by the model are presented in Table 3-1. It should be noted that the half saturation constants in these tables are not fitting parameters and are based on literature values (Amos, 2006; Ramezanzadeh et al., 2023). The initial concentrations of each chemical simulated in the reaction network are provided in Table 3-2. The parameters of flow and reactive transport processes used in numerical simulations are provided in Table 3-3. The diffusion coefficients, Henry's law constants, and diffusion activation energies for different substances in Table 3-3 are based on literature values. However, r_{max} , T_{min} , T_{max} , and T_{opt} were the fitting parameters that were fit to the data.

Table 3-1: List of reactions included in the microbial reaction network and their reaction rate constants, half saturation constants, and other parameters.

Reaction name	Chemical reaction	Reaction parameters		
		Rate constant, $r_{max,i}$ [$\frac{mol}{m^3 \cdot sec}$]	Half saturation constant, K_{ED} [$\frac{mol}{m^3}$]	Half saturation constant, K_{EA} [$\frac{mol}{m^3}$]
Methane oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	1.8e-9	1.0e-6	3.41e-6
Glucose aerobic oxidation	$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	1.5e-7	0.001	0.025
Glucose fermentation	$C_6H_{12}O_6 + 0.857H_2O \rightarrow 0.857 CO_2 + 2.57C_2H_3O_2^- + 1.714H_2 + 2.576 H^+$	2.6e-8	0.004	-

Table 3-2: Initial concentrations of each species modeled in the microbial reaction network.

Substance	Initial concentration	Units
$C_6H_{12}O_6$	1.82	[mol m ⁻³]
DOC	10.93	[mol m ⁻³]
CO_2 (g)	11.82	[g]
O_2 (g)	8.94	[g]
CH_4 (g)	0	[g]
(before injection)		

Table 3-3: Parameters of flow and reactive transport processes used in the numerical simulation.

Parameter	Value	Units	Reference
$K_{CH_4}^{H_s}$	0.034	[mol m ⁻³]	Linstrom & Mallard (2001)
$K_{CO_2}^{H_s}$	0.83	[mol m ⁻³]	Linstrom & Mallard (2001)
$K_{O_2}^{H_s}$	0.032	[mol m ⁻³]	Linstrom & Mallard (2001)
$D_{CH_4}^g$	1.9e-5	[m ² sec ⁻¹]	Langenberg et al. (2020)
$D_{CH_4}^{aq}$	1.6e-9	[m ² sec ⁻¹]	Cussler (2009)
$D_{CO_2}^g$	1.1e-5	[m ² sec ⁻¹]	Haynes (2016)
$D_{CO_2}^{aq}$	1.2e-9	[m ² sec ⁻¹]	Cussler (2009)
$D_{O_2}^g$	1.6e-5	[m ² sec ⁻¹]	Haynes (2016)
$D_{O_2}^{aq}$	2.1e-9	[m ² sec ⁻¹]	Cussler (2009)
D_{Gluc}	6.14e-10	[m ² sec ⁻¹]	Stein & Litman (2014)
E_{A,CH_4}	12.8	[kJ.mol ⁻¹]	Maharajh & Walkley (1973)
E_{A,CO_2}	17.9	[kJ.mol ⁻¹]	Tamimi et al. (1994)
$E_{A,Gluc}$	16.74	[kJ.mol ⁻¹]	Koirala et al. (2022)
$T_{min}, T_{opt}, T_{max}$ for CH ₄ oxidation	-7, 30, 40	[°C]	-
$T_{min}, T_{opt}, T_{max}$ for Glucose Oxidation	-2, 47, 65	[°C]	-
ϕ_e	0.34	--	-
ρ_b (kg m ⁻³)	1230	kg m ⁻³	-

3.3 Results

3.3.1 *CH₄ consumption rates*

The maximal average CH₄ consumption rate was 330±12.3 nmol h⁻¹ g DW⁻¹ (± SD; standard deviation), observed at moderate soil moisture and temperature conditions (60% WFPS and 25°C; Figure 3-2). The rate of CH₄ consumption was consistently highest at 60% WFPS across all temperatures and follows a similar moisture pattern across the temperatures (Figure 3-2A). CH₄ consumption was generally highest at 25°C for all moistures except 20% WFPS, and there was also comparable CH₄ consumption at 15°C, especially at the moderate soil moistures between 40 to 80% WFPS (Figure 3-2B). There was less variability (~27% difference) in the rates at 20% WFPS across different temperatures, while the effect of the different temperatures was more pronounced (~125% difference for 80% WFPS) at the higher WFPS conditions (Figure 3-2B). Overall, CH₄ consumption rates increased up to the optimal soil moisture or temperature condition, then decreased after the optimal condition. The rate of CH₄ consumption did not show clear patterns with subsequent injections (Figure AII-2A). For example, 20% WFPS exhibited a higher rate for injection 1, then decreased but remained constant for injections 2 to 5 (108% difference for 1°C), whereas rates for 60% WFPS were relatively constant for injections 1 to 5 (12.9% difference for 1°C).

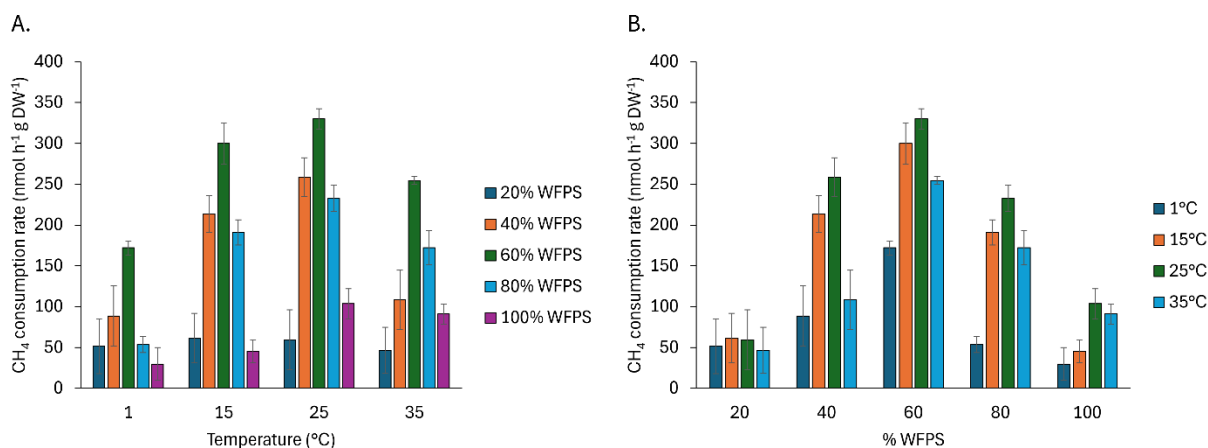


Figure 3-2: Average CH₄ consumption rates at each temperature and soil moisture condition versus temperature (A) or versus % WFPS (B). Error bars are the standard deviation of the 5 injections at a given temperature and soil moisture.

3.3.2 CO₂ efflux rates

The maximal average CO₂ efflux rate of 652±85.0 nmol h⁻¹ g DW⁻¹ was observed at the greatest soil moisture and temperature conditions of the experiment (100% WFPS and 35°C; Figure 3-3). CO₂ fluxes were highest at 80% WFPS in the 15 and 25°C incubations, at 40% WFPS in the 1°C incubations, and at 100% WFPS in the 35°C incubation (Figure 3-3A). CO₂ efflux was typically highest at 35°C for the higher WFPS conditions from 40 to 100%, or 15°C for 20% WFPS (Figure 3-3B). For moistures other than 20% WFPS, the CO₂ efflux gradually increased with temperature up to 35°C. The CO₂ efflux magnitudes were generally lower than the CH₄ consumption rate magnitudes, except for at 100% WFPS and 35°C (Figures 3-2 and 3-3). The rate of CO₂ efflux did not show much variation with subsequent injections, but similar to CH₄ consumption rates, a higher rate for injection 1 was observed at 20% WFPS for all temperatures, and at 1°C for most moistures (Figure AII-2B).

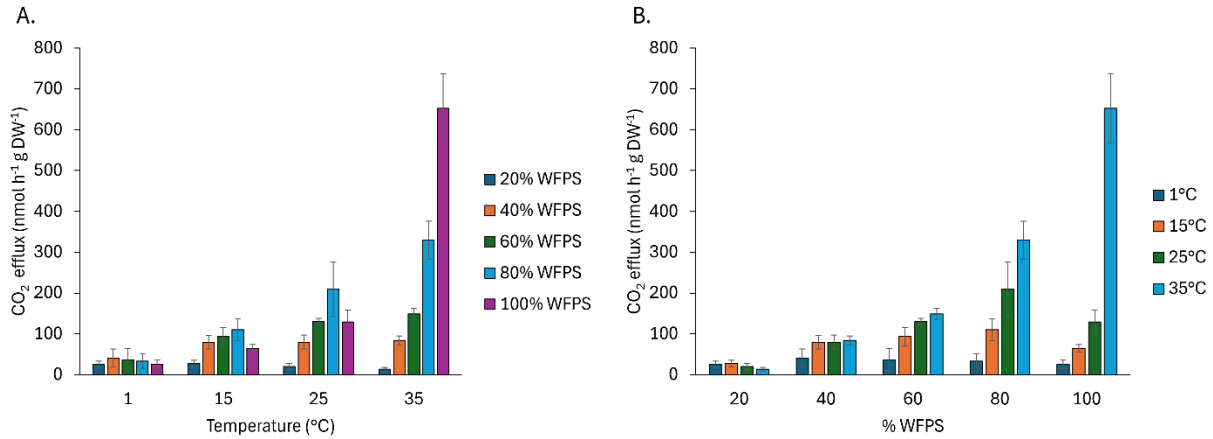


Figure 3-3: Average CO₂ effluxes at each temperature and soil moisture conditions versus temperature (A) or versus % WFPS (B). Error bars are the standard deviation of the 5 injections at a given temperature and soil moisture. Note the different y-axis scale compared to Figure 3-2 for CH₄ consumption.

3.3.3 Model simulation results

The experimental and model simulation results showed a similar moisture pattern for CH₄ consumption (Figure 3-4A), with a goodness of fit or R-squared value of 0.71. The model underestimated the rate of CH₄ consumption at 1°C, while the other temperatures were generally aligned (Figure 3-4B). The simulation results indicate that the maximum CH₄ consumption rate occurs at 60% WFPS and 24°C, which is aligned with the maximal rates observed in the experimental results under the tested conditions (60% WFPS and 25°C). The experimental and modeled CO₂ effluxes were also in good agreement, with an R-squared value of 0.59, or 0.83 excluding the highest moisture and temperature condition (100% WFPS, 35°C) where the experimental fluxes were much higher than those predicted by the model (Figure 3-4C and 3-4D). Overall, most of the model results followed a similar pattern as the experimental results, deviating the most at the high temperature and high moisture conditions.

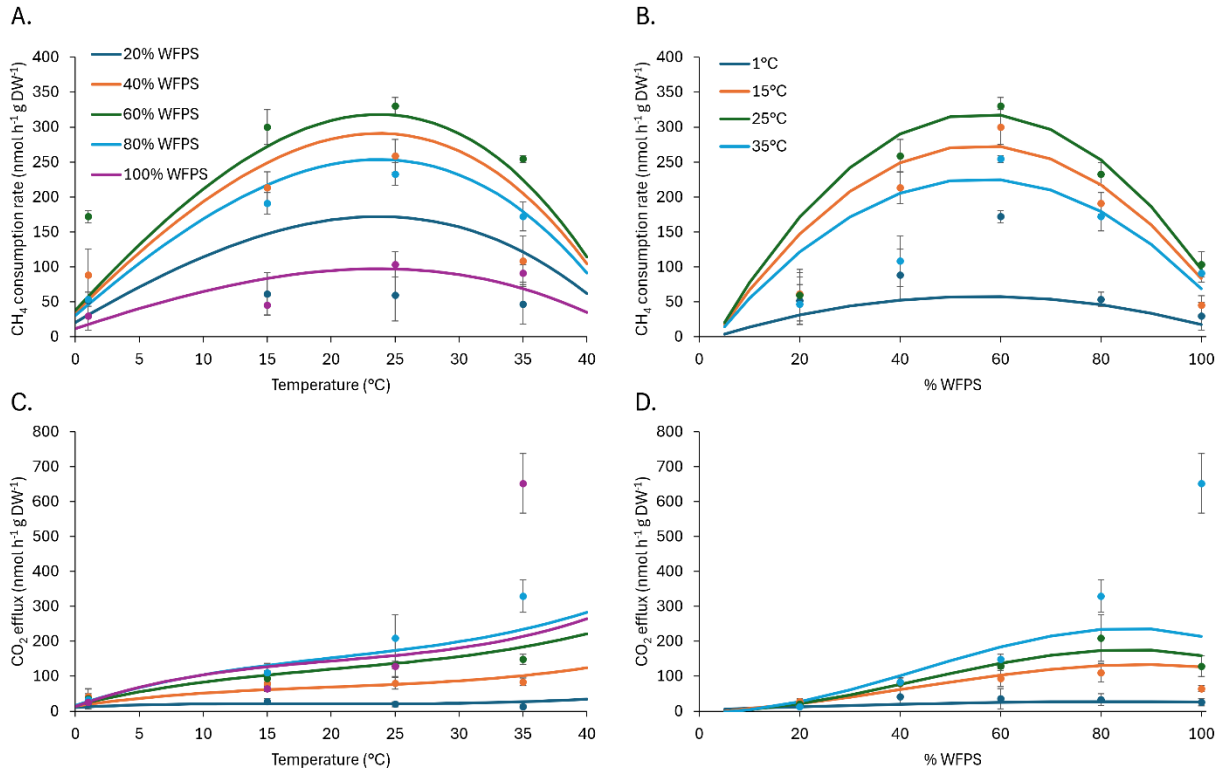


Figure 3-4: Modeling simulation results of CH₄ consumption rate versus temperature (A) and versus soil moisture as % WFPS (B), and modeling simulation results for CO₂ efflux versus temperature (C) and versus soil moisture as % WFPS (D). The points represent experimental data, while the lines represent the model simulation results.

3.3.4 Temperature sensitivity results (Q_{10})

The highest Q_{10} value for CH₄ consumption was 2.57 for 80% WFPS, while the lowest was 1.17 for 20% WFPS (Table 3-4 and Figure 3-5A). Some Q_{10} values for CO₂ efflux were slightly higher than those of CH₄ consumption (Table 3-4 and Figure 3-5B), where the greatest Q_{10} value for CO₂ efflux from this incubation was 2.58 for 100% WFPS, and the lowest was 1.11 for 20% WFPS. Most Q_{10} values for CH₄ consumption and CO₂ efflux were relatively close to 2, aside from the lowest moisture (20% WFPS). For both CH₄ consumption and CO₂ efflux, the highest Q_{10} value occurred at approximately the same moisture condition as the optimal condition of those rates.

Table 3-4: Temperature sensitivity (Q_{10}) values calculated for CH_4 consumption and CO_2 efflux at each % WFPS. The number of data points used in the calculation of each Q_{10} value are presented in Figure 3-5.

% WFPS	Q_{10} value (CH_4 consumption)	Q_{10} value (CO_2 efflux)
20	1.17	1.11
40	1.66	1.66
60	1.54	2.05
80	2.57	2.44
100	1.70	2.58

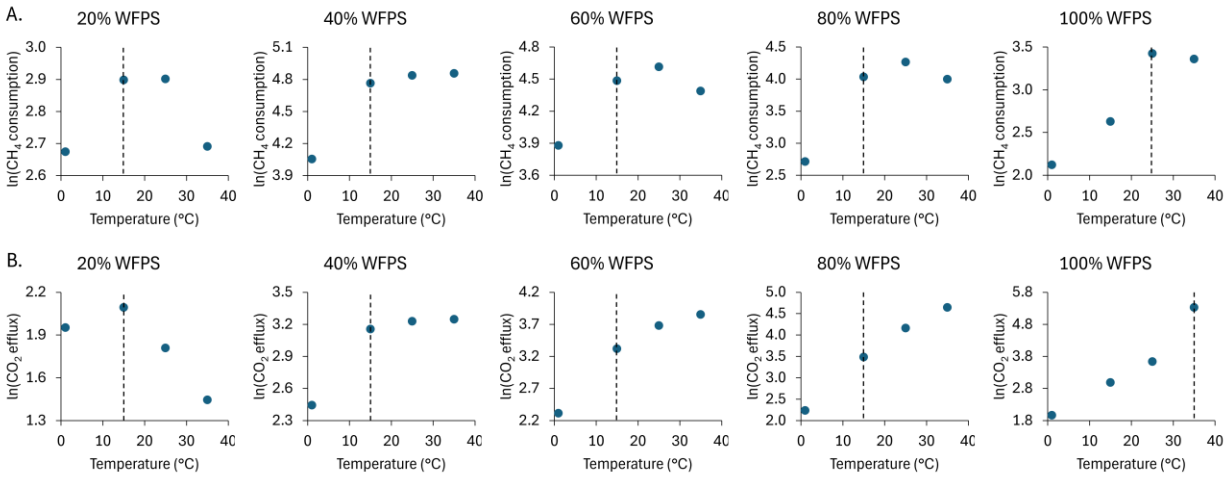


Figure 3-5: Arrhenius plots for CH_4 consumption (A) and CO_2 efflux (B) for each soil moisture condition. The dashed line denotes the experimental data points which were used in the Q_{10} values calculated in Table 3-4.

3.4 Discussion

3.4.1 Optimal soil moisture and temperature for CH_4 consumption

It is evident that both soil moisture and temperature had an effect on the CH_4 consumption rate due to the presence of an optimal condition identified in this study, with the highest average rate of CH_4 consumption ($330 \pm 12.3 \text{ nmol h}^{-1} \text{ g DW}^{-1}$) observed at moderate soil moisture and

temperature conditions (60% WFPS and 25°C; Figure 3-2). The rapid reduction in CH₄ concentration from the headspace within 5 minutes for each injection indicated an active microbial community that was capable of consuming CH₄ once supplied to the soil. This was also supported by the abiotic control samples, where there was minimal reduction in the CH₄ concentration relative to the experimental samples over the same incubation period (Figure AII-3).

The optimal soil moisture observed in this experiment (60% WFPS) is higher than reported from previous studies, as many observed the maximal rates of CH₄ oxidation at a range of 10 to 35% soil moisture (Bender & Conrad, 1995; Park et al., 2005). Low soil moistures are reported to be ideal for CH₄ oxidation, as there is a greater proportion of pore space for the diffusion of CH₄ and O₂, the two substrates of CH₄ oxidation, via gas-filled pore spaces (Gebert et al., 2022; Scheutz et al., 2009). As gases, both O₂ and CH₄ can diffuse throughout the soil faster in less saturated soils due to their higher solubility in the gas versus aqueous phase (Einola et al., 2007; Gebert et al., 2022; Hilger & Humer, 2003; Park et al., 2005; Whalen et al., 1990). Soil moisture also affects the connectivity of the soil aggregates and pore spaces, and thus the ability of the microbes to access dissolved substrates, where the air spaces become discontinuous with increasing water (Borowik & Wyszowska, 2016; Gebert et al., 2022; Reddy et al., 2014). Microbial processes in soil require some amount of water for basic cell function, as very low moisture content could result in water stress and desiccation, leading to a decline in microbial activity (Manzoni et al., 2016; Park et al., 2005; Scheutz et al., 2009).

While lower moistures are reported in the literature as being optimal for CH₄ oxidation, 60% WFPS is consistently the moisture content that yielded the highest CH₄ consumption rate for all temperatures of the experiments in this study, and this is also in agreement with the modeling simulation results (Figure 3-4). 60% WFPS is still a moderate moisture, and for this soil, was the

optimal point where there was sufficient moisture content for microbial activity and a sufficient percent of unsaturated pore volumes for gas exchange. This difference from literature may be due to the varying ways that soil moisture is expressed in literature (*i.e.*, gravimetrically or volumetrically), as well as the effect that soil texture that could have on moisture content, and thus gas exchange and CH₄ oxidation potential. Some studies suggest representing soil moisture as water holding capacity or soil moisture potential for more standard comparison (Einola et al., 2007; Spokas & Bogner, 2011).

The optimal temperature for CH₄ consumption was 25°C (Figure 3-2), and while on the lower end, has also been observed by studies including Bender and Conrad (1995) in natural soils and Hanson and Hanson (1996) in peat soils. In landfill environments, the reported optimal temperature for CH₄ oxidation is typically higher, ranging from 30 to 36°C (Gebert et al., 2022; Hilger & Humer, 2003; Scheutz et al., 2009). However, there was still considerable CH₄ consumption observed outside this range in this study, and in previous studies, can range from 1 to 40°C (Einola et al., 2007; Park et al., 2005). The proposed optimal range of 20 to 35°C would be expected for methanotrophs, which are typically mesophiles that thrive in moderate temperatures (Hanson & Hanson, 1996). Temperature is a key factor for the kinetics of microbial reactions and can also affect gas solubility in water (Scheutz et al., 2009; Velasco et al., 2018).

For temperature sensitivity, the highest observed Q_{10} value for CH₄ consumption was 2.57 for 80% WFPS (Table 3-4 and Figure 3-5A). Overall, the Q_{10} values for CH₄ consumption from this experiment are generally lower than in literature, though relatively close to 2 as described for biological processes (Davidson & Janssens, 2006). Q_{10} values for CH₄ oxidation have been typically observed from 1.9 to 4.1 (Boeckx et al., 1996; Scheutz et al., 2009), with some studies reporting values greater than 8 (Christophersen et al., 2000; Einola et al., 2007) from landfill cover

soils. The lower Q_{10} values from our data may be due to our study site being a former landfill, where the inherent microbial community of this soil may have lower CH_4 consumption capacity than an active landfill cover soil regularly exposed to high CH_4 concentrations (Boeckx et al., 1996). The conditions of the experiment may also have an impact, considering the lower relative CH_4 concentration supplied to the headspace. For comparison, Park et al. (2005) reported Q_{10} values of 2.57 and 2.69 using an initial headspace CH_4 concentration in batch incubations of 400,000 ppm, demonstrating that CH_4 consumption via CH_4 oxidation is also affected by the concentration of CH_4 supplied in the incubation (Bender & Conrad, 1995; Bogner et al., 1997).

3.4.2 *Optimal soil moisture and temperature for CO_2 efflux*

For the CO_2 efflux, the maximal average rate observed was $652 \pm 85.0 \text{ nmol h}^{-1} \text{ g DW}^{-1}$ at 100% WFPS and 35°C (Figure 3-3). Typically, CO_2 effluxes are expected to be optimal at moderate soil moistures with lower CO_2 effluxes at higher soil moistures because of the limitation of O_2 diffusion and, thus, of aerobic microbial metabolisms (Byun et al., 2021; Fairbairn et al., 2023). This was the case for the temperature conditions other than 35°C , where CO_2 effluxes decreased at 100% WFPS (Figure 3-3A), demonstrating the optimal rates at moderate conditions. The high CO_2 production observed at 100% WFPS in the 35°C incubation could be due to anaerobic degradation of soil organic matter, leading to production of CO_2 at high temperatures (Chen et al., 2021; Fairbairn et al., 2023).

The optimal temperature for CO_2 effluxes was 35°C , which was within the expected range for methanotrophs (Hanson & Hanson, 1996; Reddy et al., 2019). The Q_{10} values for CO_2 efflux were slightly higher than those of CH_4 consumption, indicating that this process was more temperature sensitive for most moistures (Table 3-4 and Figure 3-5B). We observed lower Q_{10} values for CO_2

efflux associated with CH₄ consumption compared to previous studies, as the greatest Q_{10} value from this incubation was 2.58. Einola et al. (2007) reported a range of 5.7 to 5.8 for CO₂ production from their CH₄ assays, though their study showed some of the highest Q_{10} values for CH₄ oxidation and CO₂ production among studies from landfill cover soils. The different response of CO₂ effluxes is likely driven by other microbial groups, outside of the methanotrophs of this study.

3.4.3 *CH₄ consumption to CO₂ production ratio*

Given the reaction stoichiometry for CH₄ oxidation, the ratio of CH₄ consumed to CO₂ produced during CH₄ oxidation is 1 mol CH₄ consumed:1 mol CO₂ produced (Le Mer & Roger, 2001; Scheutz et al., 2009). Although the relative rates measured in the headspace of the CO₂ effluxes and CH₄ consumption observed in this study did not reflect this ratio, with CH₄ consumption exceeding CO₂ production at most combinations of soil moisture and temperature conditions (16 of 20 combinations), we still interpret that the CH₄ consumption observed in the experiments was the result of microbial CH₄ oxidation. This interpretation is supported by the abiotic controls, where CH₄ concentrations remained stable and accumulated with subsequent injections of CH₄ over the course of the incubation as expected, with minor decreases in concentration likely due to the collection of gas samples from the headspace for analyses (Figure AII-3). In addition, the CO₂ headspace concentrations (and therefore the CO₂ effluxes) in the “soil, no CH₄” control were much lower than in the experimental bottles where CH₄ was added, providing additional evidence that the CO₂ effluxes produced in the experimental bottles was attributable to the CH₄ consumption via CH₄ oxidation (Figure AII-4).

Higher CH₄ consumption rates compared to CO₂ efflux rates have also been observed in other studies, where it has been attributed to the assimilation of CO₂ into the microbial biomass

(Megraw & Knowles, 1987; Whalen et al., 1990), accumulation of CO₂ in the soil (Einola et al., 2007; Megraw & Knowles, 1987), or the dissolution of CO₂ as DIC in the porewater (Ferdush & Paul, 2021; Ramnarine et al., 2012). Because the incubations used in this study were short incubations lasting approximately 25 minutes, it is unlikely that there was substantial CO₂ consumption via CO₂ assimilation into biomass within this time frame. Therefore, the lower CO₂ efflux relative to CH₄ consumption is possibly due to the accumulation of CO₂ in the pore spaces which do not reach the headspace, or its presence as bicarbonate (measured as DIC, Figure AII-5) in the porewater. Headspace gas was collected from the bottles, so those samples would not capture gas accumulated in the pore spaces. In addition, there was an increase in DIC concentration from the initial soil porewater to the end-of-experiment porewater (0.14 and 0.05 mM for 80 and 100% WFPS, respectively), suggesting that the CO₂ present in the headspace may have been converted to DIC in the porewater (Figure AII-5). The pH of the porewater samples was also around neutral and where CO₂ could be present as DIC, supporting the idea that there was dissolution to DIC (Ferdush & Paul, 2021). Accumulation of CO₂ in the pore spaces may be more likely for lower moisture contents as less of the pore space is filled with water, while dissolution of CO₂ to DIC in the porewater may be more likely for higher moisture contents. Some studies also reported a molar ratio between moles of CH₄ consumed and CO₂ produced, where a ratio of CO₂:CH₄ less than one indicates less CO₂ produced than CH₄ consumed. Einola et al. (2007) reported ratios between 0.49 to 0.93, and Megraw and Knowles (1987) reported a ratio of 0.27, and this ratio ranges from 0.21 to 0.90 in our study for cases where the CO₂ efflux rate is less than CH₄ consumption rate (16 of 20 combinations).

3.5 Conclusion

This study assessed the combined effects of variations in soil moisture and temperature on CH₄ consumption rates in landfill cover soil collected from a hot-spot of a former landfill. The rate of CH₄ consumption was optimal at moderate conditions (330±12.3 nmol h⁻¹ g DW⁻¹ at 60% WFPS and 25°C), and the CO₂ efflux rate was optimal at higher conditions (652±85.0 nmol h⁻¹ g DW⁻¹ at 100% WFPS and 35°C). Overall, these results highlight that soil moisture and temperature are two important factors modulating microbial CH₄ consumption via CH₄ oxidation, and the net CH₄ consumption observed is a result of the interactions of the different transport and microbial reaction processes occurring in the soil. The different optimal conditions highlight that there are different microbial groups responsible for the various processes, resulting in the observed fluxes. The results were further supported by the temperature sensitivity analysis (Q_{10}) and the diffusion-reaction model. The experimental results, combined with the modeling simulations, provide insight into the optimal conditions for microbial CH₄ oxidation. These results can be further used in larger-scale modeling of CH₄ oxidation in landfill cover soils and/or in the practical design of landfill cover soils.

4 Conclusion

4.1 Summary of key findings

The objective of this thesis was to advance the understanding of the simultaneous effects of soil moisture and temperature on the rates of CH₄ consumption and associated CO₂ efflux in a landfill cover soil. In Chapter 2, I designed and conducted a preliminary soil incubation experiment with varied temperature and moisture, and identified preliminary optimal conditions for CH₄ consumption and CO₂ production as well as advancements to the methods. In Chapter 3, I further developed the experimental design of the soil incubation, incorporating a wider range of soil moistures, temperature sensitivity analysis, and a diffusion-reaction model to support the observed trends in CH₄ consumption and CO₂ production.

In Chapter 2, soil from a CH₄ hot-spot location at a former landfill was incubated under various soil moistures and subjected to a changing temperature regime. Following an injection of CH₄ into the headspace, this preliminary experiment assessed the capacity for CH₄ consumption, and subsequent CO₂ production, in the soil. CH₄ consumption was optimal at low soil moisture and moderate temperature at 25% WFPS and 25°C, respectively. These results showed that there was CH₄ consumption at nearly all combinations of soil moisture and temperature in this soil from a CH₄ hot-spot, and this activity was optimal where temperature was ideal for methanotrophs, and where there was sufficient water and pore space for gaseous diffusion of CH₄ and O₂ (substrates for CH₄ oxidation). However, this experiment used a lower CH₄ concentration that resulted in a smaller range of CH₄ consumption rates (0.08 to 1.86 nmol h⁻¹ g DW⁻¹) in comparison to Chapter 3; while an optimal condition can be identified, there is not a large difference between the rates across conditions in this chapter, relative to Chapter 3. In addition, the optimal conditions for CO₂

production were the highest conditions of the experiment (47% WFPS and 35°C), suggesting that there are different microbial communities throughout the soil contributing to these different fluxes. The findings from Chapter 2 were an initial assessment of the method for measuring CH₄ consumption, and the initial capacity for CH₄ consumption activity from a CH₄ hot-spot under varied soil moisture and temperature conditions. These findings served as a baseline for the design of the incubation experiments in Chapter 3, incorporating a broader range of soil moistures and temperatures and multiple injections of a higher CH₄ concentration.

In Chapter 3, the same CH₄ hot-spot field site was used for a series of soil incubation experiments over a greater range of soil moistures and temperatures to assess the CH₄ consumption and associated CO₂ effluxes. Soil was incubated under various combinations of soil moisture and temperature, where they received subsequent injections and higher concentrations of CH₄ to saturate the system with CH₄. As a result, greater rates of CH₄ consumption and similar rates of CO₂ production were observed relative to Chapter 2, indicating a greater response by the microbial community. The optimal conditions for CH₄ consumption were moderate soil moisture and temperature conditions at 60% WFPS and 25°C, where the temperature was in line with Chapter 2 and expected for methanotrophs. This soil moisture was higher than in Chapter 2, however Chapter 3 covered a wider range of moistures, and used a higher CH₄ concentration that resulted in a larger range of CH₄ consumption rates (29.7 to 330 nmol h⁻¹ g DW⁻¹). Interpretation of the optimal condition is likely more accurate, as there were greater differences among rates of CH₄ consumption across conditions. Differences in the soil texture and expression of soil moisture also influence the comparison of rates across studies. CO₂ production was, again, highest at the optimal conditions of the experiment, which may be due to abiotic activity at 100% WFPS and 35°C. Different optimal conditions for CH₄ consumption and CO₂ production, again, suggest different

dominant microbial groups driving these fluxes. These experimental results were coupled with temperature sensitivity analysis (Q_{10}) and a diffusion-reaction model, further supporting the CH_4 consumption observed from this landfill cover soil. The findings from Chapter 3 emphasize that soil moisture and temperature play an important role in the capacity of CH_4 consumption activity which was modeled reasonably well with the diffusion-reaction model presented in this chapter.

The findings from Chapters 2 and 3 together demonstrated that CH_4 consumption was evident, and that moderate soil moisture and temperature conditions were optimal for this activity. The results also provided insight into patterns of CH_4 consumption under variable soil moisture and temperature conditions, which can be useful in understanding the potential impacts of climate change and changing seasonality. These moderate optimal conditions observed are aligned with literature, where CH_4 oxidation requires both sufficient water for nutrients and pore space for diffusion of gases. The lower soil moisture favoured in Chapter 2 may have been due to the lower concentration used in that experiment, relative to Chapter 3, resulting in vastly different ranges of CH_4 consumption rates (range of 1.78 and 300 $\text{nmol h}^{-1} \text{g DW}^{-1}$ for Chapters 2 and 3 respectively). In all experiments presented in this thesis, soil moisture seemed to have a greater effect on the CH_4 consumption rates, showing greater differences in those rates when moisture was varied. In addition, the results showed that the CO_2 production associated with CH_4 oxidation was not necessarily observed at the same optimal conditions, and there were other processes at play (*i.e.*, dissolution into porewater, or accumulation of CO_2) that resulted in different magnitudes of these fluxes. The difference in optimal conditions for CH_4 consumption and CO_2 production highlights that there are different groups of microbes responsible for these processes.

4.2 Recommendations for future research

The results from this thesis contribute to the understanding of CH₄ consumption activity under simultaneous variations of soil moisture and temperature from a landfill cover soil. They demonstrate that CH₄ consumption is optimal at moderate soil moisture and temperature conditions, which can support future studies on CH₄ oxidation in landfills, and can potentially aid in landfill management and design. The understanding developed from the methods and model in this study can be further expanded on and/or used for different landfill sites to assess and compare their CH₄ consumption activities.

In Chapter 2, a challenge of the experiment was the relatively small CH₄ consumption rates observed, likely attributable to the low concentration of CH₄ injected into the headspace. A recommendation would be to increase the concentration of CH₄ injected, which made a direct difference to the results of Chapter 3 given the higher rates of CH₄ consumption. In Chapter 3, multiple subsequent injections of CH₄ were also introduced to address this, in attempts to continually saturate the soil with CH₄. While the rates of CH₄ consumption did not change much with each injection, a continuous source or flow of CH₄ into the headspace could be a modification to the experimental design. Differences in the model-predicted rates and experimental rates observed also show that further work could be done to the initial model, or a different modeling approach could be used, to better represent the CO₂ effluxes from the incubations.

From both experiments presented in this thesis, there were several aspects that could be modified for future research. The incubations were relatively short (25 minutes to 2 hours), thus longer-term incubations could be insightful to changes in the CH₄ consumption and microbial community as environmental conditions (*i.e.*, moisture, temperature, and CH₄ concentration) change. Additional analyses could also be done to further support CH₄ consumption activity and understand the

transformations of carbon. For example, porewater analyses could be performed in greater detail (*i.e.*, measuring dissolved organic and inorganic carbon at multiple points of the incubation) to assess the dynamics of CO₂, or carbon isotopes could be incorporated to trace the carbon when supplied as CH₄ throughout the incubation. Characterization of the microbial community would also be valuable in confirming which microbial groups are present and responsible for the various soil processes. Future studies may also benefit from assessing the effect of soil texture, as this property affects the overall soil moisture and thus the interpretation and comparison of CH₄ consumption rates to previous studies.

Overall, this research has contributed to existing methods in quantifying CH₄ oxidation rates, as well as the response when challenged under seasonal simulations. These results can be used to develop tools for use by municipalities to monitor and reduce landfill emissions. For example, refining the diffusion-reaction model can help predict CH₄ emissions from hot-spots in landfills, and future research can also lean into identifying and developing these active microbial communities as inoculum for use on hot-spots as a natural control on CH₄ emissions.

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<https://doi.org/10.1016/j.rser.2012.04.008>

Appendix I: Additional results from Chapter 2

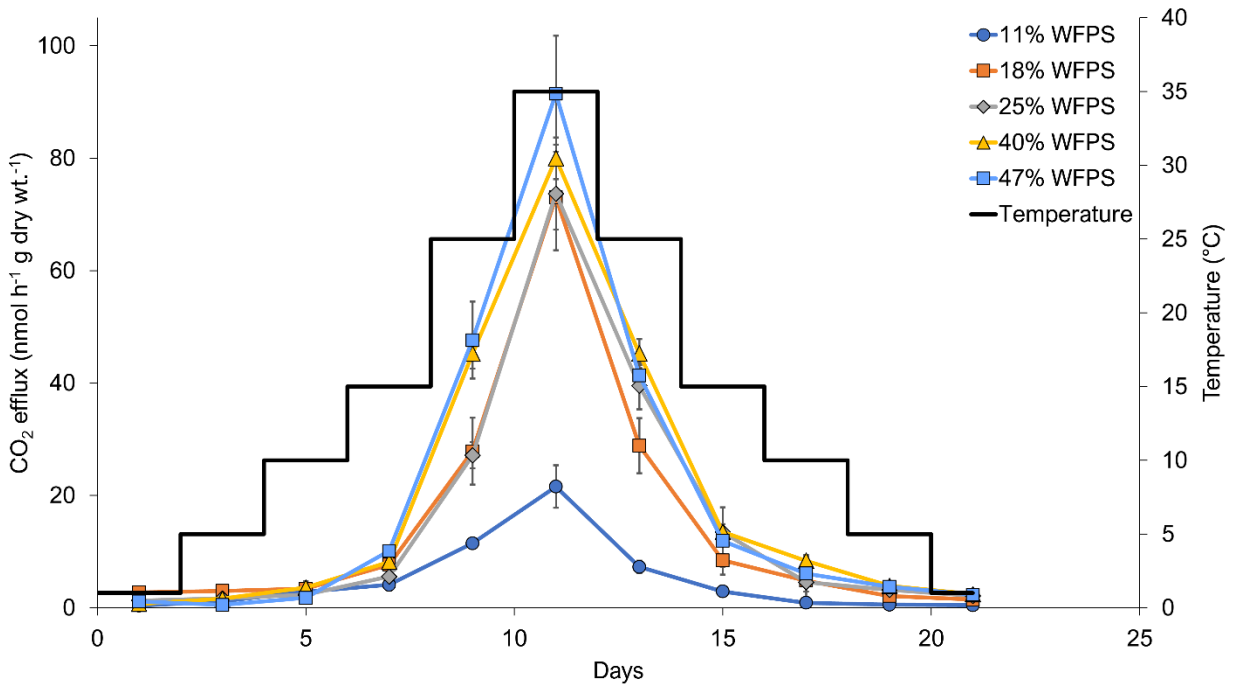


Figure AI-1: Time series results of CO₂ fluxes from headspace gas concentrations under different moisture contents and incubation temperatures over the 21-day experiment. Error bars are the standard deviation of the triplicate measurements.

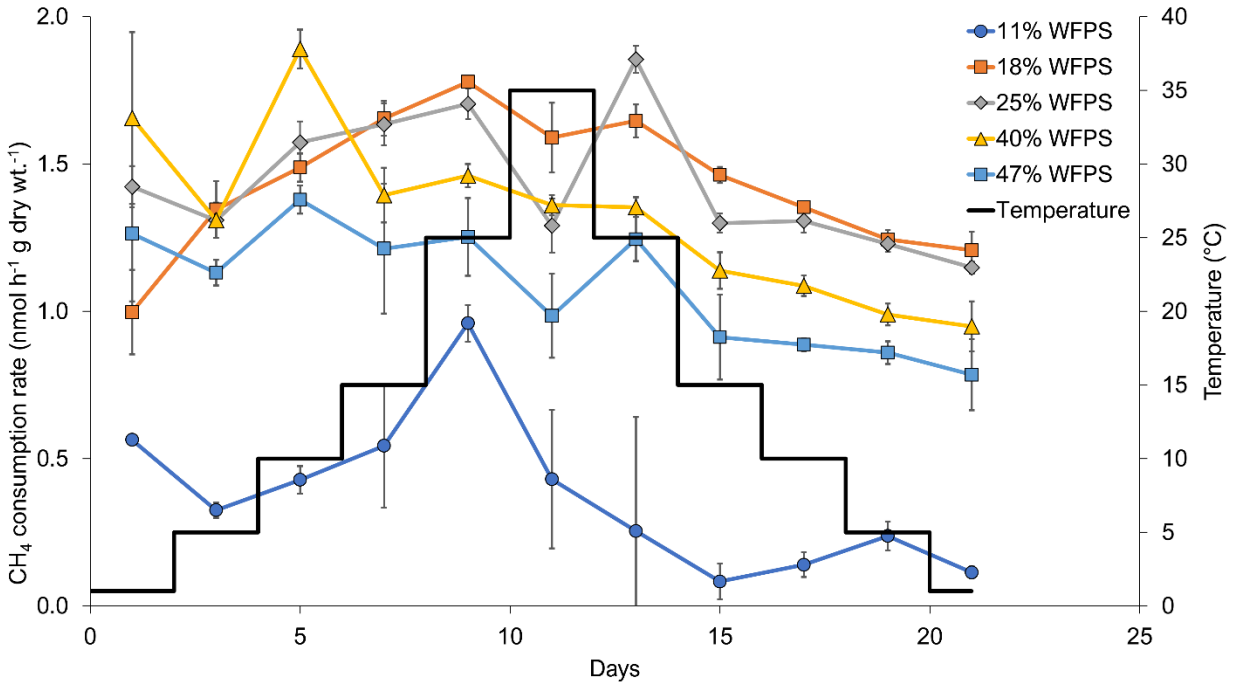


Figure AI-2: Time series results of CH₄ consumption rates from headspace gas concentrations under different moisture contents and incubation temperatures over the 21-day experiment. Error bars are the standard deviation of the triplicate measurements.

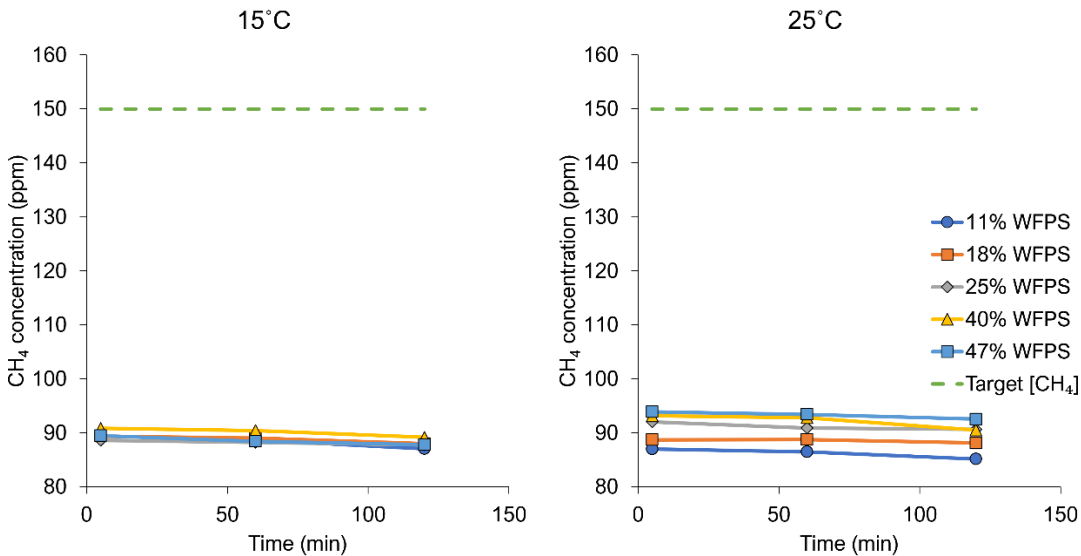


Figure AI-3: CH₄ concentrations in an additional incubation experiment to test for CH₄ consumption in the sterilized soil (treated with mercuric chloride (HgCl₂) and dried at 100°C for 48 hours). All 5 moisture contents were prepared and incubated at 15 and 25°C. All gas sampling was performed in the same manner as the experimental jars.

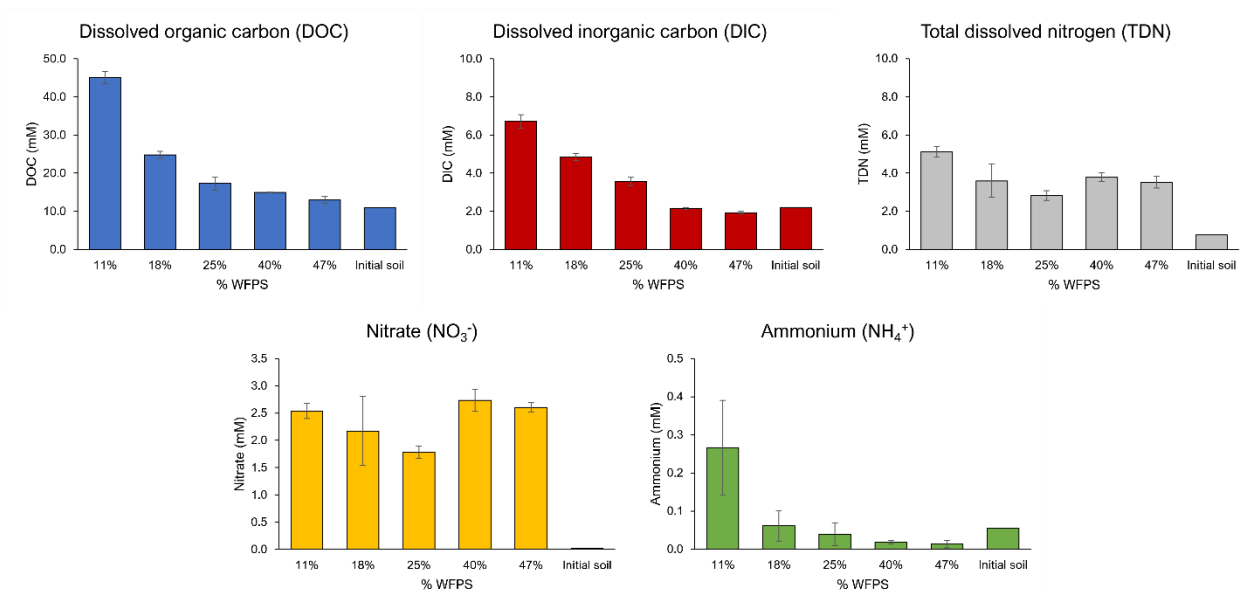


Figure AI-4: Porewater concentrations of DOC, DIC, TDN, NO₃⁻, and NH₄⁺ measured at the end of the experiment. Error bars are the standard deviation of the triplicate measurements.

Appendix II: Additional results from Chapter 3

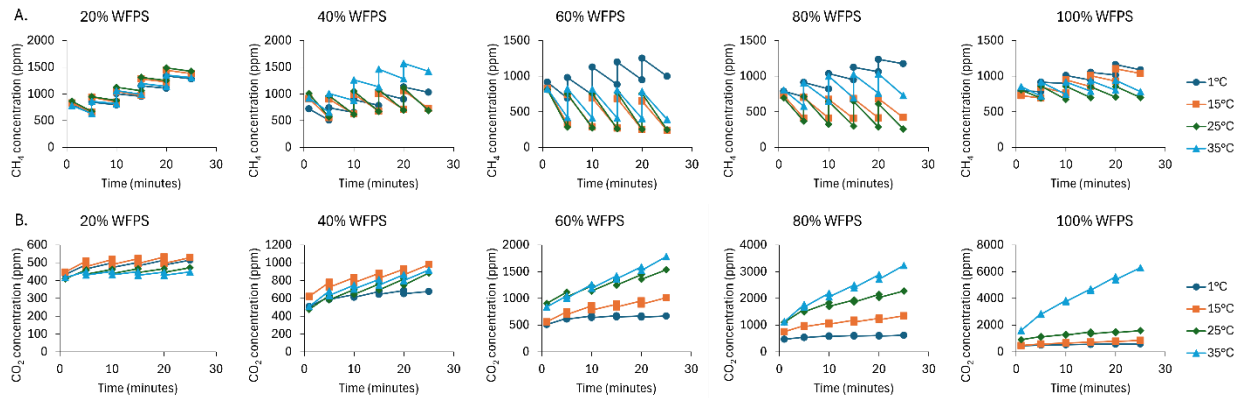


Figure AII-1: CH₄ (A) and CO₂ (B) concentrations from headspace gas samples at each temperature and soil moisture condition for experimental samples.

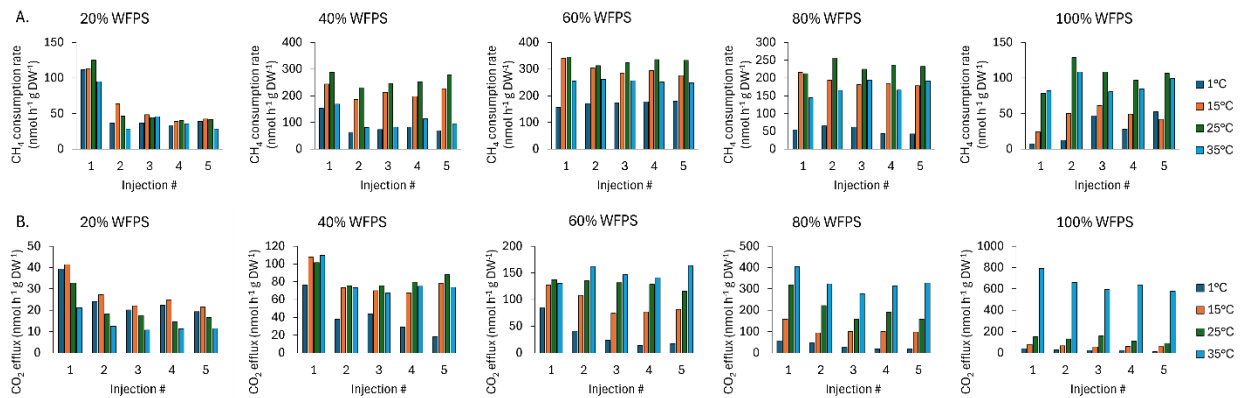


Figure AII-2: Rates of CH₄ consumption (A) and CO₂ efflux (B) calculated from headspace CH₄ and CO₂ concentrations at each temperature and soil moisture conditions per injection for experimental samples.

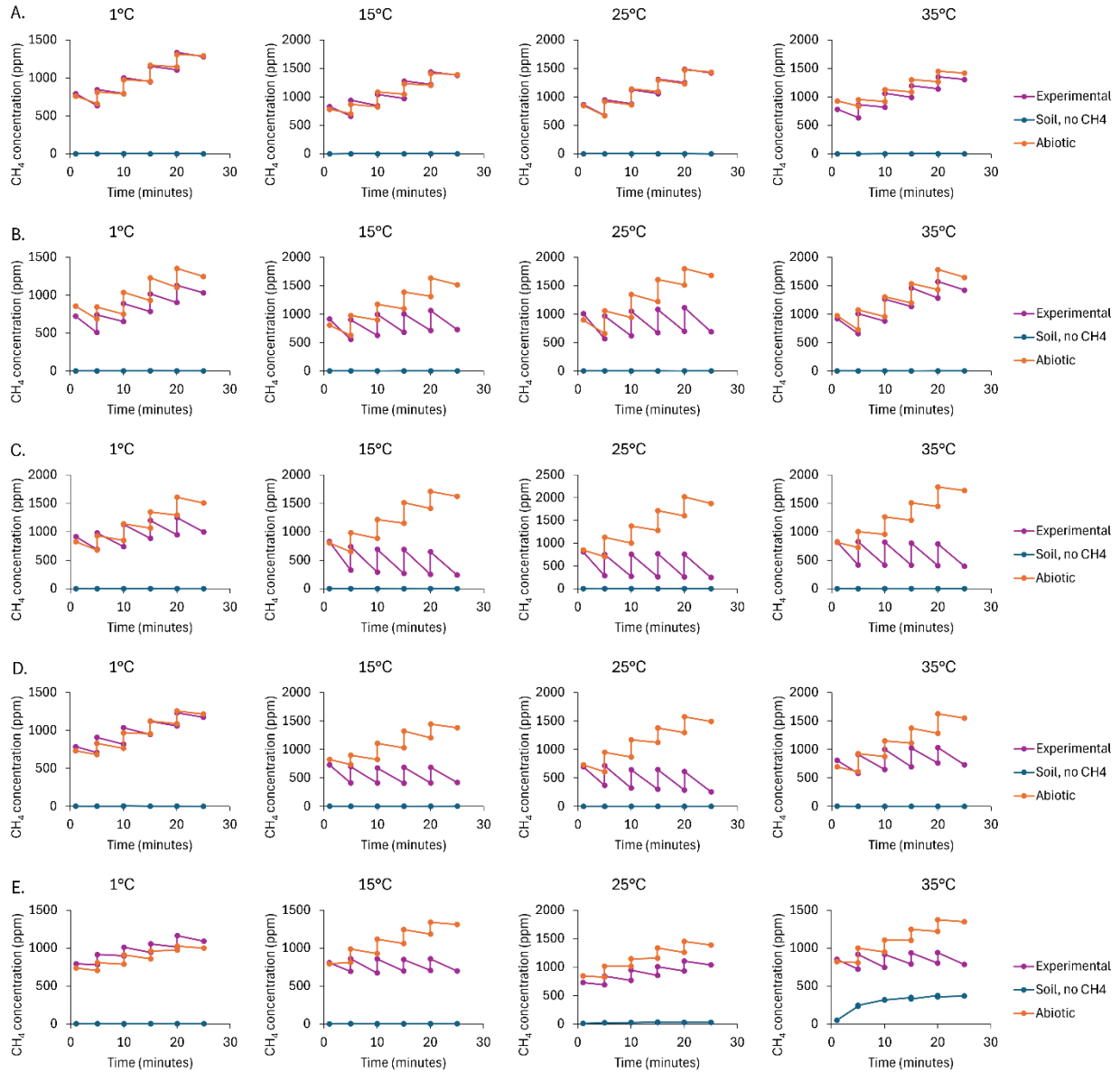


Figure AII-3: CH₄ concentrations from headspace gas samples at each temperature and moisture combination for experimental, “soil, no CH₄”, and “abiotic” samples. Concentrations are split by moistures: 20% WFPS (A), 40% WFPS (B), 60% WFPS (C), 80% WFPS (D), and 100% WFPS (E).

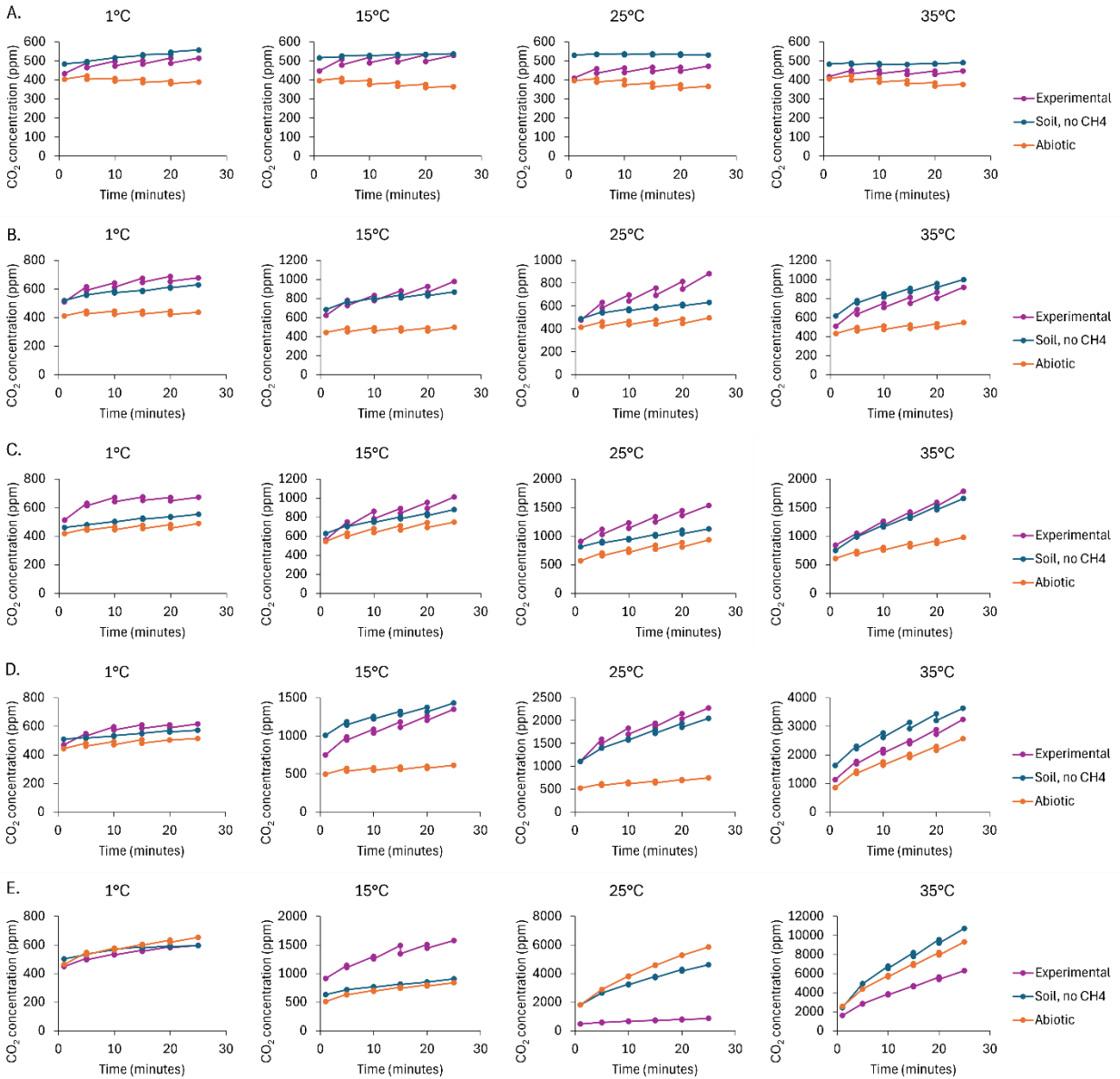


Figure AII-4: CO₂ concentrations from headspace gas samples at each temperature and moisture combination for experimental, “soil, no CH₄”, and “abiotic” samples. Concentrations are split by moistures: 20% WFPS (A), 40% WFPS (B), 60% WFPS (C), 80% WFPS (D), and 100% WFPS (E).

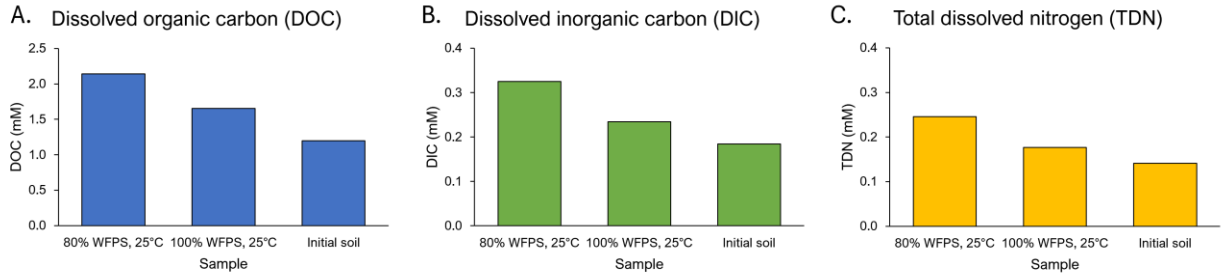


Figure AII-5: Porewater concentrations of DOC, DIC and TDN from selected experimental samples (80% WFPS, 25°C and 100% WFPS, 25°C) at the end of the experiment and from the initial soil sample.