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Andrews Dwomoh

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A Case Study of Monitoring Methane Emissions and Mitigation Efforts at a Municipal Solid Waste Landfill: Insights from Mining Field Data and Laboratory-Based Column Experiments on the Effectiveness of Soil Cover Amendments

by

Andrews Dwomoh

Under the Direction of Nadine Kabengi, PhD

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

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ABSTRACT

This thesis focused on understanding and mitigating methane emissions from landfills. Chapter 2 analyzed quarterly methane emissions from a municipal solid waste landfill using ordinary kriging in ArcGIS Pro to map spatiotemporal trends and evaluate soil cover effectiveness in reducing methane emissions. Soil covers reduced methane emissions within 10–30 days at certain locations; however, variations in emission reductions highlight the need for additional measures and continued monitoring to assess their long-term effectiveness. Chapter 3 evaluated biochar, compost, and woodchip-amended soil, as well as unamended landfill soil, in laboratory column experiments. Landfill soil showed moderate methane adsorption and low methane removal efficiency. Biochar enhanced methane adsorption and removal due to its high porosity and large surface area, while compost improved methane removal efficiency by supporting the growth of methanotrophic bacteria. These findings underscore the potential of biochar and compost as effective amendments to conventional landfill soil covers for enhancing methane mitigation.

INDEX WORDS: Landfill Methane, Soil Covers, Column Experiment, ArcGIS Pro.

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by

Andrews Dwomoh

Committee Chair: Nadine Kabengi

Committee: Adrian Gale

Ashwin Ashok

Dajun Dai

Electronic Version Approved:

Office of Graduate Services

College of Arts and Sciences

Georgia State University

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DEDICATION

To the Almighty God.

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LIST OF ABBREVIATIONS

GWP – Global Warming Potential

IPCC – Intergovernmental Panel on Climate Change

LEL – Lower Explosive Limit

LFG – Landfill Gas Emissions

LSC – Landfill Soil Cover

MRE – Methane Removal Efficiency

MSW – Municipal Solid Waste

NMVOC – Non-Methane Volatile Organic Compounds

USEPA – United States Environmental Protection Agency

1 INTRODUCTION

Landfill gas (LFG) emissions are of significant concern to the scientific community and policymakers due to their harmful impact on the atmosphere and human health of the populace living near landfills (Wang et al., 2022). Methane (CH_4) is a major component of LFG and a potent greenhouse gas with a global warming potential (GWP) 28 times greater than carbon dioxide (CO_2) over 100 years, according to the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report published in 2014. Municipal solid waste (MSW) landfills are the third-largest anthropogenic source of CH_4 emissions in the United States, contributing approximately 14.3% of the total CH_4 emissions in 2021 according to the United States Environmental Protection Agency (USEPA, 2023). CH_4 emissions from landfills have gained more attention in recent decades because they can be recycled and purified to generate electricity and gas for profit, or they can be mitigated using soil covers and gas collection systems to prevent their release into the atmosphere. Previous research has suggested that landfill cover soil is an economical solution to reducing CH_4 emissions from landfills with or without gas-recovery systems, with the former offering a near-complete CH_4 removal (Reddy et al., 2014). Meanwhile, the continual rise of CH_4 emissions from landfills and the significant need for and importance of developing a better technology has led researchers to explore different methods to enhance methane removal efficiency (MRE) of landfill soil covers using organic-rich materials such as compost, biochar, and sewage sludge, either alone or as an amendment to existing landfill cover soils (Sadasivam and Reddy, 2014). While several studies (Gebert et al., 2022; Majdinasab et al., 2017; Sadasivam and Reddy 2014; Sadasivam and Reddy, 2015; Valenzuela-Heredia and Aroca, 2023;) have explored the use of soil cover to mitigate CH_4 emissions from landfills on a large scale, few studies have quantified the effectiveness of different landfill soil cover amendments using controlled column experiments to understand the mechanisms and processes through which biocovers reduce CH_4 emissions. This thesis aims to bridge this gap by monitoring surface CH_4 emissions from a MSW landfill. Initially, it identifies spatiotemporal hotspots (i.e. above 500 ppm) of surface CH_4 emissions from the MSW landfill using a spatial interpolation method and evaluates the efficacy of soil covers applied at the hotspot areas in reducing CH_4 emissions. Subsequently, the study quantifies the effectiveness of different soil cover amendments through column experiments to better understand the mechanisms through which soil covers reduce CH_4 emissions.

1.1 How is landfill gas generated and emitted?

LFG is predominantly made up of 40 to 60% of CH_4, approximately 40% of CO_2, nitrous oxide (N_2O), and more than 100 types of non-methane volatile organic compounds (NMVOC) (Duan et al., 2021; Osra et al., 2021) which are generated during microbially induced biochemical decomposition of organic matter in a landfill as shown in Figure 1.1. The gas generation in landfills is categorized into two processes: aerobic composting, which occurs when there is enough oxygen, and anaerobic degradation, which occurs in three phases without oxygen (Ehrig et al., 2011; Themelis and Ulloa, 2007). Shortly after MSW is deposited, the easily degradable organic compounds from the landfill's surface to a depth of about 1 to 1.5m (Ehrig et al., 2011) are oxidized aerobically. The aerobic process usually lasts only for a few days or weeks. After this stage, the landfilled waste is covered by newly deposited materials, and further decomposition occurs anaerobically. After the oxygen in the waste runs out, anaerobic digestion begins, and this is the main biochemical process in landfills; this leads to CH_4 fermentation which continues for 0.5 to 3 years. (Ehrig et al., 2011). The anaerobic process takes place in three phases, during which organic substances are converted to CH_4 and CO_2 as well as small amounts of biomass and energy (Zhao, 2019). The three steps in the anaerobic process according to (Ehrig et al., 2011; Themelis and

Ulloa, 2007) are: (1) Hydrolysis – this process involves facultative bacteria converting the organic substrate into simple organic substances such as amino acids, glucose, etc.; (2) Acetogenesis – the process through which the end products of hydrolysis are converted by acid-forming bacteria to volatile fatty acids, CO_2, and H_2. Acetogenic bacteria then convert volatile fatty acids to acetic acid, CO_2, and H_2; and (3) Methanogenesis - at this phase, CH_4 is formed by methanogenic bacteria, either by breaking down the acids to CH_4 and CO_2, or by reducing CO_2 with H_2.

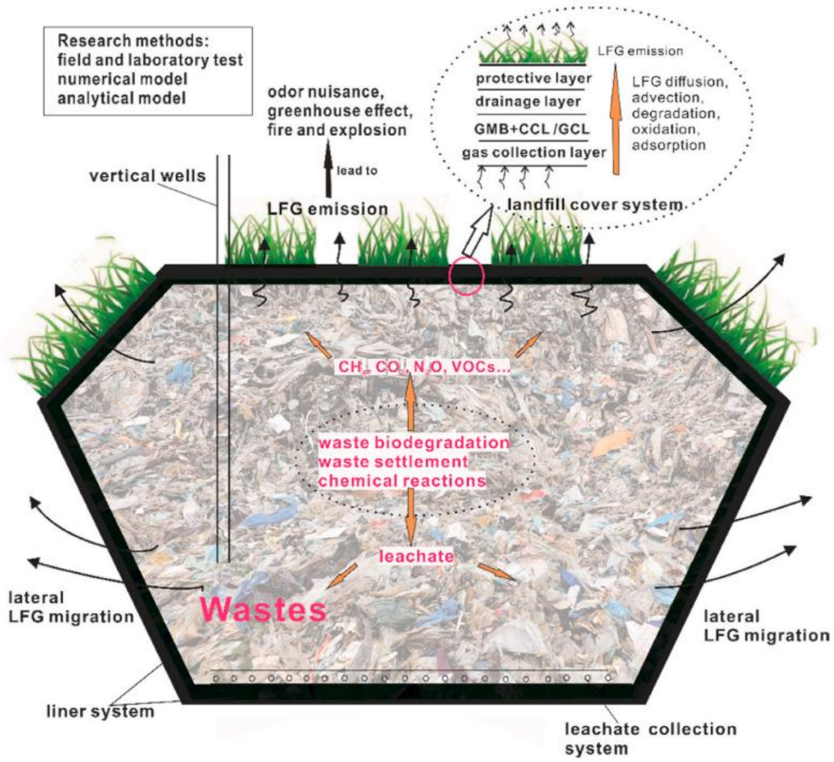


Figure 1.1. Schematic of landfill gas generation and emission (Wang et al., 2022)

1.1.1 The state of municipal solid waste landfills in the United States

In 2002, Columbia University's Earth Engineering Center partnered with BioCycle journal to conduct a nationwide survey in the US of the amount of MSW generated and how they were disposed of (Themelis and Ulloa, 2007). The results are shown and compared with USEPA numbers in Table 1.1 below.

Table 1.1. Generation and fate of municipal solid waste in the United States (Ehrig et al., 2011; Themelis and Ulloa, 2007)

	14th SOG survey		USEPA 2001 survey	
	Million tonnes/yr	(%)	Million tonnes/yr	(%)
Amount generated	336	100	211	100
Amount recycled and composted	90	26.7	65	30.8
Amount to waste-to-energy	26	7.7	65	12.8
Amount landfilled	220	65.6	119	56.4

SOG: State of Garbage

1.2 Techniques for mitigating methane emissions from landfills

Several techniques are used to mitigate CH_4 emissions from landfills. These include a pre-treatment of organic waste landfilling, promotion of aerobic conditions in landfills, landfill gas collection, and utilization of biological CH_4 oxidation in the final cover soil (Chan et al., 2023). Traditionally, landfill gas (LFG) management strategies involve a landfill cover system, LFG collection system, or a combination of both (Verma et al., 2024). The gas extraction system includes vertical wells and horizontal collectors that use cylindrical pipes with strategically placed perforations (Sadasivam and Reddy, 2014). Although these gas extraction systems are designed to capture and convert LFG to energy or flare it, their effectiveness is restricted due to a limited radius of influence of the wells and waste heterogeneity which impacts LFG generation rates, flow pathways, and the uniformity of gas capture across landfills (Spokas et al., 2006). Also, it is not economically practical to install gas collection systems in old or abandoned landfills with low CH_4 output (Mor et al., 2006) and gas collection systems cannot capture all CH_4 emissions from landfills (Spokas et al., 2006). Therefore, a portion of the biogas produced ends up escaping into the atmosphere, resulting in what is known as fugitive emissions. Furthermore, after gas collection systems are shut down, landfills are anticipated to continue releasing residual emissions (Cabral et al., 2010). Despite being low, these residual emissions can continue for decades. As such, cost-effective methods are required to significantly mitigate CH_4 emissions from landfills. Mitigating fugitive and residual CH_4 emissions from landfills is possible using microbial CH_4 oxidation in landfill-cover soils or biocovers (Ait-Benichou et al., 2009; Hilger et al., 2000). In recent years, studies have shown that microbially mediated CH_4 oxidation can mitigate CH_4 emissions from new or old landfills by providing a well-designed landfill cover and engineered biocover system (Huber-Humer et al., 2011). Biocovers are mainly composed of organic-rich materials such as composts and peats, either alone or amended with landfill cover soil, which can support and promote microbial growth and CH_4 oxidation (Huber-Humer et al., 2008, Sadasivam and Reddy, 2014). According to Scheutz et al., 2011 in landfills without gas collection systems, the soil cover's effectiveness in enhancing CH_4 oxidation is only 14%. In this regard, to significantly reduce CH_4 emissions, it is necessary to optimize the composition of the soil cover to improve microbial CH_4 oxidation in landfill cover. Previous research has shown that adding materials rich in organic matter, such as compost and biochar, increases CH_4 oxidation rates by enhancing the growth of CH_4-oxidizing bacteria in the cover materials (Reddy et al., 2014). Several studies have investigated different amendments to landfill cover soil to improve CH_4 oxidation (Nikiema et al., 2005; Darnault, 2011; Hilger et al., 2000; Reddy et al., 2014; Xin et al., 2023; Stern et al., 2007). Xin et al., (2023) reported that due to the electron storage capacity of soil reef biochar, it can reduce microbial CH_4 production by acting as an electron acceptor, promoting anaerobic respiration, and inhibiting methanogenesis. Moreover, Reddy et al., 2014 reported in their work that amending soil with biochar can promote the growth of methanotrophic bacteria to achieve greater oxidation capacity. Similarly, Darnault, (2011) reported that biochar amendment improves landfill cover soil's chemical and physical properties, promoting methanotroph growth and CH_4 mitigation. In laboratory soil column simulations, mature and porous compost enhanced CH_4 uptake, showing markedly higher and rapidly increasing oxidation rates than conventional landfill cover soils (Huber-Humer et al., 2011). For instance, Stein and Hettiaratchi, (2010) reported a steady-state oxidation efficiency of 32.3% for dark soil. Similarly, Rachor et al., (2011) observed an oxidation efficiency of 40% for sand, and Chiemchaisri et al., (2012) documented oxidation efficiencies ranging from 30% to 40% for sandy loam. Roncato and Cabral (2012) recorded steady-state oxidation efficiencies ranging from 83% to 95% for a compost-sand mixture in a 5:1 ratio, and Rose et al., (2012) reported an efficiency of 90% for a compost-sand mixture in a 3:1 ratio. The year-round CH_4 removal rate in optimally designed compost covers is 95–99% depending on the type of compost used (Huber-Humer 2004b). While soil cover provides a cost-effective method for reducing CH_4 emissions, few studies have investigated how different amendments of soil covers mitigate CH_4 emissions in a controlled column experiment. This thesis aims to contribute to these efforts by evaluating the effectiveness of different landfill cover soil amendments in reducing CH_4 emissions through a laboratory column experiment.

1.3 Overview

The goal of this work is two-fold: first, to use data mining techniques to assess surface CH_4 emissions from a municipal solid waste landfill in Jackson, South Carolina, and second to evaluate the effectiveness of soil cover amendments in mitigating CH_4 releases in a laboratory column experiment. Chapter 2 analyzes surface CH_4 emissions data from the landfill. These data were collected from the first quarter of 2017 to the first quarter of 2023 and shared with us by the landfill authority. The primary objectives are to identify locations on the landfill with preferential CH_4 leakage and ascertain the effectiveness of current mitigation practices in reducing fugitive $CH_{4.}$ Here, we utilized ordinary kriging tool in ArcGIS Pro to create heat maps to visualize the spatial and temporal CH_4 emission trends from the landfill and investigate the efficacy of soil cover application in reducing CH_4 emissions at hotspots areas of the landfill. Our analyses indicate significant historical sampling data gaps persist throughout the monitoring regimen. These inconsistencies in the landfill sampling data made it challenging to create an accurate picture of CH_4 leakage or develop a model to predict CH_4 fluxes. In addition, we observed that applying a soil treatment to “hotspots” (i.e., locations with CH_4 concentrations above 500 ppm) after a leakage event reduces CH_4 as measured after 10 and 30 days. However, the longevity of this practice remains unclear as re-monitoring beyond 30 days and at locations previously flagged as hotspots was not performed. In Chapter 3, we evaluate the effectiveness of landfill cover soil amendments in reducing CH_4 releases through a laboratory column experiment. Four different soil cover types - biochar, compost, woodchips, and landfill surface soil - were tested by packing each into a 7-inch height glass column. The same CH_4 loading rate was introduced at the bottom of each of the columns, and an MG5 gas sensor was used to measure the CH_4 concentration exiting through the top of the column. Three replicates were conducted for each type of soil cover to ensure verification and validation of the study’s findings. The breakthrough curve for each cover type was analyzed to evaluate the CH_4 retention time and CH_4 adsorption capacity of the soil covers. The methane removal efficiency (MRE) of each cover soil was calculated to determine which soil amendment is most effective for CH_4 mitigation. The landfill soil showed a moderate CH_4 adsorption capacity, which is consistent with previous studies that unamended landfill soil has low CH_4 removal efficiency. Biochar enhanced the CH_4 adsorption capacity and increased the CH_4 removal efficiency in the landfill soil due to its high porosity and large surface area, which allow for extended CH_4 retention time. The organic content of the compost improved CH_4 removal efficiency and CH_4 retention of the landfill soil cover by providing nutrients to support the growth of methanotrophic bacteria which consume CH_4 as their source of carbon and energy. Woodchips did not improve the effectiveness of the landfill soil due to their limited surface area and lack of adsorptive sites for CH_4. The findings of this thesis highlight the potential of biochar and compost as productive and cost-effective amendments to conventional landfill cover soils for enhancing CH_4 mitigation.

REFERENCES

Ait-Benichou, S., Jugnia, L. B., Greer, C. W., & Cabral, A. R. (2009). Methanotrophs and methanotrophic activity in engineered landfill biocovers. Waste Management, 29(9), 2509–2517. https://doi.org/10.1016/j.wasman.2009.05.005

Basic Information about Landfill Gas | US EPA. (n.d.). Retrieved August 26, 2024, from https://www.epa.gov/lmop/basic-information-about-landfill-gas

Cabral, A. R., Moreira, J. F. V., & Jugnia, L.-B. (2010). Biocover Performance of Landfill Methane Oxidation: Experimental Results. Journal of Environmental Engineering, 136(8), 785–793. https://doi.org/10.1061/(asce)ee.1943-7870.0000182

Chan, R., Chiemchaisri, W., & Chiemchaisri, C. (2023). Exploring Effective Bio-Cover Materials for Mitigating Methane Emission at a Tropical Landfill. Applied Sciences (Switzerland), 13(3). https://doi.org/10.3390/app13031990

Chetri, J. K., Reddy, K. R., & Grubb, D. G. (2022). Investigation of different biogeochemical cover configurations for mitigation of landfill gas emissions: laboratory column experiments. Acta Geotechnica, 17(12), 5481–5498. https://doi.org/10.1007/s11440-022-01509-5

Chiemchaisri, C., Chiemchaisri, W., Kumar, S., & Wicramarachchi, P. N. (2012). Reduction of Methane Emission From Landfill Through Microbial Activities in Cover Soil: A Brief Review. Critical Reviews in Environmental Science and Technology, 42(4), 412–434. https://doi.org/10.1080/10643389.2010.520233

Darnault, C. (2011). Development of Biochar-Amended Landfill Cover for Landfill Gas Mitigation Submitted as partial fulfillment of the requirements Defense Committee : Amid Khodadoust.

Duan, Z., Kjeldsen, P., & Scheutz, C. (2021). Trace gas composition in landfill gas at Danish landfills receiving low-organic waste. Waste Management, 122, 113–123. https://doi.org/10.1016/j.wasman.2021.01.001

Ehrig, H., Schneider, H., & Gossow, V. (2011). Waste, 7. Deposition. Ullmann’s Encyclopedia of Industrial Chemistry. https://doi.org/10.1002/14356007.o28_o07

Gebert, J., Huber-Humer, M., & Cabral, A. R. (2022). Design of Microbial Methane Oxidation Systems for Landfills. Frontiers in Environmental Science, 10(September), 1–28. https://doi.org/10.3389/fenvs.2022.907562

Hilger, H. A., Cranford, D. F., & Barlaz, M. A. (2000). Methane oxidation and microbial exopolymer production in landfill cover soil. Soil Biology and Biochemistry, 32(4), 457–467. https://doi.org/10.1016/S0038-0717(99)00101-7

Huber-Humer, M., 2004b. Abatement of landfill methane emissions by microbial oxidation in biocovers made of compost. University of Natural Resources and Applied Life Sciences Vienna, Vienna

Huber-Humer, M., Gebert, J., & Hilger, H. (2008). Biotic systems to mitigate landfill methane emissions. Waste Management and Research, 26(1), 33–46. https://doi.org/10.1177/0734242X07087977

Huber-Humer, M., Tintner, J., Böhm, K., & Lechner, P. (2011). Scrutinizing compost properties and their impact on methane oxidation efficiency. Waste Management, 31(5), 871–883. https://doi.org/10.1016/j.wasman.2010.09.023

Inventory of U.S. Greenhouse Gas Emissions and Sinks | US EPA. (n.d.). Retrieved September 6, 2024, from https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks

Majdinasab, A., & Yuan, Q. (2017). Performance of the biotic systems for reducing methane emissions from landfill sites: A review. Ecological Engineering, 104, 116–130. https://doi.org/10.1016/j.ecoleng.2017.04.015

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. https://doi.org/10.1016/j.wasman.2005.11.005

Nikiema, J., Bibeau, L., Lavoie, J., Brzezinski, R., Vigneux, J., & Heitz, M. (2005). Biofiltration of methane: An experimental study. Chemical Engineering Journal, 113(2–3), 111–117. https://doi.org/10.1016/j.cej.2005.04.005

Osra, F. A., Ozcan, H. K., Alzahrani, J. S., & Alsoufi, M. S. (2021). Municipal solid waste characterization and landfill gas generation in kakia landfill, makkah. Sustainability (Switzerland), 13(3), 1–13. https://doi.org/10.3390/su13031462

Rachor, I., Gebert, J., Gröngröft, 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. https://doi.org/10.1016/j.wasman.2010.10.006

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), 1–11. https://doi.org/10.1061/(asce)gt.1943-5606.0001148

Roncato, C. D. L., & Cabral, A. R. (2012). Evaluation of Methane Oxidation Efficiency of Two Biocovers: Field and Laboratory Results. Journal of Environmental Engineering, 138(2), 164–173. https://doi.org/10.1061/(asce)ee.1943-7870.0000475

Rose, J. L., Mahler, C. F., & Izzo, R. L. dos S. (2012). Comparison of the methane oxidation rate in four media. Revista Brasileira de Ciência Do Solo, 36(3), 803–812. https://doi.org/10.1590/s0100-06832012000300011

Sadasivam, B. Y., & Reddy, K. R. (2014). Landfill methane oxidation in soil and bio-based cover systems: A review. Reviews in Environmental Science and Biotechnology, 13(1), 79–107. https://doi.org/10.1007/s11157-013-9325-z

Sadasivam, B. Y., & Reddy, K. R. (2015). Adsorption and transport of methane in landfill cover soil amended with waste-wood biochars. Journal of Environmental Management, 158, 11–23. https://doi.org/10.1016/j.jenvman.2015.04.032

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. https://doi.org/10.1016/j.wasman.2010.11.019

Spokas, K., Bogner, J., Chanton, J. P., Morcet, M., Aran, C., Graff, C., Golvan, Y. M. Le, & Hebe, I. (2006). Methane mass balance at three landfill sites: What is the efficiency of capture by gas collection systems? Waste Management, 26(5), 516–525. https://doi.org/10.1016/j.wasman.2005.07.021

Stein, V. B., & Hettiaratchi, J. P. A. (2010). Methane oxidation in three alberta soils: Influence of soil parameters and methane flux rates. Environmental Technology (United Kingdom), 22(1), 101–111. https://doi.org/10.1080/09593332208618315

Stern, J. C., Chanton, J., Abichou, T., Powelson, D., Yuan, L., Escoriza, S., & Bogner, J. (2007). Use of a biologically active cover to reduce landfill methane emissions and enhance methane oxidation. Waste Management, 27(9), 1248–1258. https://doi.org/10.1016/j.wasman.2006.07.018

Themelis, N. J., & Ulloa, P. A. (2007). Methane generation in landfills. Renewable Energy, 32(7), 1243–1257. https://doi.org/10.1016/j.renene.2006.04.020

Understanding Global Warming Potentials | US EPA. (n.d.). Retrieved August 26, 2024, from https://www.epa.gov/ghgemissions/understanding-global-warming-potentials

Valenzuela-Heredia, D., & Aroca, G. (2023). Methane biofiltration for the treatment of a simulated diluted biogas emission containing ammonia and hydrogen sulfide. Chemical Engineering Journal, 469(March), 1–9. https://doi.org/10.1016/j.cej.2023.143704

Verma, G., Chetri, J. K., & Reddy, K. R. (2024). Evaluating the efficacy of biogeochemical cover system in mitigating landfill gas emissions: A large-scale laboratory simulation. Environmental Science and Pollution Research, 0123456789. https://doi.org/10.1007/s11356-024-34558-2

Wang, Q., Gu, X., Tang, S., Mohammad, A., Singh, D. N., Xie, H., Chen, Y., Zuo, X., & Sun, Z. (2022). Gas transport in landfill cover system: A critical appraisal. Journal of Environmental Management, 321(May). https://doi.org/10.1016/j.jenvman.2022.116020

Xin, D., Li, W., Choi, J., Yu, Y. H., & Chiu, P. C. (2023). Pyrogenic Black Carbon Suppresses Microbial Methane Production by Serving as a Terminal Electron Acceptor. Environmental Science and Technology, 57(49), 20605–20614. https://doi.org/10.1021/acs.est.3c05830

Zhao, H. (2019). Master thesis - Methane emissions from Landfills. May. https://doi.org/10.13140/RG.2.2.17326.77120

2 MONITORING SURFACE METHANE EMISSIONS AND MITIGATION EFFORTS AT A MUNICIPAL LANDFILL, A CASE STUDY AT THREE RIVERS SOLID WASTE

2.1 Introduction

Productive and cost-effective methods to monitor and mitigate surface landfill methane (CH_4) emissions are important for reducing greenhouse gas emissions as landfills are both a long-lived and substantial source of anthropogenic CH_4 (Bogner, 2006). The main challenge in measuring CH_4 emissions from landfills is the spatial and temporal variability of emissions, combined with the sheer size of a modern landfill (Oonk, 2010). Emissions at one spot can be 1 to 1000-fold of emission from a spot located a few meters away (Verschut et al., 1991). According to Czepiel et al. (1996), there is no correlation between emission at a spot at the landfill and the emission six meters away. Rachor and Gebert (2009) studied variation in CH_4 emissions within the square meter and even at this small scale CH_4 emissions proved to be highly heterogeneous. Reports indicate that between 2000 and 2009, the yearly CH_4 emissions from landfills were 75 Tg, constituting 22% of all anthropogenic CH_4 emissions (IPCC, 2013). The 100-year GWP of CH_4 is about 28 times higher than that of CO_2, as shown in Table 2.1, according to IPCC assessment reports.

Table 2.1 Comparison of methane and carbon dioxide global warming potential over 100 years (IPCC,2013).

Gas	SAR	AR4	AR5	AR5 with feedback
CO_2	1	1	1	1
CH_4	21	25	28	34

SAR – IPCC Second Assessment Report, AR4 – IPCC Fourth Assessment Report, AR5 – IPCC Fifth Assessment Report.

LFG emissions can continue for extended periods after a landfill is closed, based on the landfill operations, types, and amounts of waste disposed, and the conditions under which the waste degrades (Darnault, 2011). Prolonged accumulation beyond explosive thresholds can threaten lives and damage property near landfills (Verma et al., 2024). Due to these potential dangers, regulations for MSW landfills (40 CFR 60) mandate the capture of LFG emissions if CH_4 emissions exceed 500 parts per million (ppm) or non-methane organic compounds (NMOC) emissions exceed 34 Mg/year for open landfills and 50 Mg/year for closed landfills (USEPA, 2016). In this regard, it is necessary to monitor surface CH_4 emissions from landfills and mitigate these emissions.

Over the years, different approaches and techniques have been employed by researchers (Abichou et al., 2012; Cambaliza et al., 2015; Rolston, 1986; Krautwurst et al., 2017; Schroth et al., 2012) to understand and estimate CH_4 emissions from landfills. While some researchers (Govindan and Agamuthu, 2014; Sormunen et al., 2013) utilize gas generation modeling such as LandGEM to estimate CH_4 emissions from landfills, others employ field monitoring techniques such as surface flux chambers, eddy covariance, mass balance using aerial measurements, radial plume and tracer gas dispersion. These studies have, alone and in tandem, led to significant advancements in understanding CH_4 emissions from landfills, improving both the accuracy of CH_4 estimates and the development of more effective mitigation methods for reducing LFG emissions. Figure 2.1 shows how measurements are undertaken from the landfill surface to several kilometers away and over different timescales from minutes to weeks or months (Mønster et al., 2019). The heterogeneous nature and spatial variability of LFG emissions make it challenging to accurately measure fugitive gas emissions (Engineers, 2008). To achieve the target for reducing LFG emissions, the International Solid Waste Association (ISWA. 2009) emphasized the importance of accurate measurements of greenhouse gas emissions for setting and monitoring feasible reduction targets. In pursuit of this target, different methods have been devised to identify and measure CH_4 emissions from landfills and these methods can be categorized into three groups: (i) above-ground techniques, (ii) below-ground techniques, and (iii) ground-surface enclosure techniques (Gonzalez-Valencia et al., 2015). EPA recommends a quarterly frequency for monitoring landfill surface CH_4 emissions so that the effects of seasonal variability are accounted for (EPA Victoria, 2018). In this work, a ground surface monitoring technique was utilized where an Inficon Irwin SX CH_4 Leak Detector was used to monitor surface CH_4 emissions from Three Rivers Solid Waste Authority Landfill from the first quarter of 2017 to the first quarter of 2023. The main objectives were to identify areas of the landfill with high CH_4 emissions (that is above 500 pm) as part of CH_4 mitigation efforts and to recheck CH_4 emissions within 10 and 30 days at these spots after applying soil covers. The aim was to analyze spatial and temporal trends of CH_4 emissions and evaluate the effectiveness of the soil cover used in mitigating CH_4 emissions.

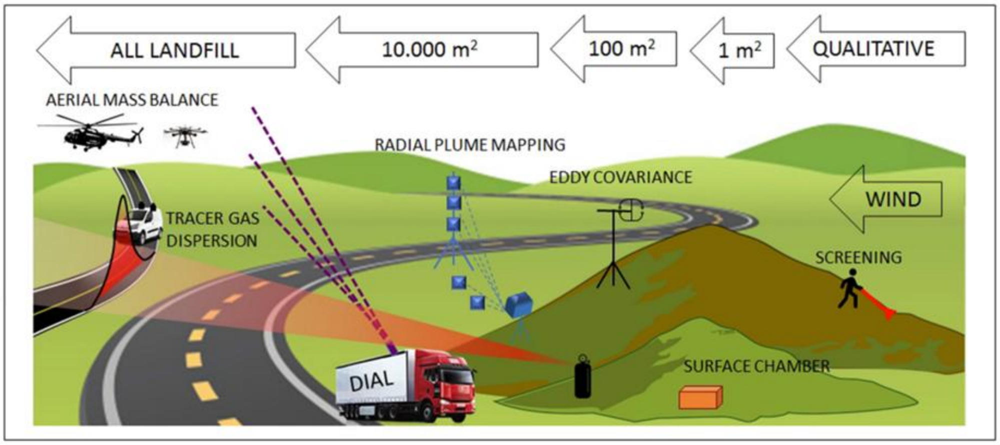


Figure 2.1. Overview of the most common field methods used to detect and measure methane emissions from landfills (Mønster et al., 2019).

2.2 Materials and Methods

2.2.1 Landfill site description

Three Rivers Solid Waste Authority Landfill is located off Highway 225 on the Department of Energy's Savannah River Site (DOE-SR) in Jackson, South Carolina. Three Rivers Solid Waste Authority Landfill is a 1400-acre landfill complex as shown in Figure 2.2.

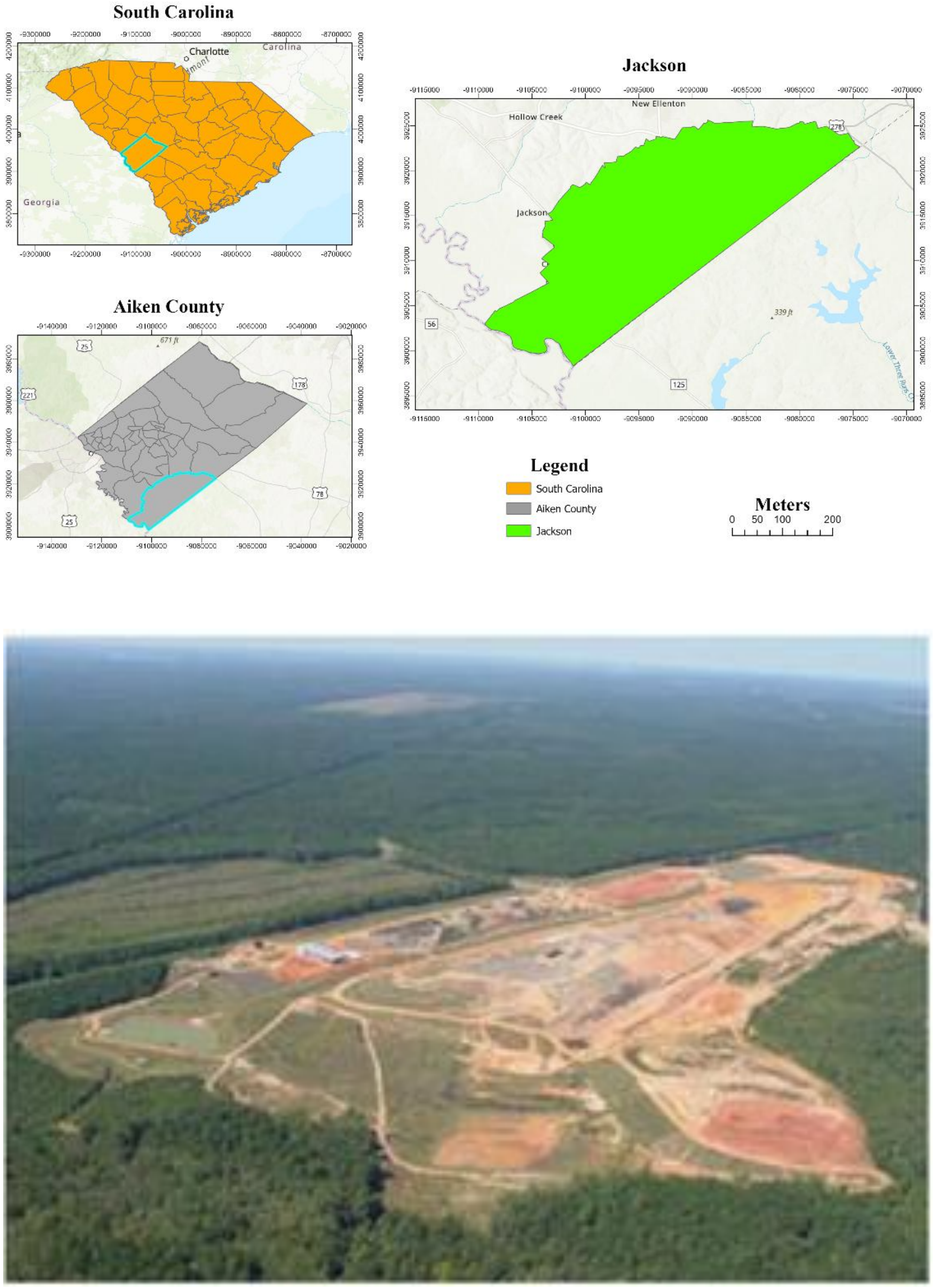


Figure 3.2. (a) A map showing the location of Three Rivers Solid Waste Authority Landfill and (b) an aerial view of Three Rivers Solid Waste Authority Landfill (https://trswa.org/landfill.shtml)

Three Rivers Solid Waste Authority Landfill was opened on July 1, 1998, for the disposal of municipal solid waste, commercial waste, and industrial waste from nine-member counties and DOE-SR. The landfill has a 300-acre footprint with remaining airspace over 38 million cubic yards of waste over a projected lifespan above 120 years. The landfill receives about 1,000 tons of waste per day or about 250,000 tons per year. Around 210,000 tons come directly from the nine-member counties. The landfill is regulated under the Federal Resource Conservation and Recovery Act (RCRA) Subtitle D and applicable South Carolina regulations and is sited and constructed in accordance with these regulations. The landfill provides for six layers of environmental protection as shown in Figure 2.3: 1) environmental regulations that require waste screening by generators, 2) waste screening at the transfer stations 3) waste screening at the landfill, 4) protection of groundwater by leachate (wastewater) collection and liner systems, 5) protection of air quality by landfill gas collection and control systems, and 6) protection of groundwater through a site selection process that requires location above an aquifer with an upward hydraulic gradient.

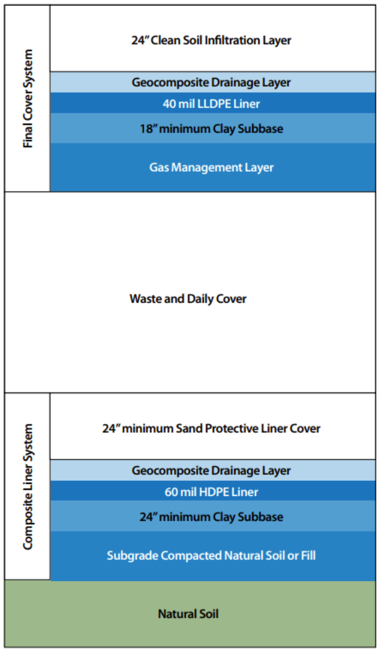


Figure 4.3. Liner and final cap construction at Three Rivers Solid Waste Authority Landfill (https://trswa.org/landfill.shtml)

2.2.2 Data collection

Surface CH_4 emissions at the Three Rivers Solid Waste Authority Landfill in Jackson, South Carolina were monitored quarterly from 2017 to 2023 by a trained landfill technician using a calibrated Inficon IRwin SX (IRwin) CH_4 Leak Detector. The collected surface CH_4 emission data were provided to us by the landfill authorities. CH_4 emissions were not continuously monitored in each quarter. CH_4 emissions points were selected through a walking survey of the landfill, identifying locations on the landfill with CH_4 emissions exceeding the 500-ppm threshold above the background concentration. These locations were recorded and flagged as exceedance points (i.e. hotspots). Corrective actions at the exceedance locations were completed timely by adding soil cover and making valve adjustments to increase vacuum to gas collection and control system (GCCS) devices in the vicinity of the exceedance locations. CH_4 emissions were rechecked at all exceedance locations within 10 and 30 days after the soil cover application. No re-monitoring was done from the fourth quarter of 2019 to the third quarter of 2020 because the initial CH_4 emissions were below 500 ppm and geographic position system (GPS) coordinates for the first quarter of 2017 to the second quarter of 2018 were not recorded. As a result, data analysis was conducted from the fourth quarter of 2021 to the first quarter of 2023. CH_4 emissions were monitored along the landfill's site-specific surface emissions monitoring route and around the perimeter of the collection area. CH_4 emissions were also monitored along areas exhibiting distressed vegetation, washouts, and other indications of compromised cover integrity on the landfill's surface.

2.2.3 Dataset preparation

For this work, we utilized a quarterly surface CH_4 emission dataset provided by the landfill authorities in a portal document format (pdf) report. The dataset covering a temporal period from the fourth quarter of 2021 to the first quarter of 2023 included measurements from 43 different surface CH_4 emission points. The dataset was manually entered into Microsoft Excel, categorized into initial, 10-day, and 30-day CH_4 emissions, and saved as a comma-separated value "CSV" file. The CSV file was then uploaded into ArcGIS Pro to visualize the latitude and longitude of CH_4 emission points. The ordinary kriging tool in ArcGIS Pro was used to create spatial interpolation prediction surfaces to observe the spatiotemporal trends for initial, 10-day recheck, and 30-day recheck CH_4 emissions. Ordinary kriging is an advanced geostatistical method that generates an estimated surface from a scattered set of points. It was chosen for this thesis because it provides standard errors to assess the uncertainty in the surface prediction and showed the lowest root mean square and mean standardized errors compared to other geostatistical methods. CH_4 emissions data points were transformed during the kriging process to normalize the data and improve prediction accuracy. Standard error maps of the initial, 10-day recheck, and 30-day recheck CH_4 emissions along with scatter plots comparing the predicted versus measured CH_4 emissions generated from the ordinary kriging interpolation were analyzed to evaluate the reliability and accuracy of the spatial interpolation predictions. Consequently, recommendations were provided on how to improve monitoring surface CH_4 emissions for effective mitigation efforts on the landfill site.

2.3 Results and Discussion

2.3.1 Initial methane emissions

During the monitoring period from the fourth quarter of 2021 to the first quarter of 2023, initial measurements of CH_4 concentrations across the landfill varied significantly, ranging from 508 ppm to 13,849 ppm as illustrated in Figure 2.4. This spatial and temporal variation of CH_4 emission highlights the complex dynamic processes during CH_4 formation on a landfill, influenced by various factors such as waste composition, moisture content, landfill management practices, and meteorological conditions (Bogner et al., 1997). CH_4 emissions were monitored at forty-three different locations throughout this period. The lowest CH_4 emission was recorded in the third quarter of 2022 while the highest CH_4 emission was observed in the first quarter of 2023. These changes over time suggest that CH_4 production is influenced by landfill operations, waste content, and seasonal environmental factors, such as temperature, pressure, wind speed, and rainfall as reported in previous studies (Aghdamet al., (2019), Christophersen et al. (2001), Czepiel et al. (1996).

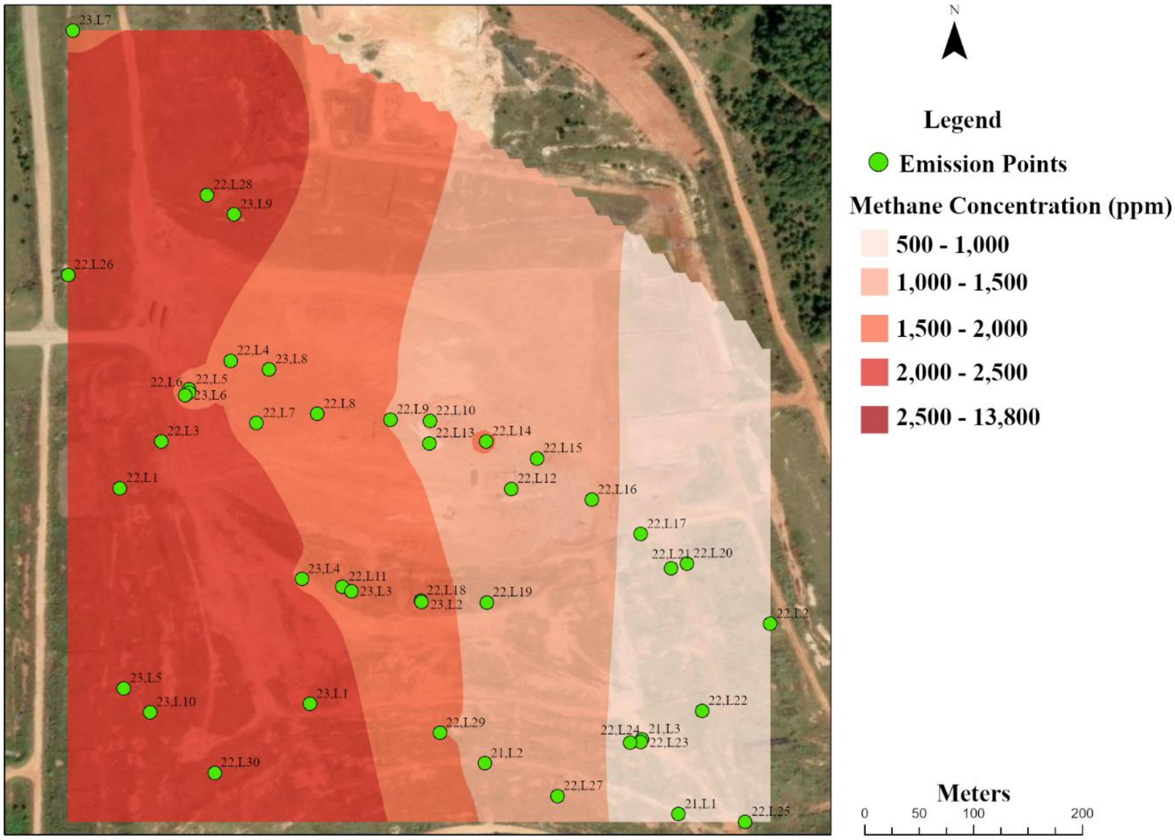


Figure 5.4. Initial surface methane emissions on the landfill site from the fourth quarter of 2021 to the first quarter of 2023.

2.3.2 Standard error map of initial methane emissions

The uncertainty of the ordinary kriging predictions for initial CH_4 concentrations is illustrated in Figure 2.5. The low standard errors in the central portion of the landfill indicate higher prediction confidence, which is associated with the several number of emission points in that area. The higher standard errors observed in the northern section of the landfill are due to the fewer emission points, leading to reduced prediction accuracy of CH_4 concentration. These high-uncertainty areas suggest the need for additional field measurements to improve the prediction accuracy. Future monitoring efforts should prioritize the northern sections on the landfill site to achieve a more uniform prediction accuracy across the landfill. This analysis demonstrates the importance of optimizing sampling point distribution to minimize spatial prediction uncertainty in landfill methane emission studies.

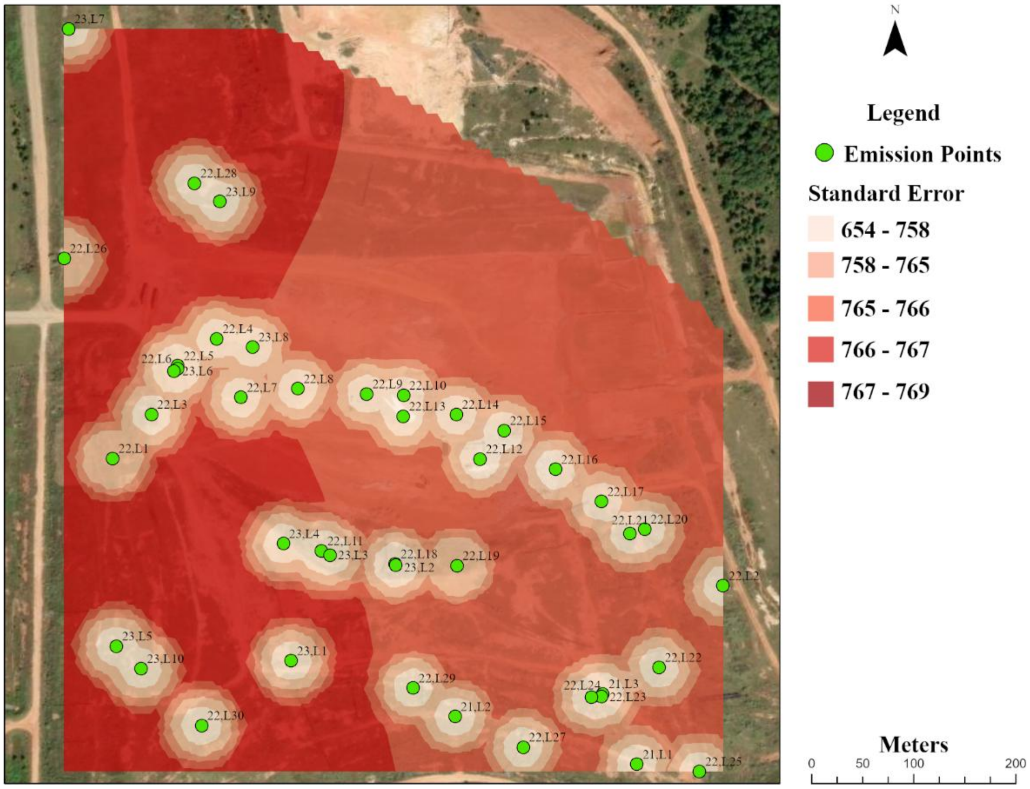


Figure 6.5. Standard error map for predicted initial surface methane emissions on the landfill site from the fourth quarter of 2021 to the first quarter of 2023.

2.3.3 Evaluation of the performance of ordinary kriging for initial methane emissions

The scatter plot comparing predicted and measured CH_4 concentrations in Figure 2.6 highlights the performance of ordinary kriging. More than half of the CH_4 emission points are clustered at the low concentration range with a few outliers at higher values. The standard root mean square error observed was 1.32. The regression line deviates from the reference line, indicating a tendency of the model to underpredict CH_4 concentrations, particularly in high-emission areas. This underprediction could be attributed to the high spatial variability of CH_4 emissions or few data points in high CH_4 emissions locations. The model demonstrates better prediction accuracy for lower CH_4 values where data points are more clustered, indicating it is more effective at predicting CH_4 emissions in areas with closely spaced measurement points rather than in areas where emission points are widely scattered. These findings emphasize the need for additional data collection in areas with high CH_4 emissions and few emission points to improve the accuracy of the kriging model to better interpolate the spatial variability of CH_4 emissions on the landfill surface which would enhance the development of targeted landfill management strategies for effective CH_4 mitigation planning.

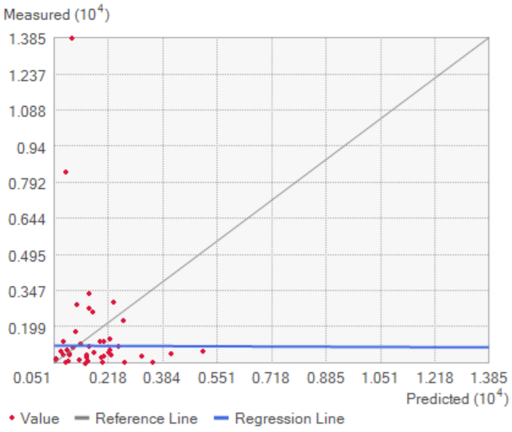


Figure 7.6. Scatter plot of measured versus predicted initial surface methane emissions generated using ordinary kriging interpolation.

2.3.4 Methane emissions rechecked within 10 days

Re-monitoring efforts conducted 10 days after the application of soil covers revealed a reduction in CH_4 emissions, with emissions falling below 500 ppm across all monitoring points except for three locations as shown in Figure 2.7. This decrease suggests that the soil covers are effective immediate mitigation measures for reducing CH_4 emissions. However, an exception was observed in the third quarter of 2022 at monitoring point two as highlighted by the blue rectangle in Figure 2.7 where CH_4 emissions increased from 1,394 ppm to 3,978 ppm, indicating an increase contrary to the general trend of CH_4 emissions reduction. This may point to issues such as insufficient soil cover thickness, uneven soil cover application, or subsurface CH_4 migration pathways where CH_4 escapes through underground channels or cracks through the soil cover.

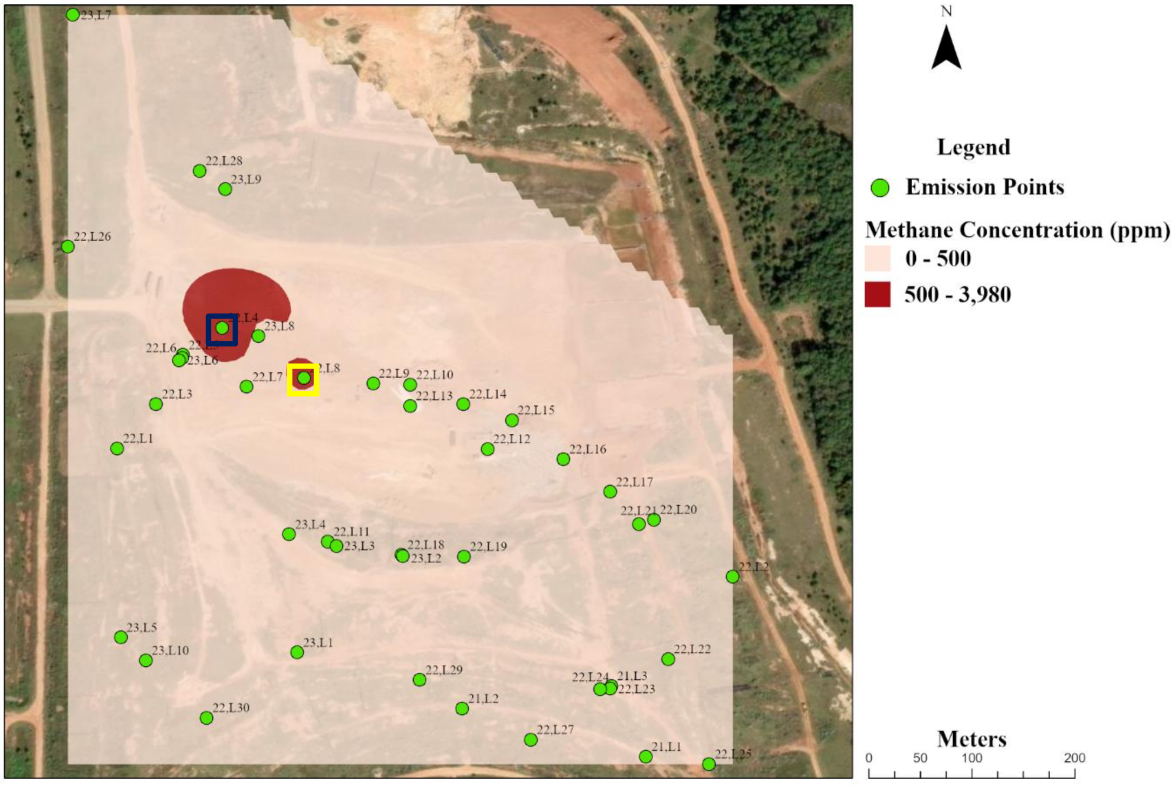


Figure 8.7. Methane emissions rechecked within 10 days after soil cover application from the fourth quarter of 2021 to the first quarter of 2023.

Further observations from the same quarter at monitoring point six as highlighted by the yellow rectangle in Figure 2.7 presented a different scenario. Here, CH_4 emissions were reduced from 2615 ppm to 1193 ppm following the application of soil covers. While this value represents a significant decrease in CH_4 emissions, it did not achieve the target of reducing CH_4 emissions to below 500 ppm, suggesting variability in the effectiveness of soil covers at different locations within the landfill. CH_4 concentrations of 0 ppm were recorded at 13 different monitoring points. This result highlights the potential for complete mitigation of CH_4 emissions in certain areas on the landfill within 10 days after the soil cover application.

2.3.5 Standard error map of methane emissions rechecked within 10 days

Figure 2.8 shows the standard error map for CH_4 emissions rechecked within 10 days, revealing a significant reduction in prediction uncertainty compared to the standard error map of initial CH_4 emissions. The reduction in the standard error is due to approximately 90% of the emission points falling below 500 ppm, which enhances the ordinary kriging model's ability to predict surface CH_4 emission with higher accuracy. With most CH_4 emission points falling below 500 ppm, the spatial variability of the CH_4 emission is significantly reduced, enabling the ordinary kriging model to accurately interpolate the monitored CH_4 emissions within the 10 days after soil cover application. Consequently, the regions with lighter shades dominate the map, reflecting improved prediction confidence across most surfaces of the landfill. The reduction in prediction uncertainty illustrates the effectiveness of the soil covers in mitigating CH_4 emissions and enhancing the spatial reliability of the ordinary kriging model. These results highlight the importance of uniform emission reductions in achieving more accurate and reliable spatial interpolation outcomes.

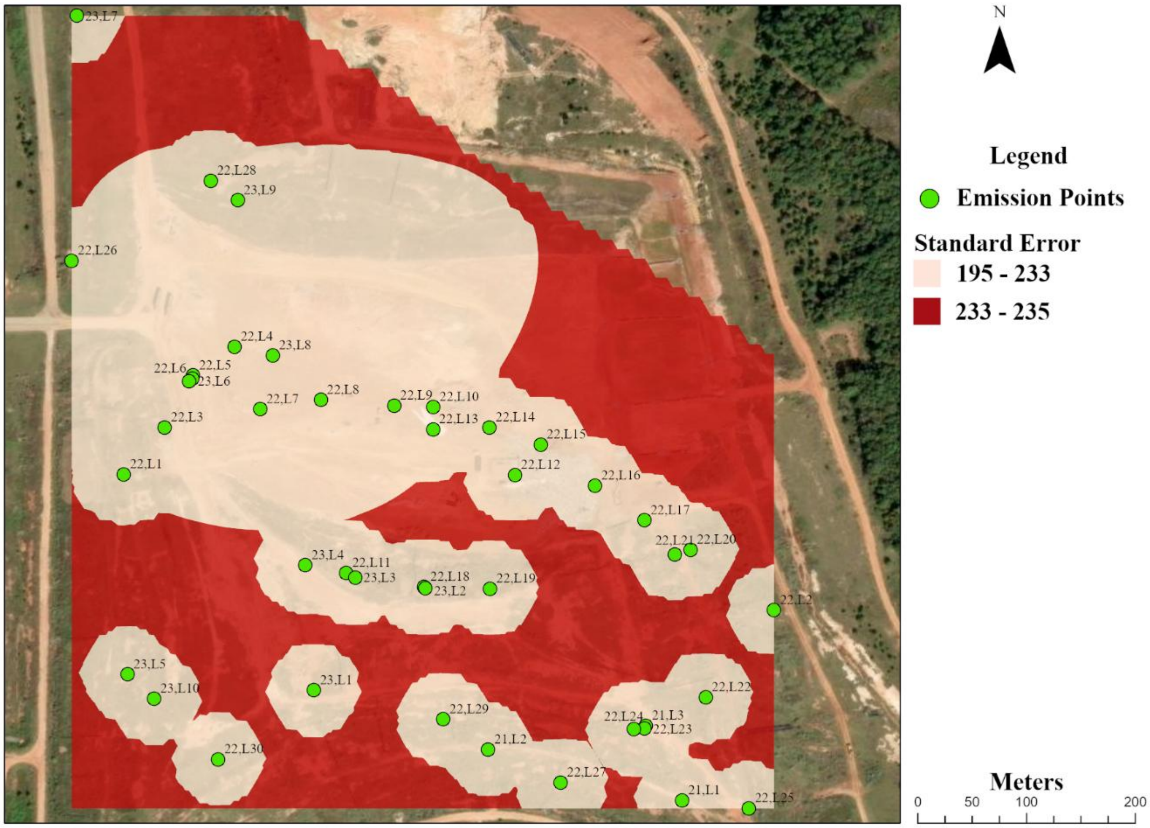


Figure 9.8. Standard error map for predicted surface methane emissions rechecked within 10 days on the landfill site from the fourth quarter of 2021 to the first quarter of 2023.

2.3.6 Evaluation of the performance of ordinary kriging for methane emissions rechecked within 10 days.

Figure 2.9 illustrates the scatter plot comparing predicted and measured CH_4 concentrations for the 10-day recheck emissions, highlighting the performance of the ordinary kriging model. The scatter plot shows that the ordinary kriging model performs relatively well in predicting CH_4 concentrations for areas with lower emissions. The clustering of points near the reference line reflects a good agreement between the predicted and measured values in these locations on the landfill site, suggesting a reliable spatial interpolation where spatial variability is minimal and the CH_4 emission points are clustered. However, as the CH_4 concentrations increase, the points deviate further from the reference line, indicating underprediction by the model in higher emission regions. This deviation highlights the model's limitation in capturing high variability in CH_4 emissions, potentially due to the dispersed or scattered CH_4 emission points in these areas. This analysis underscores the need for additional monitoring points in high CH_4 emission zones to improve prediction accuracy and the overall performance of the ordinary kriging method.

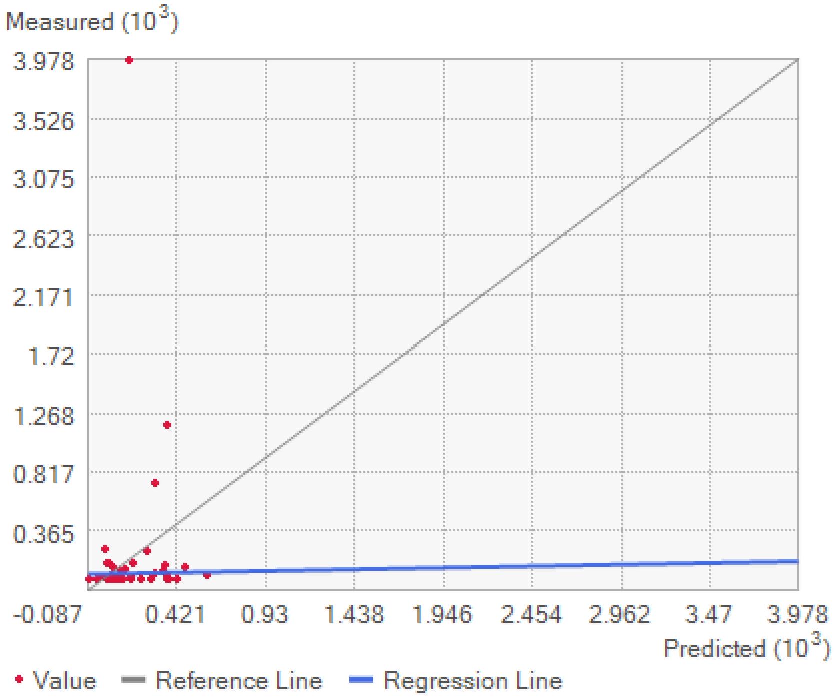


Figure 10.9. Scatter plot of measured versus predicted surface methane emissions rechecked within 10 days after soil cover application generated using ordinary kriging interpolation.

2.3.7 Methane emissions rechecked within 30 days

CH_4 emissions fell below 500 ppm across all monitored locations within 30 days. Figure 2.10 demonstrates the effectiveness of soil covers in reducing CH_4 emissions at the landfill site within 30 days. Within 10 to 30 days post soil cover application, the emissions data showed varying trends across the monitoring points: 25% of the points experienced a decrease in CH_4 emissions, 64% increased, and 11% maintained emissions at 0 ppm, indicating no detectable CH_4 emissions at these locations. The relative increase in CH_4 emissions suggests that certain landfill locations may have required additional interventions to sustain the reduction in CH_4 emissions, or they may have experienced localized CH_4 migration or soil cover degradation. Further analysis of the CH_4 emissions between the initial measurements and the 30-day review period indicates a significant reduction in CH_4 emissions. The reductions ranged from 37.04% to 100%, highlighting the substantial impact of soil cover application on mitigating CH_4 release into the atmosphere. These findings emphasize the variability in the response to soil cover application across different areas of the landfill and the overall effectiveness of this mitigation strategy in reducing CH_4 emissions within a relatively short period.

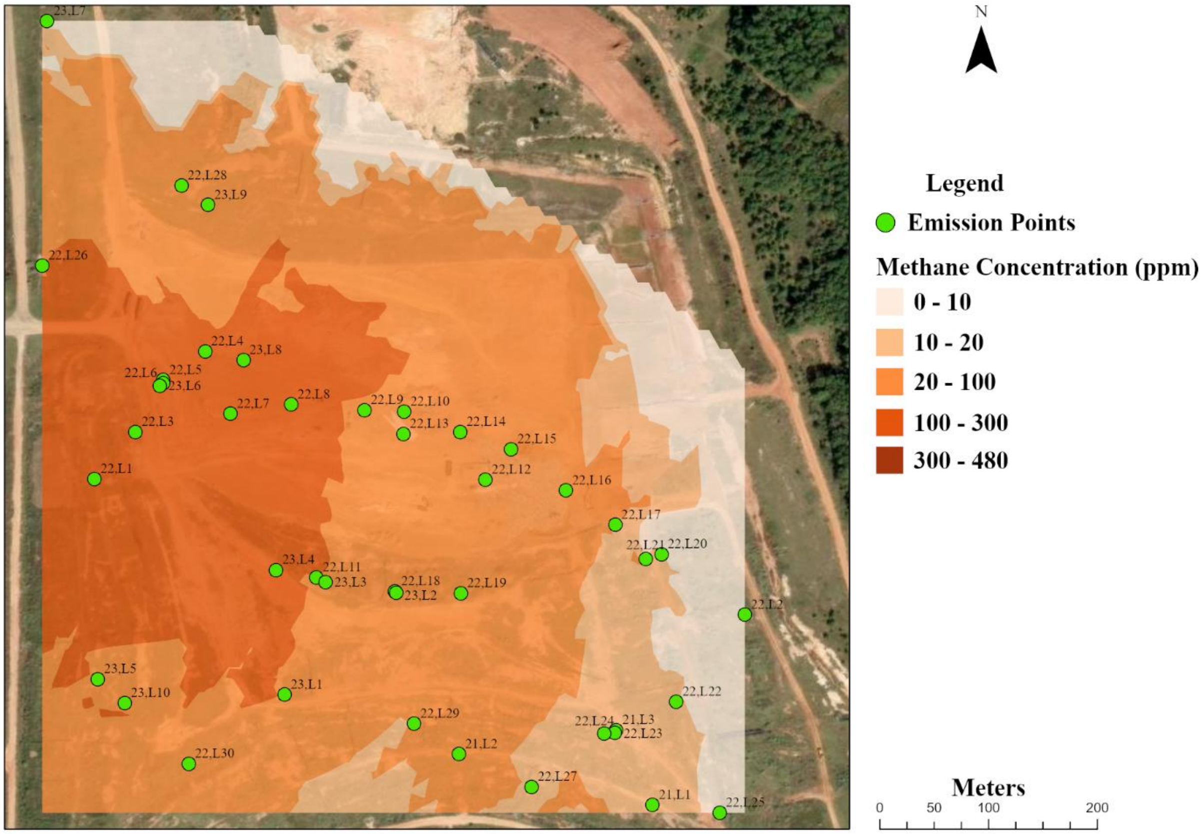


Figure 11.10. Methane emissions rechecked within 30 days after soil cover application from the fourth quarter of 2021 to the first quarter of 2023.

2.3.8 Standard error map of methane emissions rechecked within 30 days

The standard error map for the 30-day recheck period shown in Figure 2.11 illustrates improved prediction confidence compared to earlier periods, with reduced standard errors observed across almost all the areas of the landfill. The reduced standard error on the landfill surface for CH_4 emissions rechecked within 30 days, reflects a higher reliability of the kriging predictions. This improvement in prediction accuracy can be attributed to the lower spatial variability in CH_4 emissions, as all the CH_4 emission points fall below 500 ppm. However, the northern and southern portions of the landfill show relatively high standard errors, indicating the need for additional field measurements in these regions on the landfill. These findings highlight the importance of refining surface CH_4 emissions monitoring using a square grid approach to minimize underprediction or overprediction by spatial interpolation models and improve the reliability of CH_4 emission mitigation efforts.

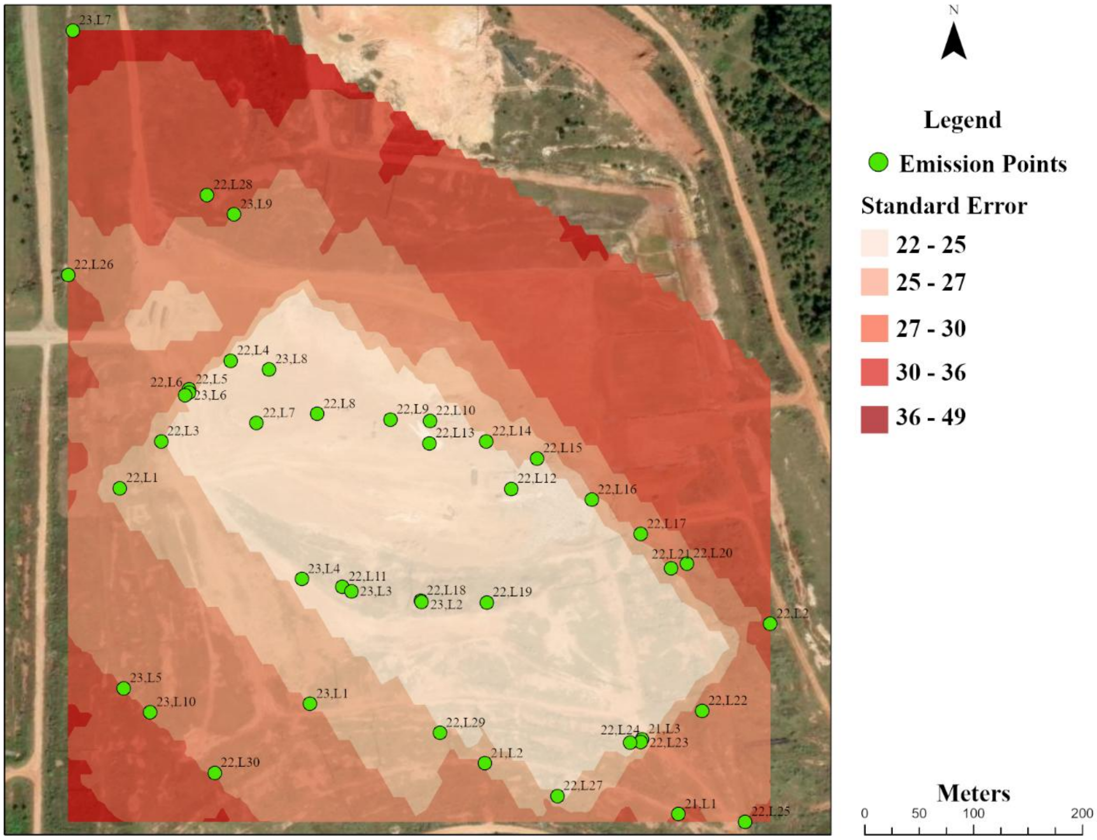


Figure 12.11. Standard error map for predicted surface methane emissions rechecked within 30 days on the landfill site from the fourth quarter of 2021 to the first quarter of 2023.

2.3.9 Evaluation of the performance of ordinary kriging for methane emissions rechecked within 30 days.

The scatter plot comparing predicted versus measured CH_4 concentrations in Figure 2.12 provides insights into the performance of the kriging model during the 30-day recheck period. The regression line closely aligns with the reference line compared to earlier CH_4 emission points, indicating a better interpolation between the predicted and measured CH_4 emissions rechecked within 30 days after soil cover application. However, the model slightly underpredicts CH_4 emissions, particularly in areas with relatively high CH_4 concentrations. This underprediction suggests potential limitations of the ordinary kriging model in interpolating localized high-emission events, reinforcing the need for enhanced spatial resolution in CH_4 emission monitoring on the landfill site.

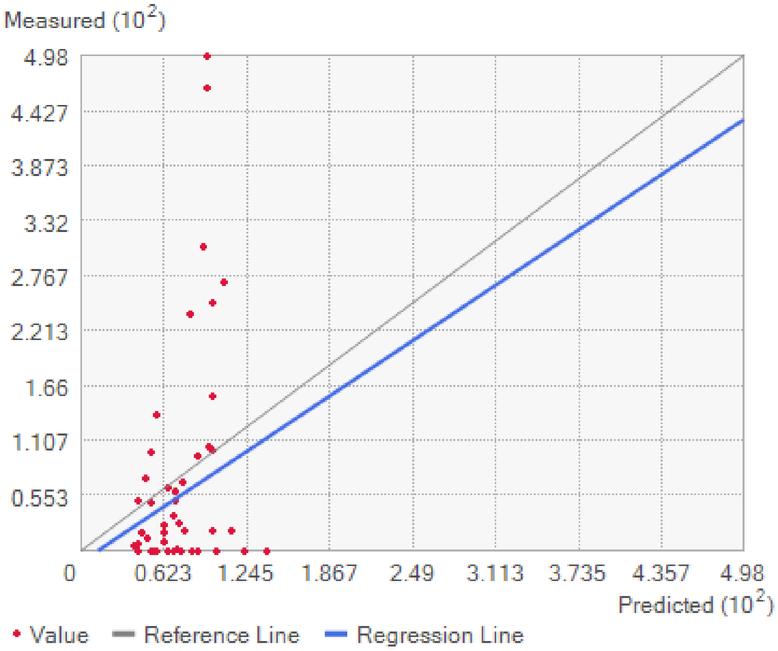


Figure 13.12. Scatter plot of measured versus predicted surface methane emissions rechecked within 30 days after soil cover application generated using the ordinary kriging interpolation.

2.4 Conclusion

In this work, quarterly surface CH_4 emissions from a municipal solid waste landfill in Jackson, South Carolina were monitored to identify spatial and temporal trends in CH_4 releases and assess the effectiveness of soil covers in reducing CH_4 emissions at hotspot areas (above 500 ppm). The data analysis highlighted significant gaps in historical sampling throughout the monitoring period, indicating a deficiency in the continuity and comprehensiveness of the data collected. One of the critical shortcomings identified is the absence of GPS coordinates for the emission locations from 2017 to 2018. This lack of precise location data made it challenging to generate a heat map for CH_4 emissions within this period and accurately quantify CH_4 flux. The missing data pose challenges for effectively modeling and predicting CH_4 emissions across the landfill site. There are a few limitations to the spatial interpolation used in the surface prediction of the CH_4 emissions. First, combining methane emissions from different quarters when soil covers were applied makes the values between locations not directly comparable, reducing the performance of the ordinary kriging method. Second, the uneven distribution of methane emission points across the landfill’s surface affected the accuracy of ordinary kriging in predicting methane emissions. Thus, there is a clear need for time series data with greater resolution to address these challenges and improve the understanding of CH_4 emission dynamics. Such enhanced data would enable a more accurate and detailed analysis of CH_4 flux trends, facilitating better-informed decisions for CH_4 mitigation and monitoring strategies in the future. It was observed that no specific locations that were monitored initially in previous quarters for CH_4 emissions were subjected to subsequent checks in the following quarters. This oversight limits the ability to assess the temporal variability of CH_4 emissions and the long-term effectiveness of the soil cover used in mitigating CH_4 emissions. While the soil covers proved to be an effective mitigation strategy for certain locations on the landfill within 10 and 30 days, the variation in performance of the soil cover suggests that additional or ongoing measures may be needed in some locations to maintain low CH_4 levels. Continued monitoring will be necessary to evaluate the long-term effectiveness of soil covers.

The standard error maps for the initial, 10-day recheck, and 30-day recheck CH_4 emissions provided insights into the reliability of the spatial interpolation of surface CH_4 predictions on the landfill generated using ordinary kriging. We observed that as CH_4 emissions decreased over time, the reduction in spatial variability resulted in improved prediction accuracy, as reflected in lower standard errors across most areas of the landfill. However, higher standard errors persisted in the northern and southern portions of the landfill, indicating the need for additional field measurements in these regions to increase the performance of the ordinary kriging model in interpolating CH_4 emissions. Using sampling grid for CH_4 emission monitoring on the landfill would enhance the reliability and accuracy of future CH_4 emission assessments and mitigation efforts.

The scatter plots comparing predicted versus measured CH_4 emissions showed an improved alignment of the regression line with the reference line over time during the monitoring period, indicating better agreement between the ordinary kriging model's predictions and the observed data. While the model demonstrated higher accuracy in predicting lower CH_4 concentrations, challenges remained in accurately estimating emissions at higher concentrations. This underprediction at higher CH_4 levels points to the need for incorporating additional parameters, such as subsurface CH_4 migration patterns or variability in soil cover application, to improve the model performance. This study emphasizes the need for continuous and comprehensive monitoring of surface CH_4 emissions to produce high-resolution data through precise and consistent sampling methods. By addressing the identified data gaps and variability in soil cover performance, more effective CH_4 mitigation strategies can be developed. The Appendix includes the root mean square error, mean standardized error, root mean square standardized error, and average standard error for the initial CH_4 emissions, the 10-day recheck CH_4 emissions, and the 30-day recheck CH_4 emissions. The quarterly changes in surface CH_4 emissions for initial, 10-day recheck, and 30-day recheck measurements from the fourth quarter of 2021 to the first quarter of 2023 by monitoring points are included in the Appendix.

REFERENCES

Abichou, T., Clark, J., Chanton, J., Hater, G., Green, R., Goldsmith, D., Barlaz, M., & Swan, N. (2012). A new approach to characterize emission contributions from area sources during optical remote sensing technique testing. Journal of the Air and Waste Management Association, 62(12), 1403–1410. https://doi.org/10.1080/10962247.2012.716384

Aghdam, E. F., Scheutz, C., & Kjeldsen, P. (2019). Impact of meteorological parameters on extracted landfill gas composition and flow. Waste Management, 87, 905–914. https://doi.org/10.1016/j.wasman.2018.01.045

AR5 Climate Change 2013: The Physical Science Basis — IPCC. (n.d.). Retrieved September 6, 2024, from https://www.ipcc.ch/report/ar5/wg1/

Babilotte, A., Lagier, T., Fiani, E., & Taramini, V. (2010). Fugitive Methane Emissions from Landfills: Field Comparison of Five Methods on a French Landfill. Journal of Environmental Engineering, 136(8), 777–784. https://doi.org/10.1061/(asce)ee.1943-7870.0000260

Bogner, J. (2006). Garbage and global change. Waste Management, 26(5), 451–452. https://doi.org/10.1016/j.wasman.2006.02.005

Bogner, J., Meadows, M., & Czepiel, P. (1997). Fluxes of methane between landfills and the atmosphere: Natural and engineered controls. Soil Use and Management, 13(4 SUPPL.), 268–277. https://doi.org/10.1111/j.1475-2743.1997.tb00598.x

Cambaliza, M. O. L., Shepson, P. B., Bogner, J., Caulton, D. R., Stirm, B., Sweeney, C., Montzka, S. A., Gurney, K. R., Spokas, K., Salmon, O. E., Lavoie, T. N., Hendricks, A., Mays, K., Turnbull, J., Miller, B. R., Lauvaux, T., Davis, K., Karion, A., Moser, B., … Richardson, S. (2015). Quantification and source apportionment of the methane emission flux from the city of Indianapolis. Elementa, 3, 1–18. https://doi.org/10.12952/journal.elementa.000037

Christophersen, M., Kjeldsen, P., Holst, H., & Chanton, J. (2001). Lateral gas transport in soil adjacent to an old landfill: Factors governing emissions and methane oxidation. Waste Management and Research, 19(6), 595–612. https://doi.org/10.1177/0734242X0101900616

Czepiel, P. M., Mosher, B., Harriss, R. C., Shorter, J. H., McManus, J. B., Kolb, C. E., Allwine, E., & Lamb, B. K. (1996). Landfill methane emissions measured by enclosure and atmospheric tracer methods. Journal of Geophysical Research Atmospheres, 101(11), 16711–16719. https://doi.org/10.1029/96jd00864

Darnault, C. (2011). Development of Biochar-Amended Landfill Cover for Landfill Gas Mitigation Submitted as partial fulfillment of the requirements Defense Committee : Amid Khodadoust.

Du, M., Peng, C., Wang, X., Chen, H., Wang, M., & Zhu, Q. (2017). Quantification of methane emissions from municipal solid waste landfills in China during the past decade. Renewable and Sustainable Energy Reviews, 78(April), 272–279. https://doi.org/10.1016/j.rser.2017.04.082

Engineers, S. C. S. (2008). Current MSW industry position and state-of-the-practice on LFG collection efficiency, methane oxidation, and carbon sequestration in landfills. Journal of Environmental Engineering, 135(916), 901–909.

EPA Victoria. (2018). Landfill gas fugitive emissions monitoring guideline. February, 1–27. https://www.epa.vic.gov.au/~/media/Publications/1684.pdf

Gonzalez-Valencia, R., Magana-Rodriguez, F., Maldonado, E., Salinas, J., & Thalasso, F.

(2015). Detection of hotspots and rapid determination of methane emissions from landfills via a ground-surface method. Environmental Monitoring and Assessment, 187(1). https://doi.org/10.1007/s10661-014-4083-0

Govindan, S. S., & Agamuthu, P. (2014). Quantification of landfill methane using modified Intergovernmental Panel on Climate Change's waste model and error function analysis. Waste Management and Research, 32(10), 1005–1014. https://doi.org/10.1177/0734242X14552551

Inventory of U.S. Greenhouse Gas Emissions and Sinks | US EPA. (n.d.). Retrieved September 6, 2024, from https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks

J., R. I. S., & Gebert, J. (2009). Spatial and temporal variability of gas emissions from old landfills, Proceedings Sardinia 2009, Twelfth International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy; 5 - 9 Oc- tober 2009. https://scholar.google.com/scholar?hl=en&as_sdt=0%2C11&as_ylo=2009&as_yhi=2010&q=Rachor+I.+Streese-Kleeberg+J.%2C+Gebert+J.+%282009%29%3A+Spatial+and+temporal+variability+of+gas+emissions+from+old+landfills%2C+Proceedings+Sardinia+2009%2C+&btnG=

Krautwurst, S., Gerilowski, K., Jonsson, H. H., Thompson, D. R., Kolyer, R. W., Iraci, L. T., Thorpe, A. K., Horstjann, M., Eastwood, M., Leifer, I., Vigil, S. A., Krings, T., Borchardt, J., Buchwitz, M., Fladeland, M. M., Burrows, J. P., & Bovensmann, H. (2017). Methane emissions from a Californian landfill, determined from airborne remote sensing and in situ measurements. Atmospheric Measurement Techniques, 10(9), 3429–3452. https://doi.org/10.5194/amt-10-3429-2017

Mønster, J., Kjeldsen, P., & Scheutz, C. (2019). Methodologies for measuring fugitive methane emissions from landfills – A review. Waste Management, 87, 835–859. https://doi.org/10.1016/j.wasman.2018.12.047

Oonk, H. (2010). Methods to quantify generation, oxidation and emission. Literature Review: Methane from Landfills, April, 75.

Rolston, D. E. (1986). Gas Flux. 9(9), 1103–1119.

Scheutz, C., Kjeldsen, P., Bogner, J. E., De Visscher, A., Gebert, J., Hilger, H. A., Huber-Humer, M., & Spokas, K. (2009). Microbial methane oxidation processes and technologies for mitigation of landfill gas emissions. Waste Management and Research, 27(5), 409–455. https://doi.org/10.1177/0734242X09339325

Schroth, M. H., Eugster, W., Gómez, K. E., Gonzalez-Gil, G., Niklaus, P. A., & Oester, P. (2012). Above- and below-ground methane fluxes and methanotrophic activity in a landfill-cover soil. Waste Management, 32(5), 879–889. https://doi.org/10.1016/j.wasman.2011.11.003

Sormunen, K., Laurila, T., & Rintala, J. (2013). Determination of waste decay rate for a large Finnish landfill by calibrating methane generation models on the basis of methane recovery and emissions. Waste Management and Research, 31(10), 979–985. https://doi.org/10.1177/0734242X13490980

Three Rivers Solid Waste Authority. (n.d.). Retrieved October 4, 2024, from https://trswa.org/landfill.shtml

Verma, G., Chetri, J. K., & Reddy, K. R. (2024). Evaluating the efficacy of biogeochemical cover system in mitigating landfill gas emissions: A large-scale laboratory simulation. Environmental Science and Pollution Research, 0123456789.

https://doi.org/10.1007/s11356-024-34558-2

Verschut, C., Oonk, J., & Mulder, W. (1991). Greenhouse gases from garbage dumps in the Netherlands; Broeikasgassen uit vuilstorts in Nederland. https://www.osti.gov/etdeweb/biblio/574805

3 EVALUATING THE EFFECTIVENESS OF LANDFILL COVER SOIL AMENDMENTS IN MITIGATING METHANE RELEASES: A LABORATORY COLUMN EXPERIMENT

3.1 Introduction

The global increase in methane (CH_4) emissions from landfills has highlighted the critical need for effective mitigation strategies to combat global warming (Sadasivam and Reddy, 2014). In terms of MSW landfill management, open dumping of solid waste was a widespread practice until researchers discovered that open dumps contributed to environmental degradation (Hettiaratchi, 2007). MSW management has transitioned from the open dump practices of the 1960s to today's integrated waste management systems (Sadasivam and Reddy, 2014). Integrated waste management aims to reduce waste generation at the source by integrating three features: the reuse and recycling of waste, energy recovery from waste, and residual waste management (Kollikkathara et al., 2009). Despite ongoing efforts to adopt alternative waste management strategies to reduce the amount of waste going to landfills, recent studies in the United States show that over 50% of the MSW generated still ends up in landfills, indicating that landfilling remains the most widely used method for MSW management (Weitz et al., 2002). A significant environmental problem associated with landfills is the generation of landfill gas (LFG), primarily made up of CH_4 and CO_2. Landfills are a major source of anthropogenic CH_4 emissions and addressing these emissions is crucial for global CH_4 reduction efforts (Grégoire et al., 2023). If CH_4 accumulates in landfills, it can pose a risk to public health and safety at landfills. Therefore, it is essential to mitigate CH_4 emissions through methods like gas collection systems or landfill covers (Yusuf et al., 2012). In small and old landfills, the gas collection is often not cost-effective, and as a result, the landfill gas produced is allowed to escape into the atmosphere, leading to what are called fugitive CH_4 emissions (Roncato and Cabral, 2012). Implementing landfill soil cover (LSC) with a natural biological capacity to consume CH_4 is a promising approach for mitigating fugitive CH_4 emissions from landfills (Gebert et al., 2022). Most of these alternate landfill covers include the amendment of cover soils with organic-rich materials (e.g. biochar and compost) either over large areas or in targeted zones of high CH_4 emissions requiring significant changes to current cover construction and monitoring practices (Yargicoglu and Reddy, 2017). CH_4 removal efficiency is influenced by the configuration and operational factors of the LSC, including inlet CH_4 loading rate, moisture content, soil depth, etc. (Stone et al., 2017). These factors control CH_4 diffusion and advection processes in LSC and impact the CH_4 mass transfer (Gebert et al., 2010a, b). For instance, to ensure sufficient CH_4 transport and maintain methanotrophic activity, optimal soil moisture is required (Yargicoglu and Reddy, 2018) while moisture deficiency would restrict microbial CH_4 oxidation (Scheutz et al., 2009). On the other hand, excess moisture would decrease the available pore space in the LSC, reducing the CH_4 mass transfer into the LSC (La et al., 2018).

The effect of the CH_4 loading rate on the CH_4 removal efficiencies is influenced by the CH_4 residence time and oxygen entering the soil cover (Huang et al., 2024). Due to the relatively high concentration of CH_4 but its low solubility in water, an appropriate residence time of CH_4 in the LSC is required (Pawłowska et al., 2011). It has been found that active CH_4 oxidation could reduce the upward pressure gradient, thereby decreasing the contribution of advective CH_4 emissions and facilitating the net flux of atmospheric oxygen into the soil cover (Molins and Mayer, 2007). A thicker soil layer ensures a longer gas retention time and usually presents a higher CH_4 removal efficiency (Huang et al., 2024). Abichou et al., (2006) found that a thick LSC of 45 cm had higher CH_4 removal capacity compared to a 15 cm thin layer. However, it is necessary to note that, CH_4 removal efficiency is not continuously increased with cover thickness but may become constant when exceeding a threshold (Bian et al., 2018; Yao et al., 2015). In general, CH_4 removal is mainly due to methanotrophic activity in the upper 30 to 40 cm of the soil cover layer where CH_4 and oxygen combine, but below 60 cm, this activity is significantly restricted due to limited oxygen (Scheutz et al., 2009). Garg and Achari, (2010) created a numerical model to simulate gas, heat, and moisture transport in sanitary landfills, as well as CH_4 oxidation in final covers, and found no significant benefit from increasing the cover depth. Similar findings were also reported in other modeling studies (Bian et al., 2018; Yao et al., 2015). In this context, it would be useful to develop an optimization design of LSC to not only ensure adequate CH_4 removal capacity but also minimize soil utilization. However, these designs need to consider other operational factors like soil moisture content and inlet CH_4 flux, as both influence gas diffusion and advection. Unfortunately, this kind of study has rarely been done with soil column studies. The methanotrophic potential of the soil material is a primary factor in determining the CH_4 removal efficiencies (La et al., 2018). Biochar has the potential to facilitate the oxidation process by increasing gas transport and microbial oxidation within landfill cover material which results in higher oxidation efficiency due to biochar’s high porosity and high-water retention capacity (Reddy et al., 2014). Using biochar amendment would improve the CH_4 removal capacity for LSC and allow for minimizing the LSC thickness to save soil and landfill capacity (Huang et al., 2024). Additionally, previous studies indicate that LSC amendments rich in compost can increase CH_4 oxidation rates to some extent by facilitating the growth of methanotrophic bacteria within the cover material (Hilger et al., 2000; Pedersen et al., 2011; Sadasivam and Reddy, 2014; Wilshusen et al., 2004). However, immature composts or compost with low air-filled porosity can produce CH_4 through methanogenesis when they become saturated and anaerobic conditions exist (Reddy et al., 2014). This work seeks to determine an optimized design of soil covers for effective CH_4

mitigation by evaluating the effectiveness of four different cover soil amendments, biochar-amended soil, compost-amended soil, woodchip-amended soil, and soil from the surface of the Three Rivers Solid Waste Authority Landfill - through a series of laboratory column experiments. The same levels of CH_4 fluxes were applied to the bottom of the column to quantify CH_4 removal efficiency and evaluate the breakthrough curve for each of the investigated materials. Here we present a novel approach by using an MQ5 gas sensor to measure the concentration of CH_4 exiting from the top of each of the columns. The performance of the soil cover amendments was compared with a conventional landfill soil cover profile.

3.2 Materials and Methods

3.2.1 Design and operations of column

The column employed in this experiment is made up of glass with 7 inches in height and 2.6 inches in diameter. Four different soil covers, namely compost, biochar, wood chips, and landfill soil, were used to set up the column types. The biochar used in this study was derived from rice husks through pyrolysis at 470°C in an oxygen-limited environment. The compost used in this work is evergreen organic compost produced from manure and contains no recycled forest products. The porosity of the soil covers used for the column experiment is provided in Table 3.1.

Table 3.1. Porosities of soil covers used for the column experiment.

Soil covers	Porosity (%)
Landfill soil	35.08 ± 1.23
Woodchips	79.03 ± 6.51
Compost	56.96 ± 1.26
Biochar	84.21 ± 4.54

The porosity of the soil covers was determined using three replicates for each material to ensure accuracy and precision were achieved. The soil covers were first weighed and placed in pre-weighed pyrex beakers, then oven-dried for 24 hours at 105°C. The oven-dried samples were then transferred into pre-weighed glass vials and carefully saturated with water to uniformly fill the pore spaces and allow the water in the soil cover to drain under gravity. The saturated weight of each sample was measured. The volume of soil in the glass vial was calculated based on the height of the soil in the glass vial and the internal diameter of the glass vial. Porosity was then determined as the ratio of the volume of voids to the total soil volume, expressed as a percentage using the equation below:

$$\text{Porosity} = \left(\frac{W_{sat} - W_{dry}}{\rho \times Volume\ of\ soil\ cover\ in\ glass\ vial}\right) \times 100\%$$

where W_{sat} is the saturated weight of soil cover and W_{dry} is the dry weight of soil cover

ρ is the density of water = 1 g / cm^3

A schematic diagram of the soil cover profiles evaluated is shown in Figure 3.1. A 0.5-inch gas distribution layer composed of gravel was placed below each column type to ensure a uniform flow of CH_4 into the base of the columns. Above the gravel, a soil cover layer was packed having different profiles as shown in Table 3.2. The column was also packed with 5 inches of each of the soil covers to analyze the breakthrough curve for each profile. A 2.5% (25000 ppm) CH_4-air balance was introduced continuously into the base of each column type at a flow rate of 2 ml/min until a breakthrough point was reached. The breakthrough point indicates when CH_4 begins to exit the column, suggesting that the soil cover has reached its CH_4 adsorption capacity. This point is critical for determining the MRE of each soil cover type. Each column type in Table 3.2 was replicated three times to increase the precision and accuracy of the results by accounting for variability within the experiment.

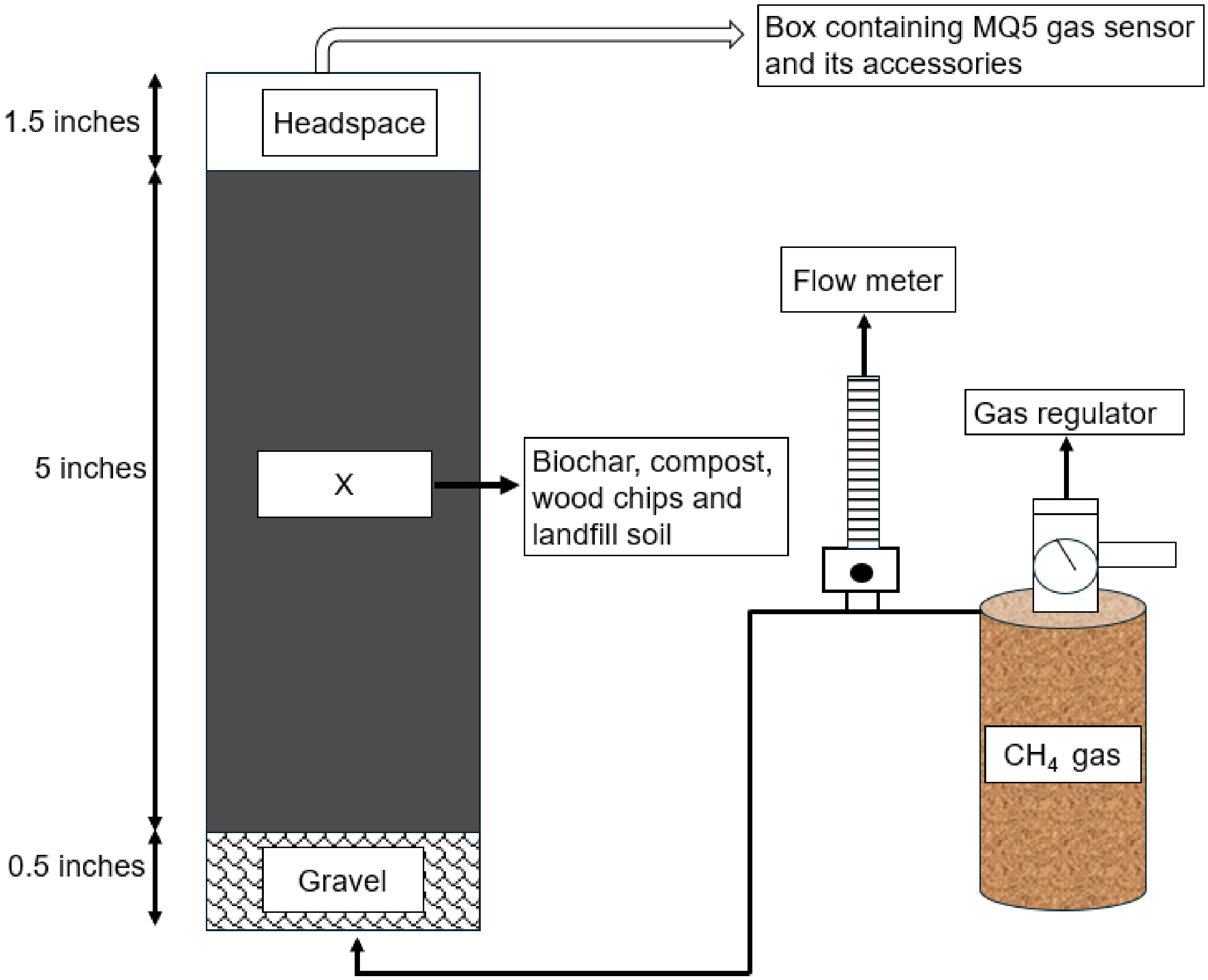


Figure 14.1. Schematic diagram of the column experiment setup.

Table 4.2. Soil cover types for column experiment.

Experiment Number	Layer composition (bottom to top)
Column 1	5 inches of landfill soil
Column 2	3 inches of landfill soil: 2 inches of woodchips
Column 3	3 inches of landfill soil: 2 inches of biochar
Column 4	3 inches of landfill soil: 2 inches of compost

The inlet and outlet flow rate of CH_4 were continuously monitored using a HARRIS GP 402 gas regulator and a Miller Brass Pipeline flow meter. The concentration of CH_4 gas exiting each column type was measured on top of the column with an MQ5 gas sensor.

The CH_4 flux entering the base of the column was calculated using the equation below:

$$J_{in} = \frac{Q_{in} \times C_{in}}{A}$$

where J_{in} is the inlet flux (g/m^2/min), C_{in} is the concentration of CH_4 gas (g/ml), Q_{in} is the inlet flow rate (ml/min), and A is the cross-sectional area of the column (m^2).

Outlet flow rates were measured separately for each column during headspace gas concentration measurements to calculate the outlet flux using the equation below:

$$J_{out} = \frac{Q_{out} \times C_{out}}{A}$$

where J_{out} is the outlet flux (g/m^2/min), C_{out} is the concentration of CH_4 gas exiting the column (g/ml), Q_{out} is the outlet flow rate of CH_4 gas (ml/min), and A is the cross-sectional area of the column (m^2).

The MRE was calculated for each cover type based on the CH_4 mass balance method using the following equation:

$$MRE = \frac{J_{in} - J_{out}}{J_{in}} \times 100\%$$

where J_{in} is the inlet CH_4 flux (g/m^2/min) and J_{out} is the outlet CH_4 flux (g/m^2/min). Several studies investigating landfill covers have employed and validated the effectiveness of this method for measuring CH_4 removal efficiencies from soil columns (Gebert et al., 2011; Rachor et al., 2011).

3.2.2 Building of MQ5 gas sensor

To start, an MQ5 gas sensor must be connected to an Arduino Uno to run. The MQ5 gas sensor has specifically been designed to work with the Arduino and needs to be connected to one to properly run. Figure 3.2 showcases a diagram of how these two devices are supposed to connect. When together, both will look like as shown in Figure 3.3. Once assembled, the system must be checked to see if it is running. To do this, the Arduino must connect to a computer, using a universal serial bus (USB)-B to USB-A cable. The USB-B side is plugged into the Arduino Uno, and USB-A side is plugged into a computer to begin the process of uploading the code to the Arduino to run the system. Long Range Radio (Lora) Transmissions are radio wave communications happening on free communication channels within the radio spectrum. LoRa offers Low Power, Wide Area (LPWA) networking protocol designed to wirelessly connect battery-operated ‘things’ to the Internet in regional, national, or global networks, and targets key Internet of Things (IoT) requirements, which for this thesis allows us to connect and send the sensor data from the sensor box to ground station set up for data analysis. It consists of a Two Dragino LoRa Kit V1 as shown in Figure 3.4.

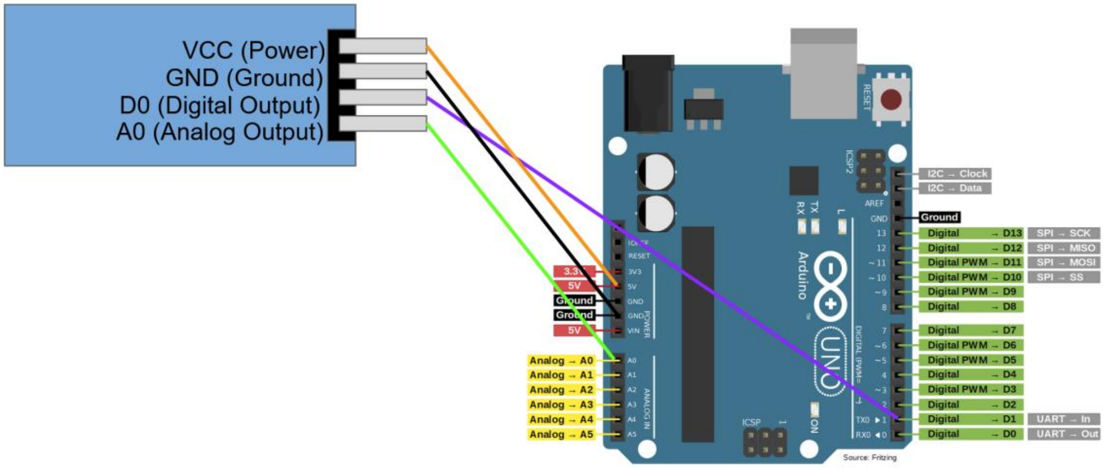


Figure 15.2. Connecting the MQ5 sensor to the Arduino Uno

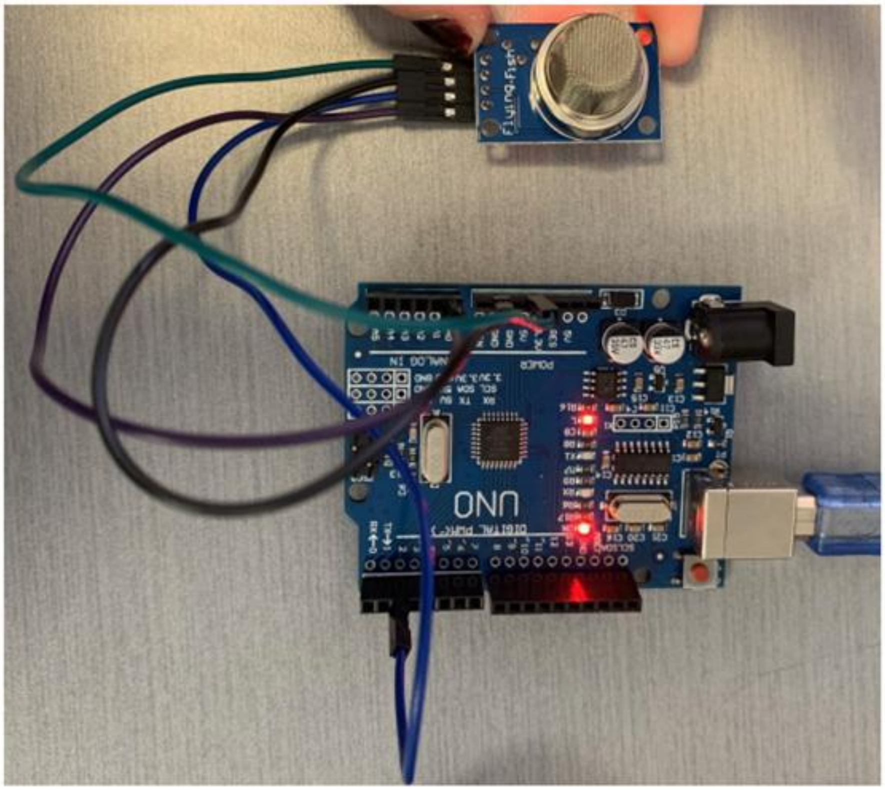


Figure 16.3. Pinout connecting the MQ5 sensor to Arduino Uno with Real Equipment

Figure 17.4. Two Dragino LoRa Kit V1

The Arduino Uno and the LoRa board are connected to a Raspberry Pi as shown in Figure 3.5. Once the Raspberry Pi is on and set up with an Operating System, a WiFi connection is set up, and a code is run within the Pi for data collection from the sensor and the LoRa board.

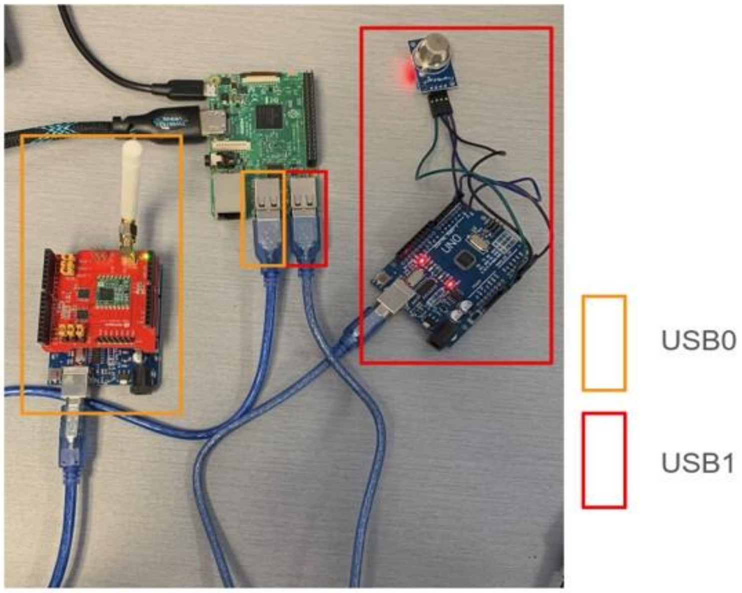


Figure 18.5. Arduino Uno and Lora board connected to a Raspberry Pi

3.2.3 Calibration of MQ5 gas sensor

Calibration of the MQ5 gas sensor was conducted using compressed air and CH_4 balance air at concentrations of 0.5%, 1.0%, 2.0%, and 2.5% of the lower explosive limit (LEL) for CH_4. The calibration was done to ensure accurate and reliable measurements, reduce potential errors, and maintain consistency with established safety standards. An R^2 value of 0.84 was obtained from the calibration curve, indicating a positive and reasonably strong correlation between CH_4 concentration and MQ5 gas sensor output value. While the R^2 value is not perfectly linear, it provides a reliable enough fit to accurately estimate CH_4 concentration trends for the column experiment. Therefore, the R^2 value of 0.84 supports the feasibility of using the MQ5 gas sensor to monitor CH_4 concentrations throughout the column experiment.

3.3 Results and Discussion

3.3.1 Column 1 – Landfill soil

The breakthrough curves for column 1 in Figure 3.6 show changes in CH_4 concentration over time until the adsorption capacity of the landfill soil is reached. The observed low CH_4 concentration at the beginning of the breakthrough curve indicates the adsorption phase, where CH_4 is adsorbed onto the porous structure of the landfill soil. The increase in CH_4 concentration marks the breakthrough point, indicating the stage at which the adsorption capacity is reached and CH_4 begins to exit the column. These findings indicate that landfill soil has a moderate capacity for CH_4 retention, which may involve adsorption or retarded transport, depending on the soil's physical and chemical properties (Huang et al., 2024b). The moderate adsorption capacity of the landfill soil is due to its small surface area and fewer active adsorption sites, which restricts its ability to retain CH_4 over extended periods (Chiu and Huang, 2020). The consistent CH_4 retention time across the three replicates of column 1 indicates that the landfill soil's physical and chemical properties provide stable and repeatable conditions for CH_4 retention.

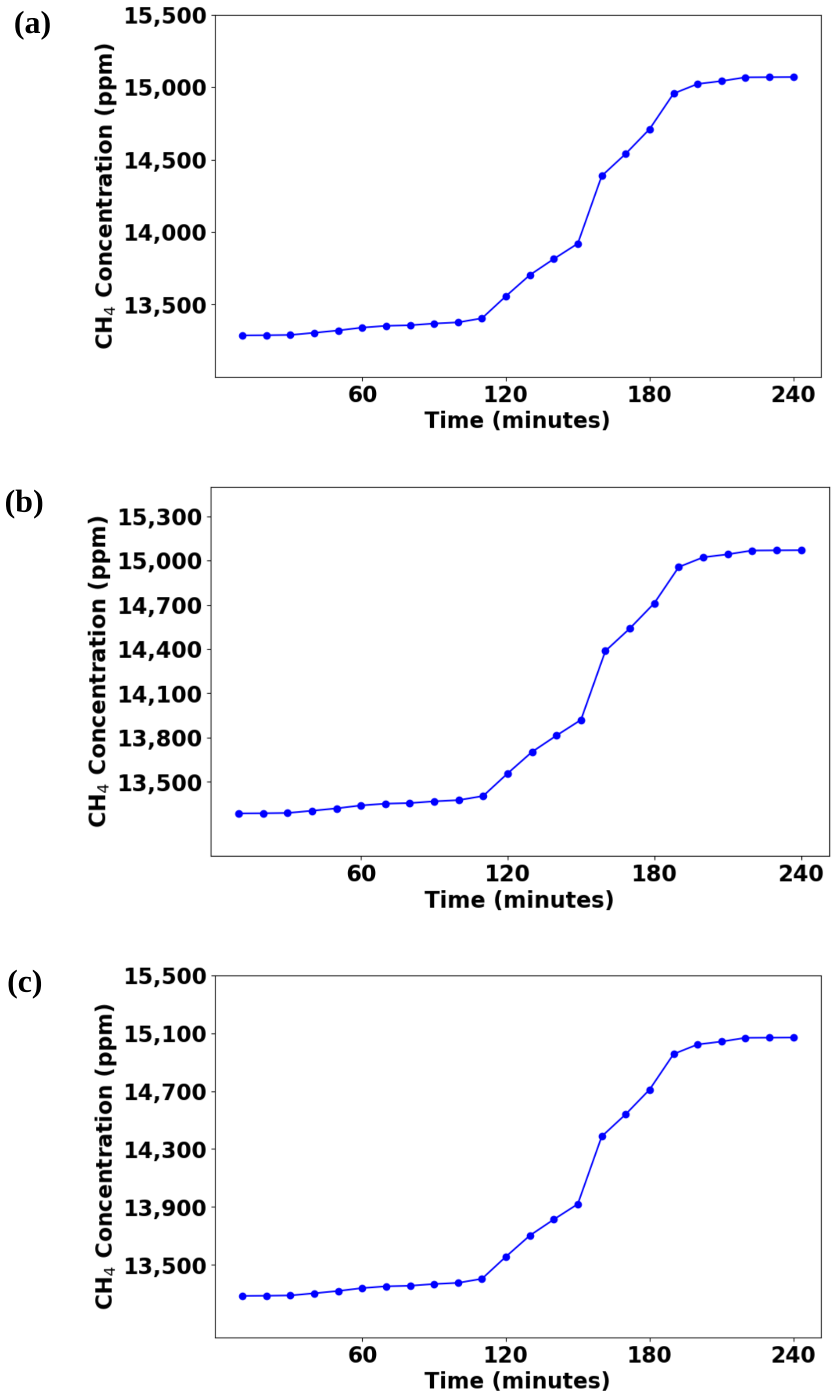


Figure 19.6. Breakthrough curves showing how methane concentration changes over time in column 1 until the adsorption capacity of the landfill soil is reached. (a), (b), and (c) represent the three replicates of the column 1 experiment.

The consistency in the results from column 1 indicates uniform accessible adsorption and pore structures within the landfill soil, yielding reproducible results and providing a baseline for evaluating how biochar, compost, and woodchips will enhance the capacity or performance of the landfill soil in reducing CH_4 emissions.

3.3.2 Column 2 - Landfill soil amended with woodchips

The CH_4 adsorption capacity of landfill soil amended with woodchips is similar to that of unamended landfill soil, as indicated in the breakthrough curves in Figure 3.7. These results suggest that woodchips did not alter the physical or chemical properties of the landfill soil to improve its CH_4 adsorption capacity. The woodchips amendment did not improve CH_4 retention time in the column, as the breakthrough curves across all three experiments remain unchanged compared to unamended landfill soil. This lack of improvement in the effectiveness or performance of the landfill soil is due to the woodchips not providing any additional active adsorption sites or pathways to improve the overall CH_4 capture efficiency of the soil. The inherent moderate adsorption capacity of the landfill soil seems to be the dominant factor controlling the CH_4 breakthrough curve. While adding woodchips to landfill soil was intended to potentially enhance CH_4 mitigation, these results indicate that it did not lead to any observable or noticeable improvements in the landfill soil's capacity to capture and retain CH_4 for prolonged periods. The breakthrough curves of the three replicates remain consistent with the previous findings for the unamended landfill soil. These findings indicate that woodchip is not an effective amendment for enhancing CH_4 adsorption in landfill soil covers.

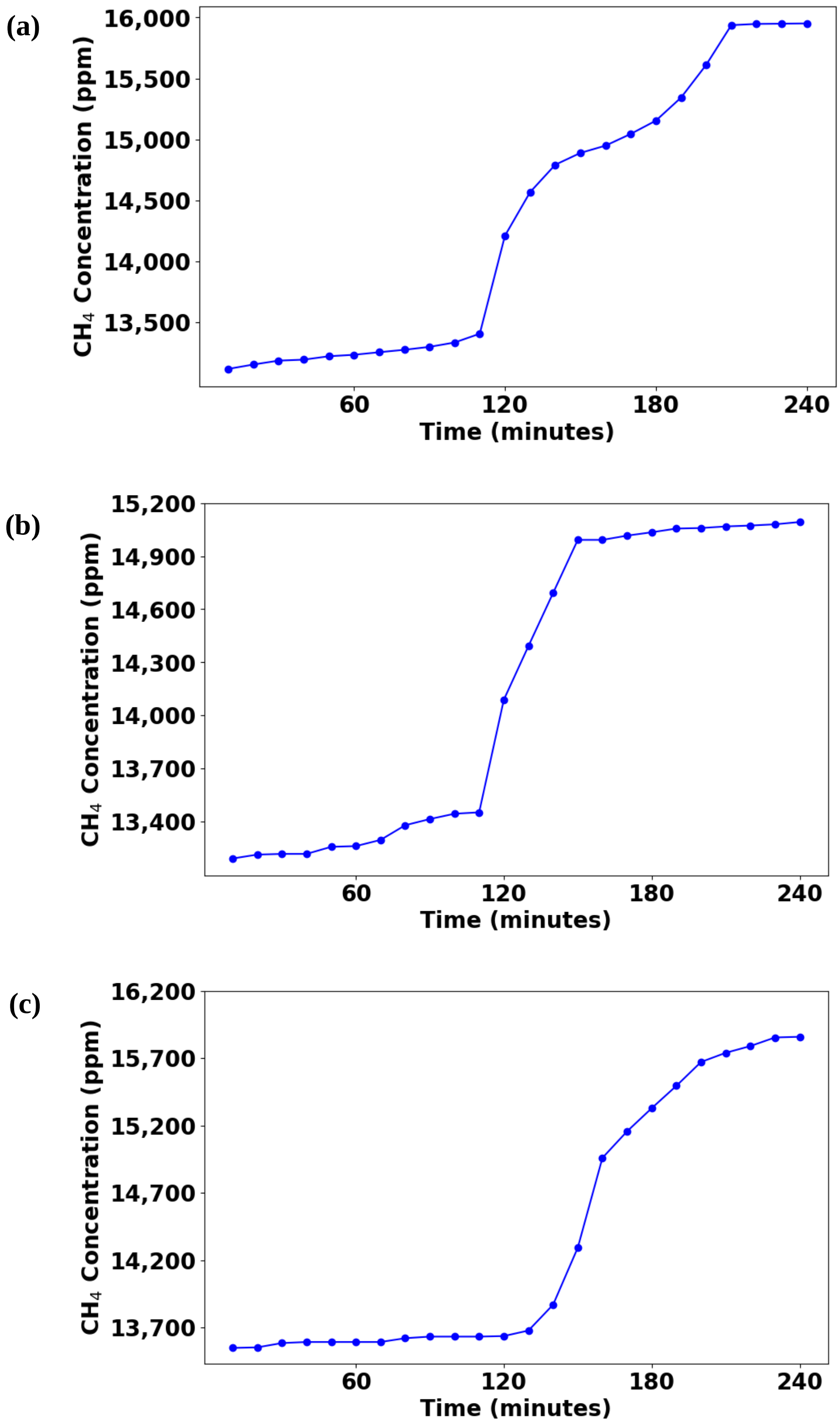


Figure 20.7. Breakthrough curves showing how methane concentration changes over time in column 2 until the adsorption capacity of the landfill soil amended with woodchips is reached. (a), (b), and (c) represent the three replicates of the column 2 experiment.

3.3.3 Column 3 - Landfill soil amended with biochar

The addition of biochar to landfill soil improved CH_4 retention time and adsorption capacity compared to unamended landfill soil, as shown by the breakthrough curves in Figure 3.8. The extended retention time across all three replicates suggests that biochar's high porosity impedes the movement of CH_4 through the column. The porous structure of biochar creates a tortuous path for CH_4 and allows more interaction with biochar, enhancing CH_4 retention time (La et al., 2019; Sadasivam and Reddy, 2015). The increase in CH_4 adsorption capacity is due to biochar's large surface area (Adlak et al., 2021; Arami-Niya et al., 2010; Hayashi et al., 2021), which provides more adsorption sites for CH_4, delaying the breakthrough point in the column. These findings show that biochar is an effective amendment to landfill soil for CH_4 mitigation. Biochar did not only improved CH_4 retention and adsorption but also increased the landfill soil's CH_4 reduction potential, making it a better soil cover amendment to the landfill soil than woodchips for CH_4 mitigation. The enhanced CH_4 adsorption capacity of biochar suggests that it could play a significant role in extending the lifespan of CH_4 mitigation systems in landfills by reducing the frequency of CH_4 emissions breakthroughs. The improved performance of the landfill soil amended with biochar implies its potential economic benefits as well, by reducing maintenance needs and extending the operational efficiency of landfill cover systems. These results underscore the potential of biochar as a sustainable and efficient amendment for CH_4 emissions mitigation.

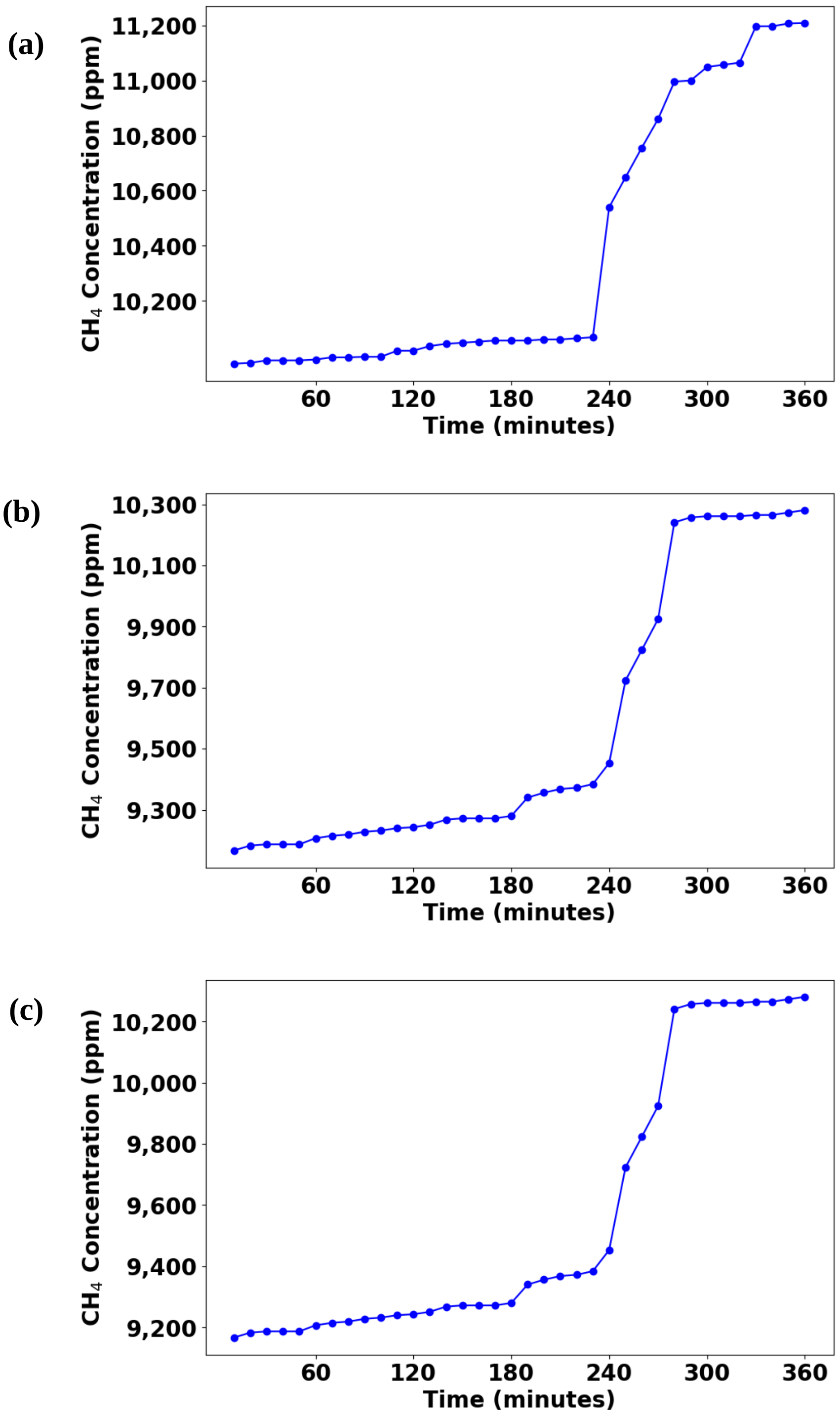
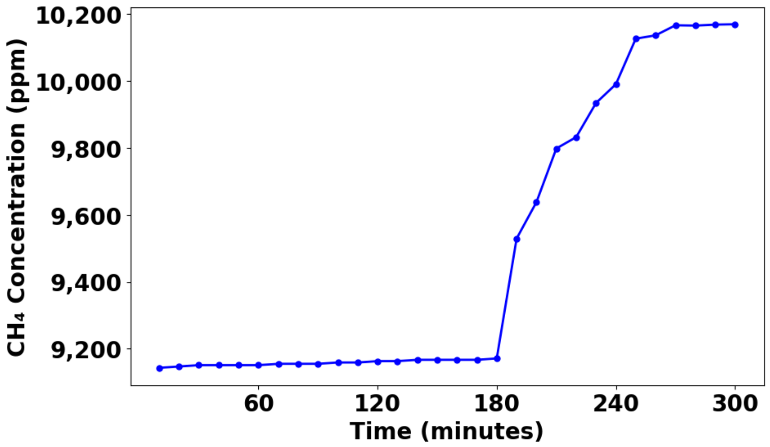


Figure 21.8. Breakthrough curves showing how methane concentration changes over time in column 3 until the adsorption capacity of the landfill soil amended with biochar is reached. (a), (b), and (c) represent the three replicates of the column 3 experiment.

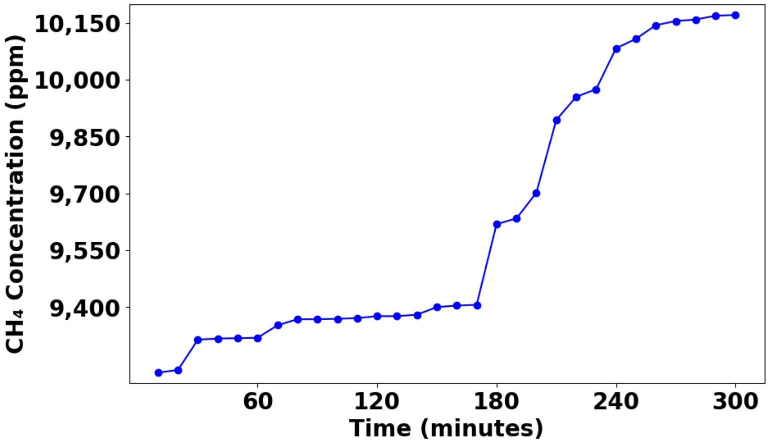
3.3.4 Column 4 - Landfill soil amended with compost

The addition of compost to landfill soil improved CH_4 retention time compared to unamended landfill soil, as shown across all three replicates in Figure 3.9. This suggests that the organic content of the compost enhances the physical and chemical structure of the soil, increasing its ability to retain CH_4 gas for longer periods. The organic matter in compost also helps retain moisture, promoting the growth of the methanotrophic bacteria (Fang et al., 2022; Syed et al., 2016) by providing essential nutrients and expanding their habitats. These methanotrophic bacteria consume CH_4 as a source of carbon and energy, effectively reducing CH_4 emissions exiting the column. The results demonstrate that compost can create a favorable environment for microbial CH_4 mitigation, making it an effective amendment for landfill soil in reducing CH_4 emissions.

(a)



(b)



(c)

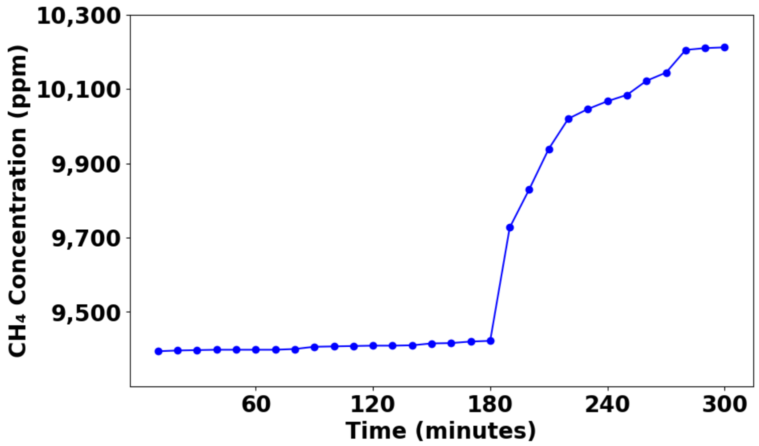


Figure 22.9. Breakthrough curves showing how methane concentration changes over time in column 4 until the adsorption capacity of the landfill soil amended with compost is reached. (a), (b), and (c) represent the three replicates of the column 4 experiment.

3.3.5 Comparison of methane adsorption potential of the soil covers

Figure 3.10 shows the breakthrough curves for biochar, woodchips, compost, and landfill soil, each packed separately into the column to a height of 5 inches. Biochar is the soil cover with the highest CH_4 retention capacity, as evidenced by its delayed breakthrough curve. CH_4 concentrations remained consistently low and stable over an extended period in the column, highlighting biochar's high porosity and large surface area, which significantly enhanced its CH_4 adsorption capabilities. The results confirm that biochar is an effective amendment material for enhancing the CH_4 mitigation potential of landfill covers. Compost is the most effective soil cover after biochar. The breakthrough shows that compost can adsorb CH_4 and retain CH_4 in the column due to its organic content and nutrient-rich composition, which creates a favorable environment for the growth of methanotrophic bacteria that consume CH_4 as their source of carbon and energy. The landfill soil exhibited a moderate CH_4 adsorption capacity when compared to biochar and compost. The moderate adsorption capacity of the landfill soil is due to the low porosity and small surface area in most landfill soils which restrict their ability to adsorb CH_4 for extended duration.

The results of the landfill soil will low methane removal efficiency align with previous studies (Chiemchaisri et al., 2012; Stein and Hettiaractchi 2010) which highlight the moderate CH_4 adsorption capacity of unamended landfill soil. Among the soil covers tested, woodchips showed the lowest effectiveness in reducing CH_4 in the column experiment. This is due to the low surface area and the lack of adequate adsorption sites of the woodchip to adsorb CH_4. The woodchips did not create conditions to support the methanotrophic bacterial activity for CH_4 oxidation in the column. These results imply that woodchips are an ineffective amendment to landfill soil covers for mitigating CH_4 emissions. The breakthrough curves for woodchips, compost, and biochar are provided in the Appendix.

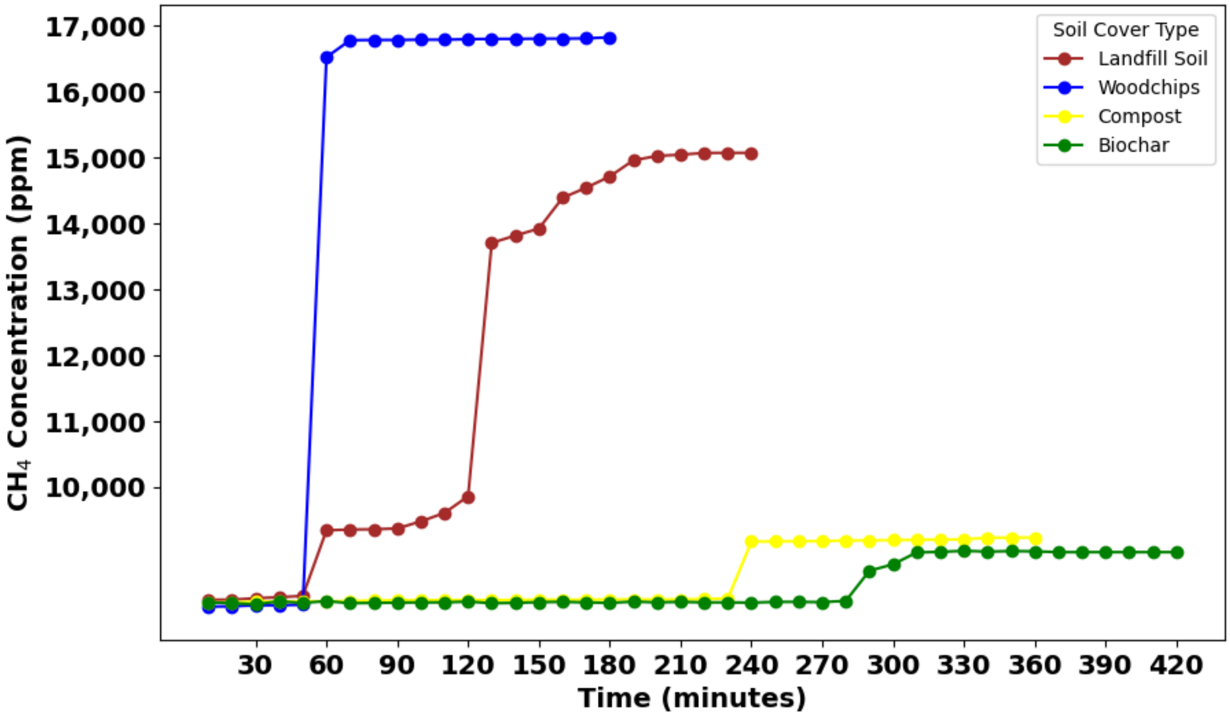


Figure 23.10. Breakthrough curves for methane concentrations over time in the column packed separately with biochar, woodchips, compost, and landfill soil to a height of 5 inches, illustrating the methane adsorption and retention performance of each cover material.

3.3.6 Comparison of methane removal efficiencies of column types

Figure 3.11 contains the methane removal efficiencies (MRE) of the column types investigated in this study, calculated using the mass balance method. The MRE calculated for column 1 and column 2 are comparatively low while that of column 3 and column 4 achieved high MRE values. MRE of column 1 is consistent with previous work by Stein and Hettiaratchi, (2010) who reported MRE of 32.0 to 37.6 % for landfill loam soil with a flow rate of 2.5 ml/min. Follow-up work by Chiemchaisri et al., (2010) observed MRE of 30 to 40% for sandy loam soil with a bottom flow rate of 3.9 ml/min. The results highlight the moderate CH_4 adsorption capacity of unamended soil covers and the importance of using organic-rich materials such as compost, biochar, and sewage sludge, either alone or as an amendment to landfill cover soils. The MRE of landfill soil amended with biochar shown in Figure 3.11 demonstrates the key role biochar plays in increasing the CH_4 adsorption and removal capacity of landfill soil. Huang et al. (2024a) reported an MRE of 59.8% to 64.3% using a 20 cm biochar layer on top of 45 cm of fresh loam soil, with a 10 cm gravel layer at the bottom of the column. The consistency in the soil amended with biochar results further validates biochar as an effective amendment for enhancing CH_4 mitigation in landfill soil. The landfill soil amended with compost showed a higher MRE compared to unamended landfill soil. This improvement is due to the organic content of compost which supports microbial activity by providing essential nutrients and retaining moisture. These conditions promote the growth of methanotrophic bacteria, which consume CH_4 as a carbon and energy source, thereby helping to reduce CH_4 emissions. The MRE of compost in this study aligns with the findings of Brandt et al. (2016), who achieved an MRE of 56% using organic leafy compost packed to a depth of 100 cm.

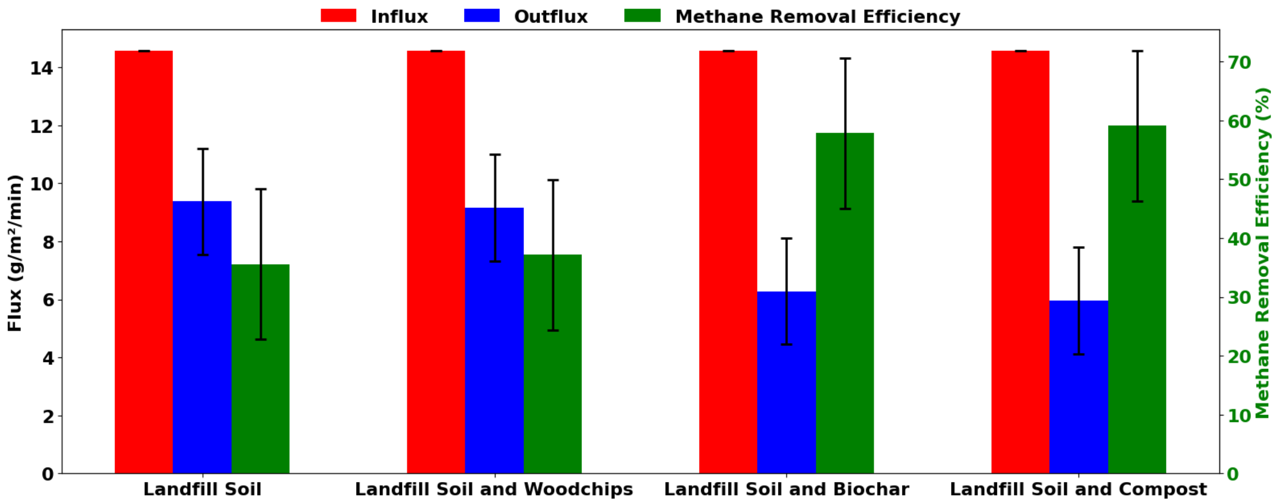


Figure 24.11. Comparison of methane removal efficiencies of the different soil cover amendments used for the column experiment.

3.4 Conclusion

In this chapter, we evaluated the effectiveness of four different soil cover amendments landfill soil, landfill soil-amended woodchips, biochar, and compost in mitigating CH_4 releases in a series of laboratory column experiments. The results demonstrated that landfill soil amended with biochar and compost significantly enhanced CH_4 retention time in the column, CH_4 adsorption, and increased CH_4 removal efficiency compared to unamended landfill soil. The high porosity and large surface area of biochar provided additional adsorption sites, effectively delaying the CH_4 breakthrough and allowing for prolonged retention within the column. Compost also showed enhanced CH_4 removal efficiency, due to its organic content, which promotes microbial activity, particularly CH_4-oxidizing bacteria, by supplying nutrients and retaining moisture in the column. However, landfill soil amended with woodchips did not yield noticeable improvements in CH_4 mitigation, due to the lack of additional adsorption sites and minimal changes to the soil's physical and chemical properties. These findings underscore the potential of biochar and compost as effective amendments for enhancing CH_4 mitigation in landfill soil covers, offering a practical and cost-efficient solution for reducing CH_4 emissions. By identifying biochar and compost amendments to landfill soil can improve CH_4 adsorption and removal efficiency, this study contributes to advancing sustainable waste management practices and reducing the release of landfill CH_4 emissions into the atmosphere.

REFERENCES

Abichou, T., Chanton, J., Powelson, D., Fleiger, J., Escoriaza, S., Lei, Y., & Stern, J. (2006). Methane flux and oxidation at two types of intermediate landfill covers. Waste Management, 26(11), 1305–1312. https://doi.org/10.1016/j.wasman.2005.11.016

Adlak, K., Chandra, R., Vijay, V. K., & Pant, K. K. (2021). Physicochemical activation and palletisation of Azadirachta indica wood carbons for increased biomethane adsorbed energy storage. Journal of Analytical and Applied Pyrolysis, 155(March), 105102. https://doi.org/10.1016/j.jaap.2021.105102

Arami-Niya, A., Daud, W. M. A. W., & Mjalli, F. S. (2010). Using granular activated carbon prepared from oil palm shell by ZnCl 2 and physical activation for methane adsorption. Journal of Analytical and Applied Pyrolysis, 89(2), 197–203. https://doi.org/10.1016/j.jaap.2010.08.006

Bian, R., Xin, D., & Chai, X. (2018). A Simulation model for estimating methane oxidation and emission from landfill cover soils. Waste Management, 77, 426–434. https://doi.org/10.1016/j.wasman.2018.04.029

Brandt, E. M. F., Duarte, F. V., Vieira, J. P. R., Melo, V. M., Souza, C. L., Araújo, J. C., & Chernicharo, C. A. L. (2016). The use of novel packing material for improving methane oxidation in biofilters. Journal of Environmental Management, 182, 412–420. https://doi.org/10.1016/j.jenvman.2016.07.075

Chiemchaisri, C., Chiemchaisri, W., Chittanukul, K., Soontornlerdwanich, W., & Tanthachoon, N. (2010). Effect of leachate irrigation on methane oxidation in tropical landfill cover soil. Journal of Material Cycles and Waste Management, 12(2), 161–168. https://doi.org/10.1007/s10163-009-0284-y

Chiemchaisri, C., Chiemchaisri, W., Kumar, S., & Wicramarachchi, P. N. (2012). Reduction of Methane Emission From Landfill Through Microbial Activities in Cover Soil: A Brief Review. Critical Reviews in Environmental Science and Technology, 42(4), 412–434. https://doi.org/10.1080/10643389.2010.520233

Chiu, C. F., & Huang, Z. D. (2020). Microbial Methane Oxidation and Gas Adsorption Capacities of Biochar-Modified Soils. International Journal of Geosynthetics and Ground Engineering, 6(2), 1–14. https://doi.org/10.1007/s40891-020-00202-5

Fang, C., Su, Y., He, X., Han, L., Qu, H., Zhou, L., & Huang, G. (2022). Membrane-covered composting significantly decreases methane emissions and microbial pathogens: Insight into the succession of bacterial and fungal communities. Science of the Total Environment, 845(April). https://doi.org/10.1016/j.scitotenv.2022.157343

Garg, A., & Achari, G. (2010). A Comprehensive Numerical Model Simulating Gas, Heat, and Moisture Transport in Sanitary Landfills and Methane Oxidation in Final Covers. Environmental Modeling and Assessment, 15(5), 397–410. https://doi.org/10.1007/s10666-009-9217-3

Gebert, J., Groengroeft, A., & Pfeiffer, E. M. (2011). Relevance of soil physical properties for the microbial oxidation of methane in landfill covers. Soil Biology and Biochemistry, 43(9), 1759–1767. https://doi.org/10.1016/j.soilbio.2010.07.004

Gebert, J., Huber-Humer, M., & Cabral, A. R. (2022). Design of Microbial Methane Oxidation Systems for Landfills. Frontiers in Environmental Science, 10(September), 1–28. https://doi.org/10.3389/fenvs.2022.907562

Gebert, J., Rachor, I., Gröngröft, A., & Pfeiffer, E. M. (2011). Temporal variability of soil gas composition in landfill covers. Waste Management, 31(5), 935–945. https://doi.org/10.1016/j.wasman.2010.10.007

Gebert, J., Röwer, I. U., Scharff, H., Roncato, C. D. L., & Cabral, A. R. (2011). Can soil gas profiles be used to assess microbial CH4 oxidation in landfill covers? Waste Management, 31(5), 987–994. https://doi.org/10.1016/j.wasman.2010.10.008

Grégoire, D. S., George, N. A., & Hug, L. A. (2023). Microbial methane cycling in a landfill on a decadal time scale. Nature Communications, 14(1). https://doi.org/10.1038/s41467-023-43129-x

Hayashi, J., Hasegawa, I., Hagihara, T., & Takara, T. (2021). Production of activated carbon with a large specific surface area from banana peel and its methane adsorption ability. Carbon, 176(293), 656. https://doi.org/10.1016/j.carbon.2021.01.100

Hettiaratchi, J. P. A. (2007). New trends in waste management: North American perspective. International Conference on Sustainable Solid Waste Management, January 2007, 9–14.

Hilger, H. A., Cranford, D. F., & Barlaz, M. A. (2000). Methane oxidation and microbial exopolymer production in landfill cover soil. Soil Biology and Biochemistry, 32(4), 457–467. https://doi.org/10.1016/S0038-0717(99)00101-7

Huang, D., Chen, Y., Bai, X., Zhang, R., Chen, Q., Wang, N., & Xu, Q. (2024a). Methane removal efficiencies of biochar-mediated landfill soil cover with reduced depth. Journal of Environmental Management, 355(October 2023). https://doi.org/10.1016/j.jenvman.2024.120487

Huang, D., Chen, Y., Bai, X., Zhang, R., Chen, Q., Wang, N., & Xu, Q. (2024b). Methane removal efficiencies of biochar-mediated landfill soil cover with reduced depth. Journal of Environmental Management, 355(February), 120487. https://doi.org/10.1016/j.jenvman.2024.120487

Kollikkathara, N., Feng, H., & Stern, E. (2009). A purview of waste management evolution: Special emphasis on USA. Waste Management, 29(2), 974–985. https://doi.org/10.1016/j.wasman.2008.06.032

La, H., Hettiaratchi, J. P. A., & Achari, G. (2019). The influence of biochar and compost mixtures, water content, and gas flow rate, on the continuous adsorption of methane in a fixed bed column. Journal of Environmental Management, 233(October 2018), 175–183. https://doi.org/10.1016/j.jenvman.2018.12.015

La, H., Hettiaratchi, J. P. A., Achari, G., & Dunfield, P. F. (2018). Biofiltration of methane. Bioresource Technology, 268(July), 759–772. https://doi.org/10.1016/j.biortech.2018.07.043

Molins, S., & Mayer, K. U. (2007). Coupling between geochemical reactions and multicomponent gas and solute transport in unsaturated media: A reactive transport modeling study. Water Resources Research, 43(5), 1–16. https://doi.org/10.1029/2006WR005206

Pawłowska, M., Rozej, A., & Stepniewski, W. (2011). The effect of bed properties on methane removal in an aerated biofilter - Model studies. Waste Management, 31(5), 903–913. https://doi.org/10.1016/j.wasman.2010.10.005

Pedersen, G. B., Scheutz, C., & Kjeldsen, P. (2011). Availability and properties of materials for the Fakse Landfill biocover. Waste Management, 31(5), 884–894. https://doi.org/10.1016/j.wasman.2010.11.020

Rachor, I., Gebert, J., Gröngröft, A., & Pfeiffer, E. M. (2011a). Assessment of the methane oxidation capacity of compacted soils intended for use as landfill cover materials. Waste Management, 31(5), 833–842. https://doi.org/10.1016/j.wasman.2010.10.006

Rachor, I., Gebert, J., Gröngröft, A., & Pfeiffer, E. M. (2011b). Assessment of the methane oxidation capacity of compacted soils intended for use as landfill cover materials. Waste Management, 31(5), 833–842. https://doi.org/10.1016/j.wasman.2010.10.006

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), 1–11. https://doi.org/10.1061/(asce)gt.1943-5606.0001148

Roncato, C. D. L., & Cabral, A. R. (2012). Evaluation of Methane Oxidation Efficiency of Two Biocovers: Field and Laboratory Results. Journal of Environmental Engineering, 138(2), 164–173. https://doi.org/10.1061/(asce)ee.1943-7870.0000475

Sadasivam, B. Y., & Reddy, K. R. (2014). Landfill methane oxidation in soil and bio-based cover systems: A review. Reviews in Environmental Science and Biotechnology, 13(1), 79–107. https://doi.org/10.1007/s11157-013-9325-z

Sadasivam, B. Y., & Reddy, K. R. (2015). Adsorption and transport of methane in landfill cover soil amended with waste-wood biochars. Journal of Environmental Management, 158, 11–23. https://doi.org/10.1016/j.jenvman.2015.04.032

Scheutz, C., Kjeldsen, P., Bogner, J. E., De Visscher, A., Gebert, J., Hilger, H. A., Huber-Humer, M., & Spokas, K. (2009). Microbial methane oxidation processes and technologies for mitigation of landfill gas emissions. Waste Management and Research, 27(5), 409–455. https://doi.org/10.1177/0734242X09339325

Spokas, K. A., & Bogner, J. E. (2011). Limits and dynamics of methane oxidation in landfill cover soils. Waste Management, 31(5), 823–832. https://doi.org/10.1016/j.wasman.2009.12.018

Stein, V. B., & Hettiaratchi, J. P. A. (2001). Methane oxidation in three alberta soils: Influence of soil parameters and methane flux rates. Environmental Technology (United Kingdom), 22(1), 101–111. https://doi.org/10.1080/09593332208618315

Stone, K. A., Hilliard, M. V., He, Q. P., & Wang, J. (2017). A mini review on bioreactor configurations and gas transfer enhancements for biochemical methane conversion. Biochemical Engineering Journal, 128, 83–92. https://doi.org/10.1016/j.bej.2017.09.003

Syed, R., Saggar, S., Tate, K., & Rehm, B. H. A. (2016). Assessment of farm soil, biochar, compost and weathered pine mulch to mitigate methane emissions. Applied Microbiology and Biotechnology, 100(21), 9365–9379. https://doi.org/10.1007/s00253-016-7794-z

Weitz, K. A., Thorneloe, S. A., Nishtala, S. R., Yarkosky, S., & Zannes, M. (2002). The impact of municipal solid waste management on greenhouse gas emissions in the United States. Journal of the Air and Waste Management Association, 52(9), 1000–1011. https://doi.org/10.1080/10473289.2002.10470843

Wilshusen, J. H., Hettiaratchi, J. P. A., De Visscher, A., & Saint-Fort, R. (2004). Methane oxidation and formation of EPS in compost: Effect of oxygen concentration. Environmental Pollution, 129(2), 305–314. https://doi.org/10.1016/j.envpol.2003.10.015

Yao, Y., Su, Y., Wu, Y., Liu, W., & He, R. (2015). An analytical model for estimating the reduction of methane emission through landfill cover soils by methane oxidation. Journal of Hazardous Materials, 283, 871–879. https://doi.org/10.1016/j.jhazmat.2014.10.035

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. https://doi.org/10.1016/j.jenvman.2017.01.068

Yargicoglu, E. N., & Reddy, K. R. (2018). Biochar-Amended Soil Cover for Microbial Methane Oxidation: Effect of Biochar Amendment Ratio and Cover Profile. Journal of Geotechnical and Geoenvironmental Engineering, 144(3), 1–15. https://doi.org/10.1061/(asce)gt.1943-5606.0001845

Yusuf, R. O., Noor, Z. Z., Abba, A. H., Hassan, M. A. A., & Din, M. F. M. (2012). Methane emission by sectors: A comprehensive review of emission sources and mitigation methods. Renewable and Sustainable Energy Reviews, 16(7), 5059–5070. https://doi.org/10.1016/j.rser.2012.04.008

Zhao, Q., Wang, Y., Xu, Z., & Yu, Z. (2021). How does biochar amendment affect soil methane oxidation? A review. Journal of Soils and Sediments, 21(4), 1575–1586. https://doi.org/10.1007/s11368-021-02889-z

4 CONCLUSION

This thesis examined surface CH_4 emissions and mitigation efforts at a municipal landfill, Three Rivers Solid Waste, and evaluated the effectiveness of soil cover amendments in reducing CH_4 emissions through laboratory column experiments. The first part focuses on understanding surface CH_4 emissions at the landfill site by creating heat maps to identify spatial and temporal hotspots of CH_4 emissions and assessing the immediate effects of soil cover application in reducing CH_4 emissions. The second section considered CH_4 retention time and breakthrough curves to evaluate the CH_4 adsorption and removal efficiencies of four different cover soil amendments. This analysis approaches the problem from two perspectives: one examines the CH_4 retention characteristics of the cover soils, while the other evaluates their overall effectiveness in reducing CH_4 releases over time.

In Chapter 2, we analyzed surface CH_4 emissions from a municipal solid waste landfill to evaluate the effectiveness of soil cover applications in mitigating CH_4 emissions. CH_4 emissions were monitored quarterly between the fourth quarter of 2021 and the first quarter of 2023 using the Inficon IRwin SX (IRwin) CH_4 Leak Detector. CH_4 emissions exceeding 500 ppm were identified as exceedance points, where soil covers were applied as corrective measures. CH_4 levels at these locations were rechecked within 10- and 30 days post soil cover application to determine the reduction in emissions. We developed heat maps using the ordinary kriging tool in ArcGIS Pro to visualize the spatial and temporal trends in CH_4 concentrations. The data revealed that CH_4 emissions peaked in the first quarter of 2023 and the lowest in the third quarter of 2022. Soil cover applications effectively reduced CH_4 emissions at most exceedance points within 10 days. However, an anomaly in the third quarter of 2022 showed a CH_4 increase from 1394 ppm to 3978 ppm at one monitoring point, caused by insufficient soil cover thickness or subsurface CH_4

migration pathways. Between 10 and 30 days, emission trends varied: 25% of points experienced further reductions, 64% showed increases, and 11% remained consistent. Despite this variability, CH_4 levels significantly reduced between the initial measurements and the 30-day review, with decreases ranging from 37.04% to 100%. These results highlight the potential of soil covers as effective short-term mitigation strategies for reducing landfill CH_4 emissions. However, the variability in performance emphasizes the need to optimize soil cover materials and amendments for improved outcomes. The study also underscores the importance of continued monitoring and consistent data collection to better understand CH_4 dynamics and enhance long-term mitigation strategies.

Chapter 3 of this work investigated the CH_4 adsorption and removal efficiencies of four different landfill cover amendments - landfill soil, biochar, compost, and woodchips - using a series of laboratory column experiments. The goal was to evaluate the CH_4 retention capacity of each soil cover and determine the effectiveness of landfill soil amended with biochar, compost, and woodchip in enhancing CH_4 mitigation compared to unamended landfill soil. CH_4 gas was introduced into the base of each column at a controlled rate, and breakthrough curves were analyzed to determine the CH_4 retention time and calculate CH_4 removal efficiencies for each cover type. Each column experiment was replicated three times, and the results were compared to identify trends in their performance. Breakthrough curves showed that biochar significantly enhanced CH_4 retention and adsorption, delaying the breakthrough point due to its high porosity and large surface area. Compost also improved CH_4 retention by supporting microbial activity through its organic content. On the other hand, woodchips showed no measurable improvement in CH_4 adsorption capacity, due to their limited surface area and lack of adsorption sites. The unamended landfill soil served as a baseline, demonstrating moderate CH_4 retention capacity. CH_4

removal efficiencies were calculated for each cover type, revealing that landfill soil amended with biochar and compost achieved the highest MREs, with reductions ranging from 55.6% to 59.3%. These findings highlight the potential of biochar and compost as effective amendments for enhancing CH_4 mitigation. The results also underscore the variability in performance among different soil covers, emphasizing the importance of selecting and optimizing soil covers for effective CH_4 mitigation.

4.1 Future work

While this study demonstrated the potential of soil cover amendments for mitigating CH_4 emissions, several avenues for future research remain unexplored. In Chapter 2, the analysis of surface CH_4 emissions relied on quarterly monitoring, but higher-frequency measurements could provide a more detailed understanding of temporal fluctuations and the dynamics of CH_4 migration pathways. Deploying a network of MQ5 gas sensors across the landfill could generate high-resolution data, helping to quantify CH_4 fluxes with greater accuracy and improve the detection of emission hotspots. Additionally, addressing the anomaly observed in the third quarter of 2022, where CH_4 emissions increased despite soil cover application, would require further investigation into factors such as soil cover degradation, subsurface gas migration, and the potential impact of environmental conditions.

In Chapter 3, the laboratory column experiments highlighted the efficacy of biochar and compost amendments in enhancing CH_4 retention and removal. However, further research is needed to optimize the composition and thickness of these amendments for field-scale applications. For instance, testing biochar produced under different pyrolysis conditions or compost with varying organic content could provide insights into the specific characteristics that maximize CH_4 mitigation. Moreover, the long-term stability of these amendments, particularly their ability to maintain CH_4 removal efficiency over extended periods, should be investigated under variable environmental conditions such as changes in moisture and temperature. Also, future research could include using a 1-D model of the system to validate the breakthrough curve results and analyzing tracer breakthrough curves for the soil covers evaluated in this study.

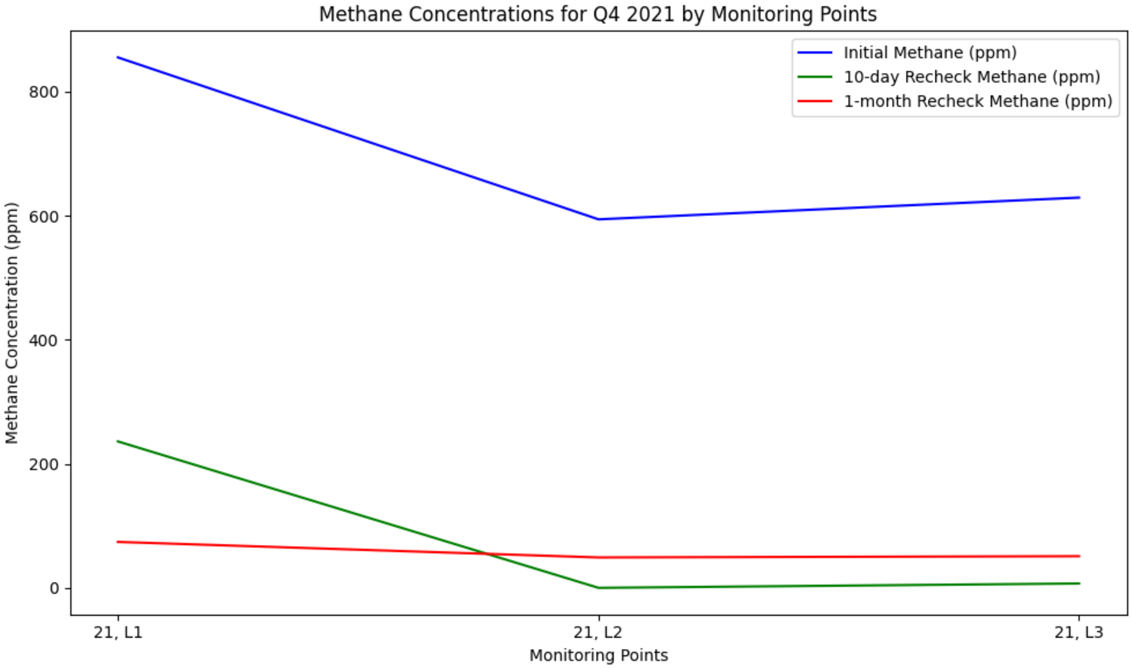
APPENDICES

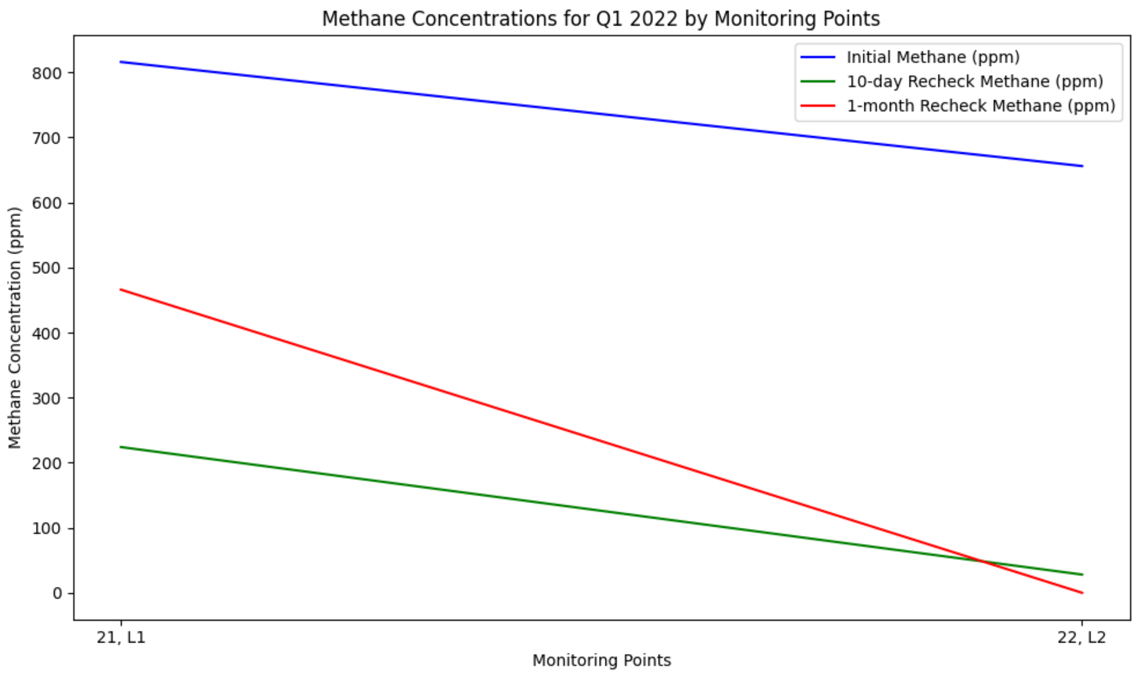
Appendix A: Root mean square error, mean standardized error, root mean square standardized error, and average standard error of ordinary kriging method used for predicting surface methane emissions from the landfill.

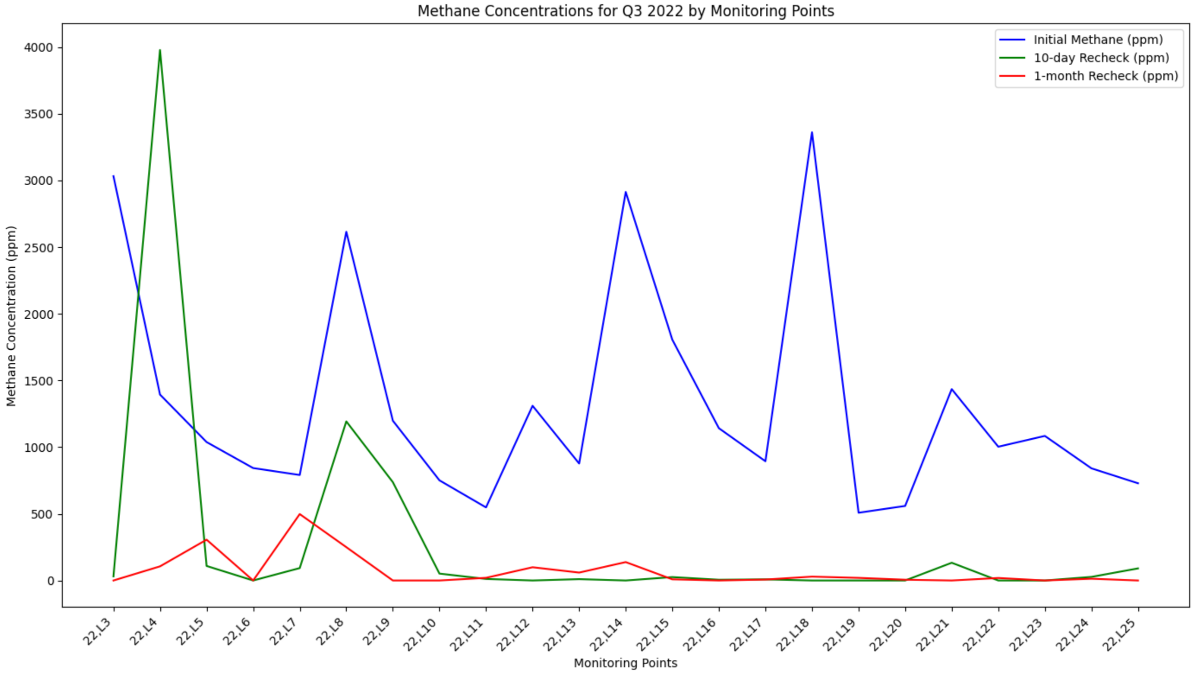
Appendix A.1 Initial, 10-day recheck, and 30-day recheck of methane emissions

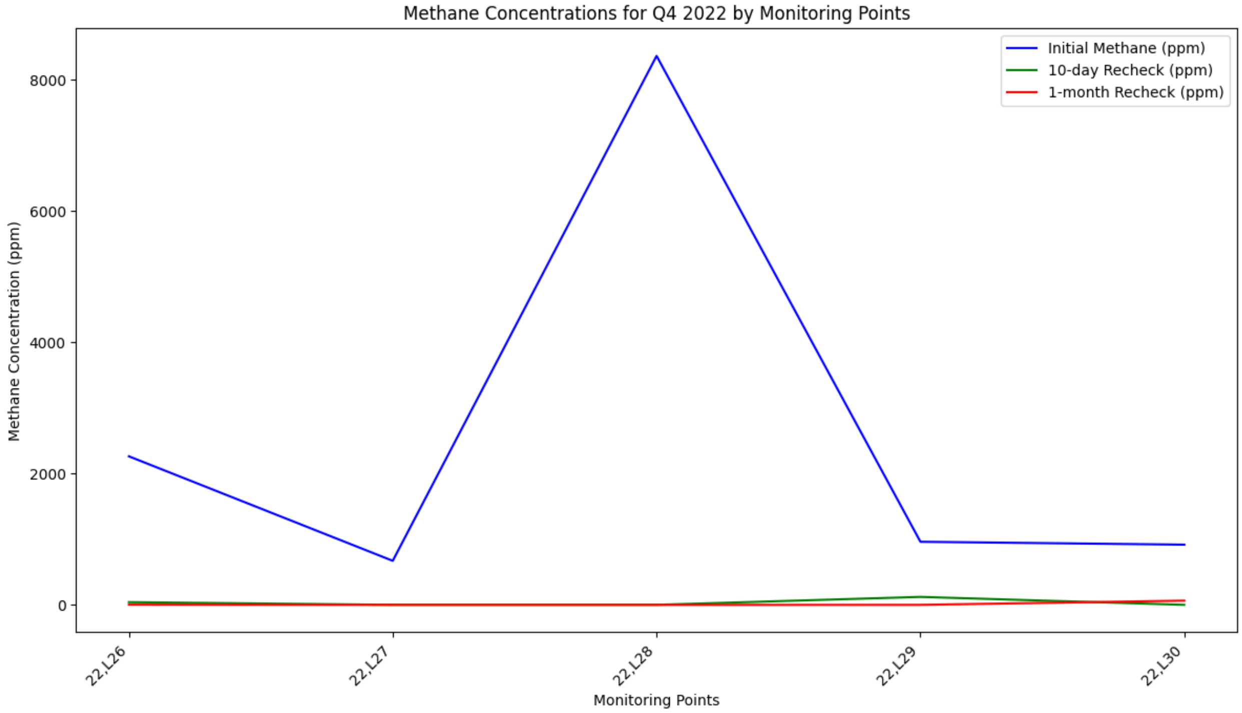
	Count	**Root Mean Square**	**Mean Standardized**	**Root mean Square Standardized**	**Average Standard Error**
Initial	43	2605	0.02	1.32	1967
10-day recheck	43	633	0.03	1.13	556
30-day recheck	43	108	0.02	1.07	101

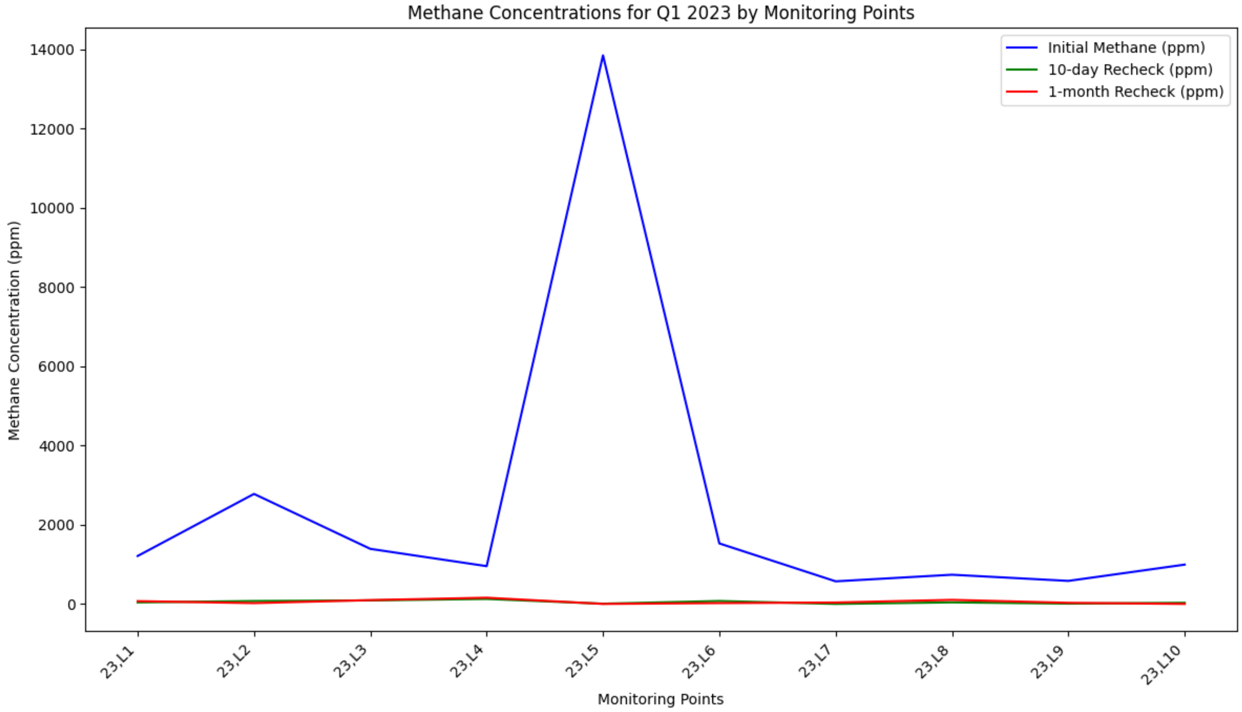
Appendix A.2 Quarterly changes in surface methane emissions for initial, 10-day recheck, and 30-day recheck measurements from the fourth quarter of 2021 to the first quarter of 2023 by monitoring points



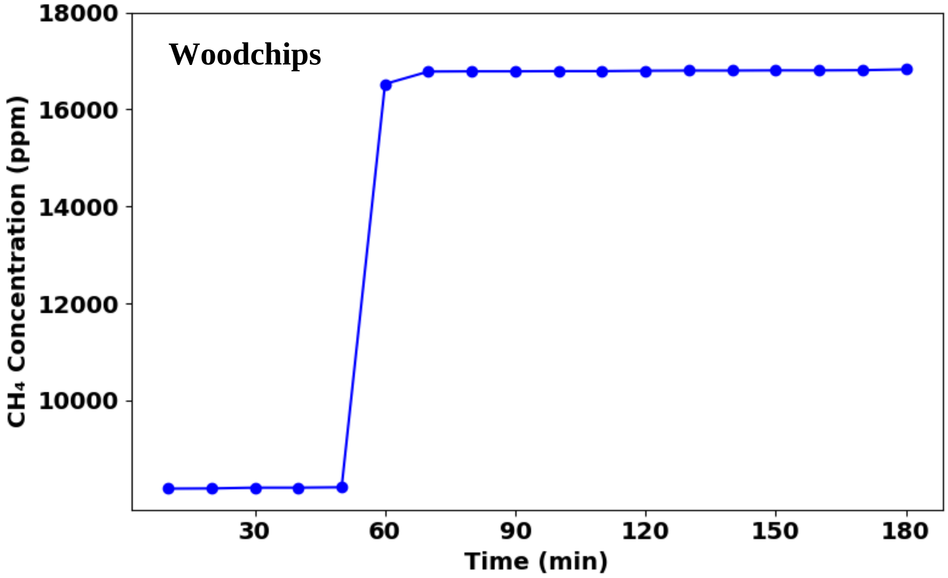

Methane Concentrations for Q1 2022 by Monitoring Points
Initial Methane (ppm)
10-day Recheck Methane (ppm)
1-month Recheck Methane (ppm)
Methane Concentration (ppm)
800
700
600
500
400
300
200
100
0
21, L1
22, L2
Monitoring Points

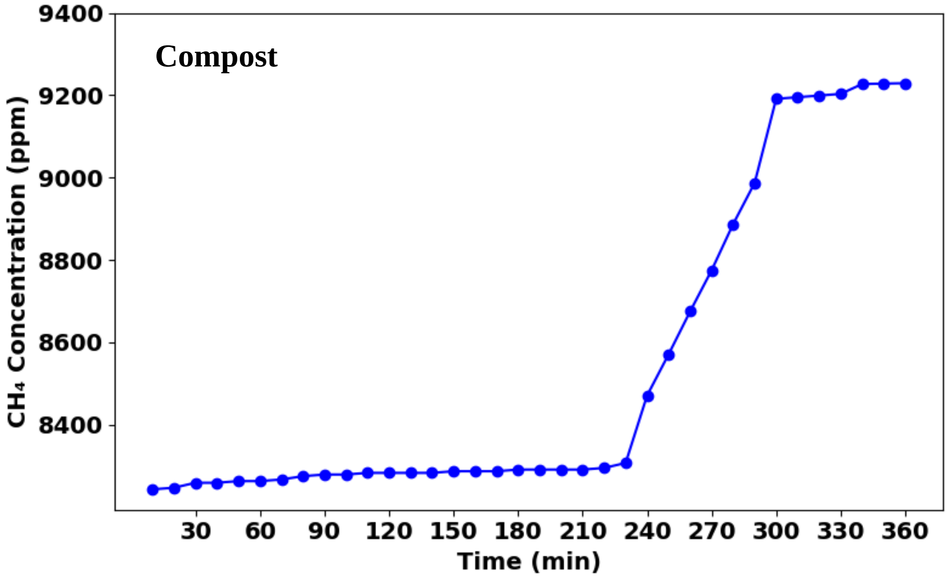

Methane Concentrations for Q3 2022 by Monitoring Points
Initial Methane (ppm)
10-day Recheck (ppm)
1-month Recheck (ppm)
Methane Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
22,L3
22,L4
22,L5
22,L6
22,L7
22,L8
22,L9
22,L10
22,L11
22,L12
22,L13
22,L14
22,L15
22,L16
22,L17
22,L18
22,L19
22,L20
22,L21
22,L22
22,L23
22,L24
22,L25
Monitoring Points

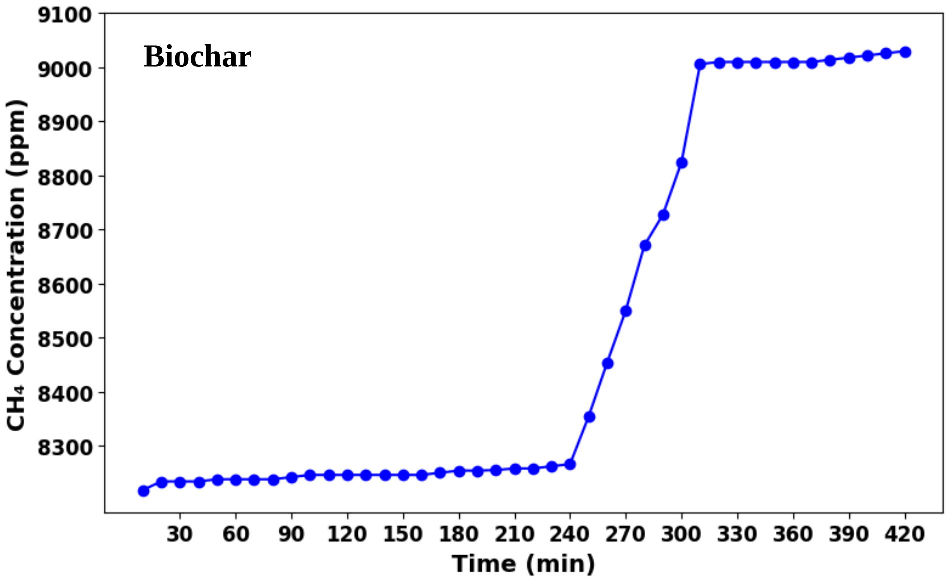

Methane Concentrations for Q4 2022 by Monitoring Points
Initial Methane (ppm)
10-day Recheck (ppm)
1-month Recheck (ppm)
Methane Concentration (ppm)
8000
6000
4000
2000
0
22,L26
22,L27
22,L28
22,L29
22,L30
Monitoring Points


Methane Concentrations for Q1 2023 by Monitoring Points
Initial Methane (ppm)
10-day Recheck (ppm)
1-month Recheck (ppm)
Methane Concentration (ppm)
14000
12000
10000
8000
6000
4000
2000
0
23,L1
23,L2
23,L3
23,L4
23,L5
23,L6
23,L7
23,L8
23,L9
23,L10
Monitoring Points

Appendix B The breakthrough curves for woodchips, compost, and biochar, each packed to a height of 5 inches within the column.






Biochar
CH₄ Concentration (ppm)
9100
9000
8900
8800
8700
8600
8500
8400
8300
30
60
90
120
150
180
210
240
270
300
330
360
390
420
Time (min)