Biochar-Based Biocovers for Landfill Methane Mitigation: Quantifying Adsorption, Transport & Oxidation

BY

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THESIS

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This thesis is dedicated to my beloved family

My father and mother

Dr. V. Sadasivam and Malleswari Sadasivam

My husband

Nirmal Kumar Prabakaran

And my brother

Dr. Balaji Sadasivam

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SUMMARY

One of the major environmental challenges associated with landfills is the generation of landfill gas which generally comprise 50% CH_4 and 50% CO_2. To mitigate the rising levels of CH_4 emissions from landfills, either bio-based cover systems are engineered and implemented in combination with efficient gas collection system during the landfill's active phase, or just the bio-based cover systems are implemented in case of an old/abandoned landfill. Microbially mediated biochemical CH_4 oxidation is the key CH_4 mitigation mechanism in landfill cover systems and the use of organic materials as landfill cover amendments was found to enhance this process. Compost has been extensively researched and advocated for use as a biocover material. Albeit, application-oriented challenges still exist due to the material's insufficient porosity and the possibility of undergoing self-degradation (if not sufficiently mature) thereby, lowering its performance. In order to design an efficient biocover system, a stable material with sufficiently good porosity and methane adsorption capacity which can promote microbial methane oxidation process needs to be selected. One such material that could potentially enhance the methane mitigation in landfill cover system is biochar. Biochar is a carbon-rich, highly porous material generated as a byproduct in the process of producing bio-energy from raw biomass (discarded wood, manure or agricultural crop residues) through pyrolysis or gasification. The physical-chemical and surface characteristics of biochars are strongly influenced by the type and composition of feedstock (raw biomass), production conditions (reactor residence time, temperature) and treatment processes (activation, particle screening, etc.). Preliminary studies show that amending biochar to soils containing a high fraction of clay content, can increase the aeration and thus limit the fraction of anoxic/anaerobic pore volume and subsequently promote microbial methane oxidation by methanotrophs.

The purpose to this study is to model the effects of amending seven different types of hardwood biochars to landfill cover soil (silty clay) on the stability of cover slopes, methane adsorption and oxidation capacities under varying levels of amendment ratios and environmental conditions such as moisture and temperature. Biochars were characterized for their physical-chemical and hydraulic properties such as particle size distribution, specific gravity, density, porosity, surface area, hydraulic conductivity, water holding capacity, organic matter and organic carbon contents, pH, oxidation-reduction potential and electrical conductivity, zeta potential, carbon, nitrogen and hydrogen (CHN) elemental composition. The biochar properties were correlated to methane adsorption capacities to develop a selection criterion for woody biochars for application as landfill cover amendments. Geotechnical properties such as compressibility and shear strength of biochars and biochar-amended cover soils were characterized to evaluate the stability aspects of the biochar-based biocover system. A series of batch and small-scale column adsorption tests were conducted to model the reactive transport of methane (1-D advection-dispersion equation) through biochars and biochar-amended soils under varying methane inflow rates and moisture levels. Batch incubation testing was performed on selected biochar-amended soils to quantify the combined methane adsorption and microbial methane oxidation capacities and model the effects of varying biochar types, biochar to soil amendment ratios, moisture and temperature on the methane oxidation rates.

Additionally, a life cycle analysis was performed to evaluate the sustainability metrics (i.e. environmental, economic and social aspects) of biochar-based landfill cover systems and conventional soil cover systems that were designed to achieve zero methane emissions for a hypothetical landfill site located in Northeastern Illinois region. Following this, Monte-Carlo simulations were used to assess the uncertainty levels in the life cycle impact assessment results

by varying the methane oxidation rates of the cover materials. Finally, design recommendations were made for the most sustainable, field-scale implementation of biochar-based cover systems which can achieve complete oxidation of methane in landfills located in Northeastern Illinois. Overall, this study presents valuable information that can be critical to the development of design guidelines for field-scale implementation of biochar-based landfill cover systems with the aim of achieving sustainable, optimum CH_4 mitigation.

1. INTRODUCTION

1.1 Problem Statement

Majority of the content in this section has been previously published by Sadasivam and Reddy (2013) during the author's doctoral work [**Sadasivam, B.Y.**, & Reddy, K.R. (2014). Landfill methane oxidation in soil and bio-based cover systems: a review. *Reviews in Environmental Science and Bio/Technology*, *13*(1), 79-107].

One of the major environmental challenges associated with landfills is the generation of landfill gas (LFG); the main components of which are methane (CH_4) and carbon dioxide (CO_2), both produced by the anaerobic decomposition of the organic waste fraction (Scheutz et al. 2009). CH_4 and CO_2 are greenhouse gases (GHGs) with a high potential to cause adverse effects on global climate change. Several researchers have determined typical gas generation rates at MSW landfills using comprehensive field monitoring programs at US landfill sites (Stern et al. 2007; Spokas et al. 2011), while a few other researchers have modeled the field gas generation rates in laboratory studies (Abichou et al. 2009, 2011). The typical composition of the LFG emissions originating from MSW landfills is 50% CH_4 and 50% CO_2 (v/v). The lifetime of CH_4 in the atmosphere is 12 years and is a short-lived GHG when compared to CO_2, which has a lifetime of 172.9 years. However, the radiative efficiency of methane is much higher with a value of 3.7×10^{-4} W m^{-2} ppb^{-1} in comparison to that of CO_2, which is 1.4×10^{-5} W m^{-2} ppb^{-1} (IPCC 2007). Consequently, methane is considered a more powerful GHG with a global warming potential (GWP) of 28 over a period of 100 years (IPCC 2013). In addition to the production of CH_4 and CO_2, landfills can also produce non-methane organic compounds such as chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs)-two greenhouse gases generated in small quantities (Bogner et al.

2010). According to a recent report released by USEPA on the US inventory of GHG emissions for 2010, landfills are the third largest source of anthropogenic CH_4 emissions and contribute to approximately 16.2% of the total anthropogenic CH_4 emissions in the US (USEPA 2012). Thus, the mitigation of LFGs through efficient LFG management systems has gained utmost importance over the past few decades.

Currently, the conventional LFG management systems incorporate the use of a landfill gas collection system, a landfill cover system or a combination of both. Many engineered landfill sites are designed with gas extraction systems that consist of vertical wells and horizontal collectors comprised of cylindrical pipes with carefully spaced perforations surrounded by a high hydraulic conductivity material (Barlaz et al. 2009). These extraction systems are placed within the waste, and the methane gas is captured and then flared or used for energy recovery. The most common principle behind the LFG capture by extraction systems is the application of negative pressure at the pipe's collection point to enhance the forceful collection and recovery of LFG generated in the waste (Park and Shin 2001; Barlaz et al. 2009). Gas collection systems are more useful during the active life of a landfill when there is a large amount of methane gas generated due to waste decomposition as this makes the gas flaring or energy recovery to be a cost-efficient process (Chiemchaisri et al. 2010). Under the US Clean Air Act New Source Performance Standards (NSPS), landfill gas collection systems must be installed within the first few years after a final cover was placed on the landfill or within 5 years from the last time that fresh refuse was disposed of in the landfill, whichever occurs earlier (Barlaz et al. 2009). In order to effectively manage the LFG that is generated, it is critical to estimate the LFG composition and its temporal variations; several landfill gas generation models have been developed to do this and are in wide use (IPCC 2007). In most of the gas generation models, zero, first or second order decay equations are

employed to determine the amount of LFG that is generated (Scheutz et al. 2011). The zero order models assume that the gas generation rates are constant over a period, unaffected by the age of waste or the waste breakdown. Some of the commonly used zero order models are EPER Germany, SWANA and IPCC zero order (Kamalan et al. 2011). The first order decay models account for the physical and chemical waste characteristics and the quantity of the waste under consideration based on the data obtained from landfills along with site specific conditions. This makes the use of first order decay models a more realistic approach by which to determine the LFG production rates. Some of the first order models include LandGEM, GasSim, Afvalzorg, IPCC, EPER France, SWANA, TNO, and Mexico (Kamalan et al. 2011), with LandGEM the most widely used gas generation model as it is specific for MSW landfills in the US.

Several studies focused on determining the efficiency of LFG extraction systems based on either a review of previously published data (Barlaz et al. 2009) or by conducting extensive field campaigns (Spokas et al. 2006). These studies demonstrated that the efficiency of the gas extraction system was highly dependent on the type of cover system (daily, intermediate or final) and the rate of efficiency varied from 50 to 95%. Gas extraction systems are designed to be coupled with methane flaring, which produces CO_2, a less powerful greenhouse gas as compared to CH_4. Nevertheless, methane flaring can release harmful byproducts into the atmosphere that are known to cause health concerns (Hettiarachchi et al. 2009). The implementation of a gas extraction system can also be both technically and economically challenging when the landfill site is old or abandoned, especially if the gas generation rates are not sufficiently high to achieve efficient flaring for energy recovery (Huber-Humer et al. 2008; Chiemchaisri et al. 2010). Case studies have shown that the extraction systems were active for less than 50% of the time that gas generation typically occurs due to economical and operational set-backs (Huber-Humer et al. 2008).

Moreover, the LFGs can escape through the vents around the collection systems, creating 'hot spots' that increase the amount of emissions into the atmosphere (Huber-Humer et al. 2008; Pedersen et al. 2011). In modern engineered landfills, the presence of a LFG extraction system serves as a major control for the emissions, but there is still a rising need to implement additional methods to control fugitive emissions that are not captured by the extraction systems. Apart from gas extraction systems, landfill cover systems can also play a key role in controlling the landfill gas emissions.

Landfill cover systems can be implemented as daily, intermediate or final cover systems based on the requirements of the specific landfill. Daily covers are used at the end of each work day after the placement of waste (Spokas and Bogner 2011), intermediate covers are designed to cover that section on which waste will not be placed for at least 1 year (Barlaz et al. 2009; Spokas and Bogner 2011), and final covers are designed to cap the landfill once its capacity to accept waste has been exhausted. Due to the rising instance of CH_4 emissions and since landfills are the third largest contributor of these gases, recent research focused on exploiting the various landfill cover systems that are used either in lieu of or in addition to gas extraction systems in order to achieve the maximum possible reduction in CH_4 emissions (Huber-Humer et al. 2008; Scheutz et al. 2009; Chiemchaisri et al. 2010). Soil cover systems are the conventional means by which landfill is capped in order to minimize LFG emissions and leachate generation. They stimulate the microbial oxidation of methane during the transport of LFGs. CH_4 oxidation in the landfill cover soil is primarily due to the presence of methanotrophic bacteria, a physiological group of bacteria called methylotrophs that assimilate CH_4 as their primary carbon and energy source for cell synthesis by using the enzyme CH_4 monooxygenase (MMO) (Scheutz et al. 2004). In the recent past, the global use of biocovers in place of soil covers has evolved as a result of innovative efforts

that target further reduction in CH_4 emissions (Sadasivam and Reddy, 2014). Unlike soil cover, a biocover is an engineered system that comprises an upper layer designed to promote the oxidation of methane plus a basal gas distribution layer (GDL) used to evenly distribute the LFG through the area to achieve effective oxidation (Scheutz et al. 2009). Generally, the oxidation layer is composed of materials rich in organic content such as composts, sewage sludge, peat, manure, etc., either alone or as amendments to the cover soil that actively support and facilitate the growth of methanotrophic bacteria.

Methane mitigation in landfill cover systems can be achieved by a combination of adsorption and microbial oxidation processes. To date, extensive research conducted in this field of interest highlights the importance of employing organic rich biocover materials to improve the microbial methane oxidation capacity in landfill cover systems. However, the long-term performance of bio-based cover systems were found to be negatively affected by major factors such as the material's ability to self-degrade, causing CH_4 to be generated rather than oxidized as well as the greater potential for forming pore-clogging exopolymeric substances which can hinder the transport of air and methane through the cover system. Researchers have seldom focused on exploring the process of methane adsorption that can also be employed to reduce methane emissions. The combined effects of both adsorption and microbial oxidation of methane need to be quantified upon employing a suitable biocover material that can facilitate both these processes. With the advent of sustainability concepts being more explicitly integrated into engineering practice, the quest for biocover materials that can reduce carbon footprint and promote the recycle and re-use of waste materials has gained greater importance. One such sustainable material proposed in this study to enhance methane adsorption and oxidation within a landfill cover system is biochar. Biochar is a highly porous, organic material derived from wood, manure or plant-based

biomass through pyrolysis under limited oxygen environments (Lehmann & Joseph, 2009). The choice of production process & treatment conditions for biochars is dependent upon the desired end product which can be biofuel for energy or biochar itself for the purpose of environmental management (Lehmann & Joseph, 2009). The presence of micropores in biochars makes it highly preferable for gas adsorption purposes. Biochar amendment to soils containing a high fraction of clay content, as in the case of commonly used landfill cover soils can increase the extent of aeration within the cover system and thus limit the fraction of anoxic/anaerobic pore volume and subsequently promote microbial methane oxidation by methanotrophs (Chan et al. 2007, Yanai et al. 2007). Biochars have found to be highly recalcitrant to decomposition in soils by at least one order of magnitude higher with a mean residence time of 1000 years as compared to the stability of other organic substances (Lehmann and Joseph, 2009).

1.2 Research Objectives

The research hypothesis is that certain types of biochars possess a strong potential to increase the methane adsorption and oxidation rates when appropriately incorporated into bio-based landfill cover systems thereby mitigating the overall methane emissions from landfills. The major goals of this research are to: (a) characterize the properties of different biochars and determine the significant factors that contribute to CH_4 adsorption for the development of a selection criteria to screen biochars prior to landfill cover application, (b) evaluate and model the effects of varying environmental factors such as moisture, temperature and exposed levels of methane concentration on the methane adsorption rates and methane adsorption capacities of different biochars, (c) evaluate and model the kinetics of methane oxidation in biochar-amended landfill soils by accounting for variations in moisture, temperature and biochar-amendment ratios and, (d) assess

the sustainability aspects of soil cover systems and biochar-based cover systems and develop design recommendations for sustainable field-scale implementation of biochar-based landfill covers to achieve optimum CH_4 mitigation.

The specific objectives of this research are to:

1. Appraise the literature on soil and bio-based cover systems, focusing on the cover material characteristics and methane oxidation mechanisms.
2. Characterize the physico-chemical and engineering properties of seven different biochars and biochar-amended landfill soils.
3. Quantify the maximum methane adsorption capacity of seven different biochars by conducting batch studies and identify the influential properties of all tested biochars which affect the methane adsorption capacity.
4. Quantify the maximum methane adsorption capacities of seven different biochars and four selected biochar-amended landfill soil at varying levels of moisture and temperature.
5. Determine the methane transport properties of seven different biochars and four selected biochar-amended landfill soil at varying levels of inlet methane loading rate and moisture.
6. Evaluate the influence of varying environmental factors on the adsorption and transport of methane through biochar and biochar-amended landfill cover soil.
7. Model the effects of moisture and temperature on the kinetic rates and maximum capacities of methane adsorption onto biochars and biochar-amended soil.
8. Quantify the microbial oxidation rates for methane in selected biochars and biochar-amended soils by conducting batch incubation studies.

9. Model the kinetics of methane oxidation in biochar-amended landfill cover soil and determine the methane oxidation rates at varying levels of moisture, temperature and biochar-amendment ratios.
10. Conduct life cycle analysis to assess the sustainability of soil cover and biochar-based landfill cover systems and develop design recommendations for sustainable, field-scale implementation of biochar-based cover system to achieve optimum methane mitigation.

1.3 Thesis Organization

This thesis is organized in nine chapters as follows:

- Chapter 2 summarizes the various technical aspects of designing an effective landfill cover system along with approaches to assess its performance and model the methane oxidation rates. Additionally, this chapter also sheds light upon the challenges associated with commonly employed CH_4 oxidation systems along with critical analysis of published case studies, which can pave way for future research and development in this field.
- Chapter 3 introduces the various biochar types tested in this research and presents information pertaining to their physical-chemical properties.
- Chapter 4 discusses the engineering properties such as compressibility and shear strength of different biochars and selected biochar-amended soils tested in this research.
- Chapter 5 discusses findings based on quantifying the kinetic rates of CH_4 adsorption, maximum CH_4 adsorption capacity and the dispersion coefficients representing the

adsorption-driven transport of CH_4 through different biochars under varying moisture and temperature conditions.

- Chapter 6 discusses the effects of adding selected biochar types to soil on its CH_4 adsorption and adsorption-driven transport properties under varying levels of biochar to soil amendment ratios, moisture and temperature conditions.
- Chapter 7 discusses the results from batch incubation tests conducted to quantify the combined adsorption and biochemical methane oxidation rates for selected biochar-amended soils under varying temperature, moisture, biochar types and biochar to soil amendment ratios.
- Chapter 8 discusses the sustainability aspects of implementing soil cover and biochar-based cover systems are evaluated by assuming a hypothetical landfill in Northeastern Illinois and design recommendations are developed for sustainable, field-scale implementation of biochar-based cover system to achieve optimum methane mitigation.
- Chapter 9 presents the overall conclusions and future research recommendations based on this study.

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2. REVIEW OF METHANE OXIDATION IN LANDFILL COVER SYSTEMS

2.1 Introduction

The content of this chapter has been previously published by Sadasivam and Reddy (2013) during the author's doctoral work [**Sadasivam, B. Y.**, & Reddy, K. R. (2014). Landfill methane oxidation in soil and bio-based cover systems: a review. *Reviews in Environmental Science and Bio/Technology*, *13*(1), 79-107].

Mitigation of landfill gases has gained the utmost importance in recent years due to the increase in methane (CH_4) emissions from landfills worldwide. This, in turn, can contribute to global warming and climatic changes. The concept of microbially mediated methane oxidation in landfill covers by using methanotrophic microorganisms has been widely adopted as a method to counter the rise in methane emissions. Traditionally, landfill soil covers were used to achieve methane oxidation, thereby reducing methane emissions. Meanwhile, the continual rise of CH_4 emissions from landfills pointing to the significant need for developing a better technology has led researchers to explore different methods to enhance microbial methane oxidation in landfill covers by using materials high in organic content such as compost. The development and field application of such bio-based systems, explored by various researches worldwide, eventually led to more widely accepted and better performing cover systems capable of reducing CH_4 emissions from landfills. In order to design an effective cover system for landfills, it is essential to have a thorough understanding of the concepts incorporated into state-of-the-art methodologies along with their pros and cons.

The purpose of this review is to summarize previous laboratory and field-scale studies conducted on various soil and bio-based cover systems, along with the modeling mechanisms

adopted for quantifying CH_4 oxidation rates. Finally, several issues and challenges in developing effective and economical soil and bio-based cover systems are presented and critically analyzed in order to highlight the existing gaps in literature.

2.2 Methane Oxidation Mechanism in Landfill Cover Systems

Aerobic methane oxidation occurs predominantly in the methanotrophic active zone located in the upper 10-20 cm of the soil profile and decreases as the depth increases (Pawlowska and Stepniewski, 2006; Het et al. 2011). In general, there are two major types of methanotrophs in the landfill soil environment, Type I and Type II. Their roles in CH_4 oxidation are presented in Table 2-1. Most methanotrophic bacteria are obligate methanotrophs and strict aerobes (Scheutz et al. 2009; He et al. 2011).

The reaction kinetics associated with methane oxidation is as found below (Pawlowska and Stepniewski, 2006; Scheutz et al. 2009; Chiemchaisri et al. 2010):

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{heat} \quad \Delta G° = -780\text{kJ/mol}\ CH_4 \qquad (2.1a)$$

Figure 2-1 illustrates this mechanism of methane oxidation in landfill soil covers. Methane generated in the waste migrates upwards through the soil cover and is oxidized to CO_2 and H_2O via methanotroph-mediated biochemical oxidation. The methane oxidation kinetics is commonly described by the Michaelis-Menten equation, shown in Equation 2.1b, which is widely used to model the single substrate enzyme kinetics:

$$r = \frac{V_{\max}\left[\mathrm{CH}_4\right]}{K_{\mathrm{m}} + \left[\mathrm{CH}_4\right]} \qquad (2.1b)$$

where r = CH_4 oxidation rate, V_{max} = Maximum CH_4 oxidation rate, and K_m = Michaelis-Menten (half-saturation) constant, equal to the affinity constant when 'r' is half of V_{max}. The values of K_m are influenced by the type of methanotrophs dominant in the methane oxidation process, which is controlled by the CH_4/O_2 mixing ratios, temperature and moisture conditions that exist within the cover soil. The typical range for K_m has been reported to be about 1000 to 25,000 ppmv (Scheutz et al. 2009). When methane oxidation by methanotrophs in landfills is modeled, CH_4 is noted to be the substrate and methane monooxygenase (MMO) is the enzyme. The Michaelis-Menten equation was derived based on the following assumptions: (1) the biochemical reaction is in equilibrium, which implies that the products formed are not converted back to the substrate; (2) the reaction is in steady-state, which implies that the rate of formation and breakdown of the intermediate, substrate-bound enzyme is constant; and, (3) the maximum rate of the reaction is obtained when all the catalytic sites in the enzyme are saturated within the substrate (Segel, 1993). The Michaelis-Menten kinetic model implies that the rate of the reaction is dependent upon the initial concentration of the substrate as observed in studies of methanotrophic methane oxidation in landfill cover systems (Abichou et al. 2011; Chanton et al. 2011).

TABLE 2-1: PROPERTIES OF TYPE I AND TYPE II METHANOTROPHS

TYPE I	TYPE II
1. Gamma proteobacteria 2. Use pMMO to oxidize CH_4 (presence of Cu) 3. HCHO is assimilated by RuMP pathway* 4. RuMP pathway – more efficient, 5. Have high CH_4 affinity 6. Favors low CH_4/high O_2 setting 7. Found in the top layers of soil cover 8. Limiting factor for cell synthesis is available CH_4 9. Cannot fix atmospheric N_2	1. Alpha proteobacteria 2. Use sMMO to oxidize CH_4 (absence of Cu) 3. HCHO is assimilated via serine pathway** 4. Serine pathway – less efficient, 5. Have low CH_4 affinity 6. Favors high CH_4/low O_2 setting 7. Found in the bottom soil layers 8. Limited by O_2 in the presence of abundant CH_4 9. Can fix atmospheric N_2 when possible

*uses only 1 ATP to assimilate 3 HCHO for synthesis

**uses 3 ATP & 2 NADH to assimilate 2 HCHO

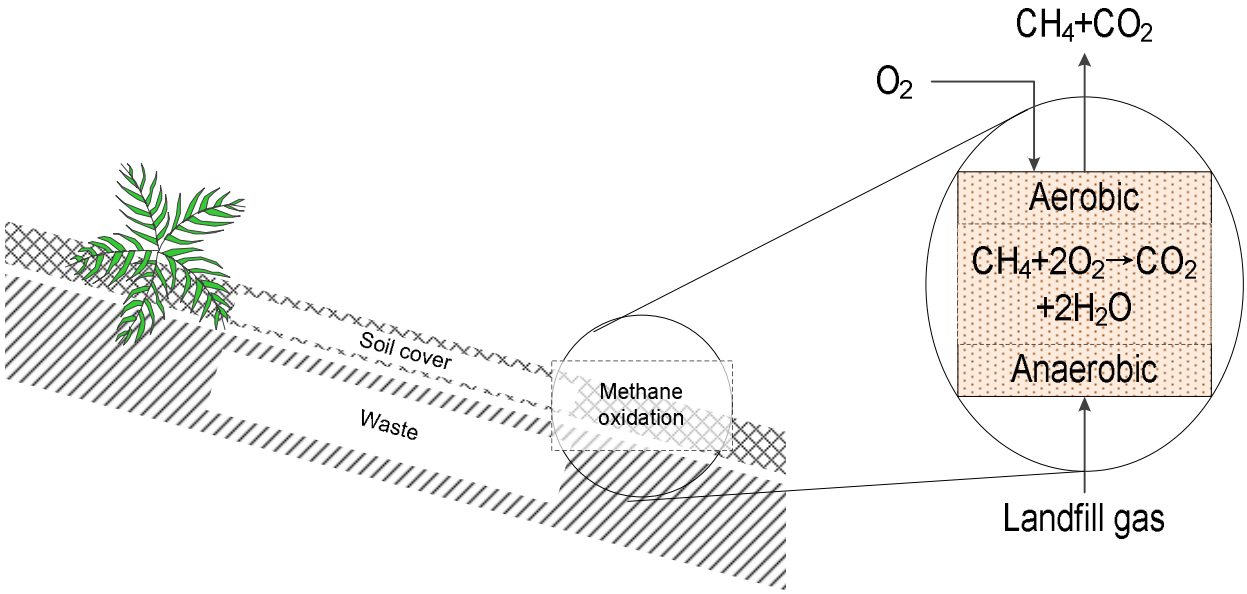

FIGURE 2-1: METHANE OXIDATION IN LANDFILL COVERS

2.3 Factors Affecting Methane Oxidation in Landfill Cover Systems

Factors such as CH_4/O_2 mixing ratio, moisture content, presence of inorganic N, formation of EPS, temperature, inhibiting chemical agents, and pH affect microbial methane oxidation in landfill covers, making it critical to understand and incorporate some of these potential factors into the technical design of a cover system. The CH_4/O_2 mixing ratio plays a vital role in controlling the oxidation activity of the soil microbial community, in particular methanotrophs (Hrad et al. 2012). As per the stoichiometric equation corresponding to methane oxidation (Eq. 2.1a), two moles of oxygen are required for the methanotrophs to oxidize one mole of methane. This in turn underscores the importance of the optimum CH_4/O_2 mixing ratios that are required to drive the methane oxidation process by Type I or Type II methanotrophs in landfill cover soils. Oxygen mixing ratios greater than 3% have no significant effects on the CH_4 oxidation rates, while ratios less than 3% negatively impact the microbial oxidation rate of landfills (He et al. 2012). According to the biochemical kinetics for CH_4 oxidation by methanotrophs, an O_2/CH_4 ratio of 3:1 is necessary to efficiently oxidize CH_4. Type I methanotrophs, abundant in the upper layers, are highly sensitive to oxygen and cannot exist under limited oxygen concentrations, which then limits the CH_4 oxidation (Chi et al. 2012). Most methanotrophs are mesophylls, meaning they can grow under moderate temperature ranges from 25 to 35°C, although the Type I methanotrophs can oxidize methane at lower temperatures ranging from 2 to 10^0C. As the temperature increases, the CH_4 oxidation rate also increases, but this only occurs below the optimum operating temperature of the methanotrophs, which is in the range of 25–35°C (Bo¨rjesson et al. 2004; Spokas and Bogner 2011).

Soil moisture helps to sustain the microbial activity in the landfill covers. But excessive soil moisture limits the transport of CH_4 through the cover soil since the rate at which CH_4 is

transported through a water medium is 104 times less than an air medium. In order to facilitate the transport of CH_4 through cover soils under wet conditions, a soil cover with a high share of pores that are greater than 50 lm is desirable (Scheutz et al. 2009a, b). Share of pores defines the air-filled porosity of the soil or the air capacity that facilitates the CH_4 transport under wet conditions. An optimum soil moisture content of 10–20% w/w is required to maintain a balanced environment in the cover soil for the CH_4 oxidation (Chanton et al. 2011a, b; Spokas and Bogner 2011), as the oxidation capacity drops significantly as its moisture content drops below 5%. Saturation of cover soils leads to increased lateral gas emissions at low temperatures and if the atmospheric pressure drops in such cases, excessive CH_4 emissions can occur; this is a significant risk. Additionally, the desiccation of the top soil layers due to dry conditions following wet conditions can result in the formation of cracks or hot spots through which excessive emissions leak (Scheutz et al. 2009a, b).

The amount of inorganic N present in the landfill cover soil also affects its CH_4 oxidation capacity. Methanotrophs have a high N-demand, so for every mole of carbon assimilated, 0.25 mol of N is used. However, excessive amounts of NH_4 competitively inhibit CH_4 oxidation since ammonia is structurally analogous to methane and can also be targeted by MMO (Bo¨rjesson et al. 2004; He et al. 2011). Type I methanotrophs use inorganic N for cell synthesis, which means that under low C:N conditions, the abundant inorganic N is available for Type I methanotrophs, which will respond with rapid initial growth. Once the excess inorganic N is consumed, the growth of Type II methanotrophs is favored as they can fix atmospheric N2 for cell synthesis under high C:N conditions. Thus, these alternating C:N ratios ensure Fig. 1 Methane oxidation in landfill covers continuous CH_4 oxidation in the microbial environment of the landfill cover soils (Scheutz et al. 2009a,b).

Exopolymeric substances (EPS) are polysaccharides secreted by methanotrophs during cell synthesis. Amorphous, slime-like substances, these act as a molecular sieve for metals and protect the bacteria and help it to adhere to the soil surface. Excessive production and accumulation of EPS can cause the soil pores to clog, impeding gas diffusion and resulting in O_2 deficiency (Hilger 1999; Wilshusen et al. 2004; Powelson et al. 2006). Interestingly, studies have shown that a higher CH_4 oxidation was achieved at 1.5% O_2 concentration (v/v) than at 10.5% O_2 concentration (v/v) since the production of EPS at 10.5% O_2 concentration (v/v) was 2.5 times higher than at 1.5% O_2 concentration (v/v) (Stein and Hettiaratchi 2010). The presence of inhibitors can also affect the CH_4 oxidation by methanotrophs. Some potential inhibitors are dichloro- and difluoro-methane, methyl fluoride, acetylene, ethylene, ammonium, certain pesticides, and hydro-HCFC. The optimum soil pH for CH_4 oxidation is between 5.5 and 8.5. Since methanotrophs have the capacity to adapt to a wide range of pH conditions, this is not a major limiting factor for microbial methane oxidation (Scheutz et al. 2009a, b).

2.4 Previous Studies On Soil Cover Systems

Several laboratory-scale studies involving batch incubation and column experimental set-ups were conducted to determine the methane oxidation rates in different types of landfill cover soils. A detailed summary of the results obtained from most of the laboratory-scale studies is reviewed elsewhere (Scheutz et al. 2009a, b). This section summarizes the technical findings from the most recent research studies along with the critical information that is required to design and optimize the performance of cover systems. Tables 2-2 and 2-3 list the design specifications and observed methane oxidation capacities for the selected laboratory-scale batch and column studies conducted on the various soil covers. Recently, Spokas and Bogner (2011) performed a comprehensive

laboratory study to investigate the CH_4 oxidation rates in six types of cover soils from two landfill sites in order to study the impact of moisture content (MC expressed in terms of soil matric potential), soil temperature and CO_2 concentration levels on the CH_4 oxidation. Batch incubation tests were conducted on the soils with and without pre-incubation under field collected MC and field capacity MC, as were the effects of diurnal temperature changes on CH_4 oxidation capacity; the latter was compared to isothermal oxidation rates. The researchers concluded that the soil wilting point (-1,500 kPa) is the lower moisture threshold for CH_4 oxidation activity and the optimum moisture potential for CH_4 oxidation is close to the soil's field capacity (- 33 kPa). Additionally, CH_4 oxidation rates under isothermal conditions were several orders of magnitude higher than the results from tests conducted by varying the temperature daily to simulate more realistic field conditions.

TABLE 2-2: SOIL COVER BATCH INCUBATION STUDIES

Material	Organic matter (% d.w.)	Optimum MC (% d.w.)	Optimum Temperature (^{0}C)	Headspace CH_4 (%), O_2 (%)	Vmax	Reference
Sandy loam	0.82	15	30	5, 21	16 mg CH_4/ kg d.w./h	He et al. 2011
Clayey silt	3.9	20, 30[1]	35	10, 30	11.2 µg CH_4/ g d.w./h 12.3 µg CH_4/ g d.w./h[1]	Albanna and Fernandes, 2009
Clay	2.4	20, 30[1]	35	10, 30	9.6 µg CH_4/ g d.w./h 10.5 µg CH_4/ g d.w./h[1]	
Sandy loam	0.82	16	25	5, ambient	13 mg CH_4/ kg d.w./h 23 mg CH_4/ kg d.w./h[1]	Yang et al. 2011
Clayey soil	--	18-20	30-35	6, 6	340 nmoles/Kg d.w./s	Abichou et al. 2011
Daily cover – Sandy soil[2]	0.5	30-40 kPa[4]	30	2ml/min[5], NA	142 µg CH_4/ g d.w./d[6]	Spokas and Bogner, 2011
Intermediate cover – Sandy loam^2	2.2	30-40 kPa[4]	30	2ml/min[5], NA	452 µg CH_4/ g d.w./d[6]	
Final Cover – Sandy loam^2	3.9	30-40 kPa[4]	30	2ml/min[5], NA	644 µg CH_4/ g d.w./d[6]	
Daily cover – Sandy soil[3]	2	30-40 kPa[4]	30	2ml/min[5], NA	112.4 µg CH_4/ g d.w./d[6]	
Intermediate cover – Sandy loam[3]	0.4	30-40 kPa[4]	30	2ml/min[5], NA	212.4 µg CH_4/ g d.w./d[6]	
Final Cover – Sandy loam[3]	0.9	30-40 kPa[4]	30	2ml/min[5], NA	212.9 µg CH_4/ g d.w./d[6]	
Sand, loamy sand & sandy loam	C/N = 6	6 kPa[4]	20	10, ambient	28.45 µg CH_4/ g d.w./h[7a] 66.64 µg CH_4/ g d.w./h[7b]	Gerbert et al. 2009
Loamy sand to sandy loam	C/N = 14.2	23	18	10, ambient	19.5 µg CH_4/ g d.w./h	Rower et al. 2011

[1] Values corresponding to the application of fertilizer
[2] Cover soil collected from Coastal Marina Landfill (Monterey, CA)
[3] Cover soil collected from Scholl Canyon Landfill (Glendale, CA)
[4] Moisture content was expressed in terms of moisture potential
[5] Headspace CH_4 concentrations were reported in terms of ml/min
[6] CH_4 oxidation rates for soils pre-incubated with 50 ml CH_4/min & 200 ml O_2/min at field capacity MC of 33 kPa
[7a] Vmax for undisturbed soil core (100 cc of soil core volume)
[7b] Vmax for disturbed soil samples (10 g soil in 10 ml water incubated in a shaker at 200 rpm)

TABLE 2-3: SOIL COVER COLUMN STUDIES

Material	MC (% dw)	Porosity, Bulk Density (g/cc)	Column Dimension (length, diameter), (m)	Bottom LFG, sweep air flow rates (ml/min)	Steady-State Oxidation efficiency (%)	Average CH_4 oxidation Rate ($gCH_4/m^2/d$)	CH_4 loading rate ($gCH_4/m^2/d$)	Duration (days)	Reference
Landfill loam	9.4	0.61, 1.142	1, 0.15	2.5 – 5.2, 300	50	-	-	300	Stein & Hettiaratchi, 2010
Dark soil	10	0.53, 1.38			32.2	-			
Peat Moss	316	0.9,0.55			55.4	-			
Sand	16[1]	0.21, 1.67	1.07, 0.19	0-19, 10 - 200	90 – 100	35 – 39	39	120	Rachor et al. 2011
Sand	22[1]	0.26, 1.38	1, 0.2	0-19, 10 - 200	65 – 95	37 – 55	57		
Sand	20[1]	0.15, 1.73	1,0.2	0-19, 10 - 200	45 – 60	36 – 48	80		
Sand	16[1]	0.18, 1.74	1, 0.2	0-19, 10 - 200	40	13	32		
Loamy sand	30[1]	0.17, 1.36	1, 0.2	0-19, 10 - 200	7	4	53		
Sandy loam	10 - 50	1.45	1, 0.15	3.9	30 – 40	6 – 12 $Mol/m^3/d$	100	275	Chiemchaisri et al. 2010
Sandy loam w/ S. virginicus	10 - 50	1.45	1, 0.15	3.9	60 – 85	9 – 14 $mol/m^3/d$	100		
Sandy loam w/ C. Plectosachyus	10 - 50	1.45	1, 0.15	3.9	35 - 45	7 – 13 $mol/m^3/d$	100		

[1] Measurement based on vol.%

In order to determine the ultimate potential for CH_4 oxidation in landfill cover soils, the researchers recommend a 60-day pre-incubation period (50 ml/L CH_4) in which the soil moisture contents are close to field capacity. Column testing is typically performed in conjunction with batch testing to assess oxidation rates attained in conditions more representative of those in field-scale applications (i.e. as part of a final cover system). Column experiments can be run for a longer period of time and are more representative of certain conditions that can occur within the soil cover, such as the formation of EPS, diffusion of LFG through the cover, and the depth of oxygen ingress into the cover layers, that play a major role in controlling the microbial CH_4 oxidation capacity of the cover soil (Scheutz et al. 2009a, b). The column tests are also used to assess the physico-chemical characteristics of the soils used in landfill cover on oxygen availability and methane oxidation.

Rachor et al. (2011) conducted laboratory column studies on four mineral soils and one sediment that was rich in organic matter and contained finer particles. The soils were compacted densely with bulk densities ranging from 1.4 to 1.7 g/cm^3 in order to simulate the actual field compaction that was expected in the landfill site; this cover material was intended for application in Germany. The CH_4 inlet loading rates were in the range of 25–100 g CH_4/m^2/day and the water content of the soil materials was adjusted to field capacity, which ranged from 16 to 48% vol. The CH_4 oxidation efficiencies for each media were determined using the mass balance approach, soil gas profile measurement, and stable isotopic measurements over 4 months. Their conclusions were like the ones previously reported in the literature except for one interesting trend with respect to the relationship between the share of pores and oxidation rates in the mineral-soil columns and the sediment column. They reported that the CH_4 oxidation potential, oxidation efficiency and the oxidation rate for the mineral soil columns were higher than those of the sediment column, which

had higher organic fraction and finer particles. This contradicts the general observations where an increase in CH_4 oxidation occurs with the increase in specific surface area, organic matter and finer particle fraction. But, since the soils and the sediment were compacted densely in this study, the effective share of pores in the organic sediment column was reduced significantly due to the clogging of the pores or EPS effect that limited the oxygen diffusion through the column.

He et al. (2011) conducted a laboratory study in China that used cover soils collected from an MSW landfill and was aimed at establishing the interaction effects of the various factors impacting CH_4 oxidation, such as water content, availability of oxygen and presence of ammonium. The methanotrophic community distribution was also investigated by DNA extraction and PCR assays. This research concludes that the highest sensitivity of CH_4 oxidation rates to moisture content in the substrate are affected by oxygen concentrations, which also affect the distribution of Type II methanotrophs, while Type I methanotrophs cannot survive under limited availability of oxygen. The optimum MC was 15% w/w and oxidation rates significantly decreased at all levels that were higher or lower than the optimum value. Additionally, the ambient oxygen concentration (20% v/v) was more favorable for CH_4 oxidation as compared to the lower value (3% v/v). Several studies have used multiple soils as landfill cover materials and that by Gebert et al. (2011a, b) established the effect of compaction on the share of pores available for gaseous transport through the soil. Three soil columns were filled with a 17 cm thick gas distribution layer (gravel) and 80 cm thick soil, which was compacted at 3 levels (75, 85 and 95%) of its Proctor density value. All the soils were adjusted for water content close to the field capacity (30 kPa). The results indicate a strong correlation between the diffusion of oxygen through the cover soil and the available share of pores, which decreased significantly at the higher compaction levels. More specifically, a sandy loam soil cover material at 75% Proctor density can completely oxidize a CH_4 influx of 3.5 g

$CH_4/m^2/day$. The researchers generalize their conclusions in order to widely apply them to the design of a cover system to oxidize CH_4 and recommend a minimum air-filled pore space (share of pores) value of 14% by volume for any substrate.

Studies by Bogner and Chanton (2011) and Chanton et al. (2011a, b) quantified the effects of seasonal and temporal variations in emissions across US landfills. Chanton et al. (2011a, b) compared the methane oxidation rates from several sampling locations that included sloped and flat top areas at two landfill sites to determine the effects of CH_4 loading on the CH_4 oxidation rates in a field-setting as a function of varying cover conditions (i.e. the presence or absence of slopes). The emissions from these locations were measured and the experimental results were compared to predictions using two numerical models (diffusion-based model and advection–diffusion-based model). Summer season was chosen to assess the emissions since the maximum CH_4 oxidation occurs in the summer due to the higher temperatures and this project aimed at determining the maximum amount of CH_4 that the chosen landfill sites could oxidize. The researchers determined that an effective way to increase methane oxidation in landfill cover soil was to limit the amount of CH_4 delivered to it. Emissions are high during the early life of landfills and they determined that a gas extraction system should be installed during this time in order to effectively control the CH_4 bottom flux to the cover. Once the waste matures, the gas extraction system can be turned off and the cover soils can enhance oxidation. Similarly, in another study conducted by Chanton et al. (2011a, b), the effects of seasonal and climatic variations on methane oxidation rates were determined by extensive seasonal sampling of over 20 landfills across various climatic zones where the results were analyzed using the stable carbon isotopic technique. The results indicated that CH_4 oxidation values obtained from the arid climatic zones were higher than other zones. Subtropical sites had the lowest value for CH_4 oxidation, and these observations were

attributed to the corresponding CH_4 loadings in each of the climatic zones. An inverse relationship was observed between the CH_4 loading and the fraction of CH_4 oxidized.

Several field scale studies have been conducted to determine the capacity of soil cover systems to oxidize methane (Powelson et al. 2006; Bogner et al. 2010; Hrad et al. 2012). Several soil cover designs were proposed for their expected efficiency and tested in the field for their methane oxidation capacities. Powelson et al. (2006) specifically focused on solving the problem of pore clogging due to the formation of EPS. They investigated the water-spreading filter consisted of a coarse gravel layer overlaid with a finer sand layer. The filter was constructed in the shape of a ridge such that there was enhanced distribution of air and water throughout the depth of the filter to help to achieve better CH_4 oxidation rates. The main objective behind this design was to achieve higher volumetric water content at the top of the filter while increasing the porosity at the bottom. To do so, a composite filter media consisting of 46 cm concrete sand with 80% w/w greater than 0.425 mm was placed at the bottom and topped by 46 cm fill sand with 60% w/w greater than 0.425 mm. This placement of the filter materials helped to achieve a gradual transition between the large pores at the bottom of the filter and the small pores at the top. Conceptually, this design used water tension and adhesion in a fining upward gradient within the soil pores against the pull of gravity on soil water such that it enhanced the CH_4 oxidation at the top layer due to increased volumetric water content, while the bottom layer facilitated enhanced transport of CH_4 through the filter with minimal clogging of the pores due to EPS.

2.5 Types of Bio-Based Cover Systems

The potential for enhanced CH_4 oxidation using efficient, suitable cover materials and amendments is being widely explored by researchers around the world. Many of these studies are

focused on using organic waste materials such as composts, sewage sludge, peat, etc., either alone or as amendments to the cover soil to induce favorable conditions for methanotrophs and enhanced methane oxidation. Such bio-based cover systems can be applied to landfill sites either alone or with an engineered gas extraction system to capture the escaping CH_4 emissions. Generally, biocovers are used at old, abandoned landfill sites where the option of using a gas collection system is technically and economically impractical due to the low CH_4 fluxes.

To date, researchers have proposed the following four types of bio-based systems to mitigate LFG (Huber-Humer et al. 2008):

- *Biocovers* require placement of the selected organic material over the entire area of the landfill like soil cover.
- *Biofilters* require placement of the engineered biotic system in pre-selected sections of the landfill area that are excavated to the required depth. Biofilters can be operated as fixed-bed reactors with a GDL beneath the methane oxidation layer, where the LFG is directed towards the oxidative layer by either an active or a passive gas extraction system. The biofilter can be operated in the up-flow or down-flow mode based on the direction in which the LFG is fed to the oxidative layer. These can also be used in combination with conventional caps (closed-bed systems) with highly engineered controls that regulate the CH_4 and O2 fluxes, temperature and MC. Biofilters can also be operated as an open-bed system with a vegetative cover layer as it does not require supplementary irrigation/ heating systems and the LFG is supplied and distributed from the bottom of the filter while oxygen ingress occurs from the top by diffusion. Although the closed-bed systems are more efficient and are isolated from negative impacts on the CH_4 oxidation efficiency due to

climatic variations, the capital and operating costs are higher than with open-bed systems; this makes it an economically infeasible option.

- *Biowindows* treat sections of the landfill site. Here, a biocover system is placed in discrete, excavated sections integrated into the landfill cover. It is economically more feasible than a full expanse biocover with respect to the quantity of cover materials required. Biowindows are usually not contained in a support structure as in the case of a biofilter and the LFG from the waste is naturally routed to the oxidative layer in the biowindows through the permeable GDL. This technique is most suitable when the landfill does not have gas collection systems to route the LFG into the biocover system.
- While biocover, biowindow and biofilter systems are final covers that lower CH_4 emissions from a landfill site, a *biotarp* is a daily cover or a temporary solution to address CH_4 releases during the active life of the landfill cell. Specifically, a biotarp mitigates early CH_4 emissions from recently placed wastes (Huber-Humer et al. 2008). A biotarp is generally a removable geotextile support impregnated with methanotrophs that is at least 15 cm thick. A variety of support materials have been laboratory tested and the major conclusion is that the materials must have good moisture holding capacity and porosity, plus be non-biodegradable and light enough to transport from one place on the landfill to another.

The fundamental mechanisms of methane oxidation in all the above bio-based systems are the same except for the differences in the system design and implementation. Commonly, the term biocover is used to refer all these systems in many published studies.

2.6 Previous Studies on Bio-Based Cover Systems

Bio-based cover systems are being recognized and acknowledged as a mechanism to help with the further reduction of LFG emissions. Several studies have been undertaken to investigate or develop effective biocovers through controlled laboratory experiments. Selected previous laboratory studies involving batch and column studies on various biocover materials are listed in Tables 2-4 and 2-5, respectively.

TABLE 2-4: SUMMARY OF BIOCOVER BATCH STUDIES

Material	MC (% d.w.)	% Organic Mater (d.w. basis)	Temperature (^{0}C)	Head space CH_4 (%, v/v)	Max. CH_4 oxidation rate	Reference
Manure Compost/Saw dust (9:1)	47-52	40±0.5/ 99.4±1.2	22	5	2.1 – 2.3 g/m^3/hr.	Perdikea et al. 2007
Garden waste compost (4 yr.)	72 ± 3	29 ± 3	Room	15	161 µg CH_4/g d.w./h	Pederson et al. 2011
Compost/Wood chips (1:1)	35.1	14	22	15	5	Scheutz et al. 2009
Compost/ Sand (1:1)	30	3.6	22	15	8	
Compost/ Sand (1:5)	11.9	1.7	22	15	3	
Supermuld	9.6	1.6	22	15	9	
Waste Biocover Soil	45%	-	35	10	9.03 µmol/g d.w./h.	Wang et al. 2011
Sandy loam	15	-	30	5	14 mg CH / kg d.w./ h	He et al. 2011
Aged refuse & Aged sludge mix (7:3)	30	12.3	22	10	78.7%	Lou et al. 2011
Mineralized refuse	55	14	30	10	14.73 µmol/g d.w./h.	Zhang et al. 2012

TABLE 2-5: SUMMARY OF BIOCOVER COLUMN STUDIES

Material	MC (%)	Porosity, dry Bulk Density (g/cc)	Temp (^{0}C)	CH_4 loading rate	Column Dimension (length, diameter), (m)	Bottom LFG, sweep air flow rates (ml/min)	Steady-State Oxidation efficiency (%)	Max. CH_4 oxidation Rate	Duration (days)	Reference
Manure Compost/ Saw Dust (9:1)	52	0.41,0.36/ 0.34,0.26	22	9.4 $g/m^3/h$	1, 0.15	2.5 – 5.2, 300	100	2 – 8 $g/m^3/h$	40	Perdikea et al. 2007
Raw Compost (4 yr.)	72	0.39/0.49	room	198 $g/m^2//d$	1, 0.2	13 – 15, 60	55	141 $g/m^2//d$	111	Pederson et al. 2011
Compost/Wood chips (1:1)	35.1	-	22	229-254 $g/m^2//d$	1, 0.08	2.4 – 2.7, 60	58	247 $g/m^2//d$	255	Scheutz et al. 2009
Compost/ Sand (1:1)	30	-	22	229-254 $g/m^2//d$	1, 0.08	2.4 – 2.7, 60	10	116	255	
Compost/ Sand (1:5)	11.9	-	22	229-254 $g/m^2//d$	1, 0.08	2.4 – 2.7, 60	12	142	255	
Supermuld	9.6	-	22	229-254 $g/m^2//d$	1, 0.08	2.4 – 2.7, 60	48	202	255	
Compost: Sand (5:1)	69	0.2	room	8 – 78 $g/m^2//d$	1, 0.15	0.2 – 2.4, 9.2 - 125	83	115	50	Roncato et al. 2012
Compost: Sand (5:1) w/ gravel	41	0.28	room	8 – 75 $g/m^2//d$	1, 0.15	0.2 – 1.4, 9.2 – 65.9	95	118	50	
Soil: Compost (3:1)	22	, 1.03	25	-	0.6, 0.09	5, 150	90	420 $g/m^3/d$	110	Rose et al. 2012
Soil: Compost (1:1)	27	, 0.95	25	-	0.6, 0.09	5, 150	93	600 $g/m^3/d$	110	
MSW Compost	39	, 0.74	25	-	0.6, 0.09	5, 150	97	1000 $g/m^3/d$	110	

Research conducted by University of Calgary, Canada, on the use of biocovers as a sustainable technology in landfills to mitigate methane emissions gives a good insight into the key aspects of the design and implementation techniques. The research group proposed the following design criteria for the field application of methane oxidation in landfill biocovers based on the findings from their several laboratory studies (Wilshusen et al. 2004; Perdikea et al. 2008; Stein and Hettiaratchi 2010; Pokhrel et al. 2011):

- Use of thin biocovers as intermediate cover system for landfills in-between the filling period for the bioreactor. A mixture with a compost (CM) to sawdust (SD) volume ratio of (10/0) or (9/1) at MC 52% w/w with a bed thickness of 30-cm operated at an inlet CH_4 load of 9.4 $g/m^3/h$ can oxidize 100% of CH_4 with a short, 2-day acclimatization period (Perdikea et al. 2008).
- Selection of an optimal soil type with appropriate MC based on site-specific temperature and climatic variables is very important. For example, in a dry environment, a soil with higher field capacity is more suitable. Hydrologic models like BROOK 90 or UNSAT2 can be used to predict the soil MC as a function of climatic variables and soil physical properties (Stein and Hettiaratchi 2010).
- Designers must account for soil's aeration status as a function of air-filled porosity. For optimal oxidation efficiency, gas must be distributed through a network of perforated pipes so that there is sufficiently low CH_4 flux (Stein and Hettiaratchi 2010). For actively aerated biofilters, the best approach is to supply O_2 through staged inlets along its length to maintain air close to the optimal concentration between 0.75 and 1.6% rather than simply supplying oxygen from the inlet (Wilshusen et al. 2004).

- If porous biocover materials with a MC greater than 30% and porosity greater than 40% are used, it is best to compact the material for field application because loosely compacted materials can form inter-particle water films and dead-end pores that can limit gas transport (Pokhrel et al. 2011).

Another group of researchers at the Danish Technical University conducted extensive laboratory-scale batch and column studies in order to evaluate different compost materials that were locally available for full scale implementation at Fakse Landfill in South Zealand, Denmark (Huber-Humer et al. 2009; Pedersen et al. 2011). They identified the following criteria for the selection of suitable compost materials for biocovers:

- Minimum level of organic matter must be 15%.
- Range for the TOC must be within 15–20%.
- Composts with a low C/N ratio achieved high oxidation rates, so the biocover must have a C/N ratio of approximately 15.
- Level of NH4-N must be below 400 mg NH_4/kg.
- Recommended value for sulfate is greater than 500 mg $SO4^-$/kg (microaeophilic or anaerobic conditions).
- Level of respiration must be less than 8 mg O_2/g/7 days

The organic contents of all the materials tested were higher than the threshold value of 15%, so were considered suitable. The water content of seven compost materials ranged between 50% (d.w.) and 90% (d.w.). From a previous study (Mor et al. 2006), tests of garden waste compost at different water contents to determine the optimum water content for methane oxidation found that the threshold limits were 70–80% DM and 100% DM. The total nitrogen range for all the compost materials were 8,480 mg/kg fine compost (FC) and 20,950 mg/kg sewage sludge compost (SC)

and fell within the criteria mentioned in studies for maximum oxidation rates. The C/N ratios for all the seven compost materials ranged from (9.5–20.3) and the threshold criteria mentioned by Humer and Lechner (2001a), which was approximately 15, was satisfied by four composts in the study by Pedersen et al. (2011). Generally, the literature shows that composts with low C/N achieved the highest oxidation rates. Humer and Lechner (2001a) also showed that the ammonium content for the seven compost materials were in the range of 736 mg/kg (FC) and 4,969 mg/kg (SC). Interestingly, the ammonium content was found to be higher than that mentioned for high methane oxidation rates of 179 g/m^2//day by Humer and Lechner (2001a, b), which was in the range of 8–348 mg/kg. The Danish researchers omitted this parameter for material selection since the methods that they used to determine the ammonium content was different from that used in previous studies. The sulfate content varied between 32 and 934 mg/kg and only few of the materials fulfilled the criteria of[500 mg sulfate/kg DM under anaerobic conditions mentioned by Huber-Humber et al. (2009).

Upon preliminary screening based on the criteria from their earlier studies, the Danish researchers conducted further testing by batch and column incubation procedures. Additionally, batch incubations were also set up to determine the compost respiration rates, which is a good indicator of the suitability of using those materials for full-scale studies (Scheutz et al. 2011b). In all, the three compost materials they tested showed similar, high values of average methane oxidation rates that ranged from 122 to 107 g/m^2//day. Using this information, the researchers selected raw leaf compost aged for 4 years for the field application since it did not require further screening or preparation prior to usage. They also took into consideration availability and production costs associated with the compost. The presence of twigs and branches in these samples was advantageous since it increased the substrate porosity and could help minimize the adverse

effects of pore clogging due to the formation of EPS. Though the practical use of the proposed approach may be questionable, Park et al. (2008) evaluated the impact of amending the landfill cover soils with earthworm casts and powdered activated carbon (PAC) in laboratory batch and column tests. The maximum CH_4 removal rate of the columns filled with landfill cover soil amended with earthworm cast was 14.6 mol/m^2/day, whereas that of the columns filled with typical landfill cover soil was 7.4 mol/m^2/day. The results from this study indicate the effectiveness of amending earthworm casts and PAC to the landfill cover soils to enhance CH_4 oxidation. The major mechanism that controlled the reduction of CH_4 in column with earthworm cast amended cover soil was CH_4 oxidation by methanotrophs, while the controlling mechanism in the case of columns containing PAC was adsorption. This observation was established from the soil gas profiles and the methanotrophic abundance along different depths of the columns. Subsequently, Park et al. (2009) studied the effects of varying the moisture contents, inlet CH_4 concentrations, CH_4 flow rates and temperature at the end of the experiments as a function of CH_4 oxidation rate. The optimum conditions for moisture content and temperature were found to fall in the range of 10–15% by weight and 25–35°C, respectively. The results also suggest that the percentage of CH_4 oxidation increases with a decrease in the inlet CH_4 concentration. The capacity of the biofilter medium, as mentioned in Park et al. (2008), to maintain a CH_4 oxidation efficiency of 100% was restricted to a gas inflow rate of 1,000 ml/ min (Empty Bed Retention Time, EBRT = 7.7 min) with 5% CH_4 concentration. In addition to these observations, the capacity of the biofilter to oxidize CH_4 was shown to increase with an increase in MC and temperature values.

A research group from Tsinghua University, China (Lu et al. 2011) has attempted to solve the problem of CH_4 oxidation being adversely affected by the limited oxygen ingression into the biocover system by using a novel passive air venting system inside a biocover, which was

simulated in a controlled laboratory condition. The mechanical air venting device was placed through the MSW such that the drainage pipe was below the MSW and the air-distributing head wheel was in the biocover area with the drainage pipe and the perforated, ring-shaped air distributing pipe being connected by an air-venting pipe. This experiment showed that the oxygen concentration significantly increased throughout the profile of the biocover system at simulated LFG flow rates ranging from 771 to 1,028 g/m^3/day and was reached the atmospheric levels in about 10 days. 100% CH_4 oxidation efficiency was observed under a LFG flow rate of 1,285 g/m^3/day. Further investigations were conducted by Chi et al. (2012) to determine the distribution of methanotrophic populations in the biocover microcosm equipped with the air venting system and without the air venting system. Yard waste compost and landfill cover soil was homogeneously mixed in a weight ratio of 7:3 and it was then placed in the columns with a thickness of 35 cm. Samples of these materials were later collected at three different depths (top, middle and bottom layers) for microbiological analyses as were gas samples. The experiment was conducted over 72 days during which the inflow of simulated LFG through the bottom of the cover material was varied. The microcosm equipped with the passive air diffusion system showed an increased level of oxygen throughout the profile with a maximum CH_4 oxidation capacity of 31.34 mol/m^3/day at a LFG flow rate of 40 ml/min and that the CH_4 concentration at the effluent was less than 6%, even at high LFG flow rates. On the other hand, for the microcosm that was not equipped with the air venting system, a CH_4 concentration of 55% was observed in the outlet gas when the LFG flow rate was 80 ml/min and the efficiency of CH_4 oxidation was significantly lower in that microcosm due to the insufficient amount of oxygen available for the biochemical oxidation of methane by methanotrophs. The molecular biology results indicated that the microcosm equipped with air venting system had excellent growth and an abundance of Type I methanotrophs, while the Type

II methanotrophs were more dominant when there was no air venting in the microcosm. Type II methanotrophs are not sensitive to the availability of oxygen and hence there were no significant differences in the Type II community in either microcosm. Although, the passive air venting system proved to be successful in promoting methane oxidation rates under laboratory conditions, its practical application under more realistic field conditions needs to be further evaluated.

Laboratory column studies and large scale lysimeter studies under field conditions to develop an efficient design for a biofilter with appropriate filter bed material to be applied in place of gas extraction system at old MSW landfill sites during in situ aeration period or waste stabilization period were conducted by Hrad et al. (2012). And, laboratory experiments using sand and compost mixtures from different sources in order to determine the potential for CH_4 oxidation under various environmental conditions were conducted by Huber-Humer et al. (2011). From their results of the column studies, it was observed that mature compost was able to control CH_4 emissions and was most suitable to be used as a landfill cover. The lysimeters comprised of filter bed medium placed above the shredded MSW served as the source of LFG during the experimental period from June to November 2010. Uniform injection of air was simulated on all the lysimeters and the one filled with compost and sand-compost mixture produced the lowest amount of leachate since the presence of compost increased the ability of the filter bed to retain water and increase plant growth. Overall conclusions from this study indicate that a layered landfill cover with compost and mineral soils can enhance the CH_4 oxidation rates during low pressure injection of air to stabilize MSW.

Gebert et al. (2003) studied the effects of many of the factors influencing CH_4 oxidation rates in a biofilter: temperature, substrate concentration, water content, salt concentration, and methane deprivation. They collected fresh field samples from the top 10 cm of a biofilter and

incubated the samples in the laboratory under different environmental conditions. The biofilter, designed to treat the passive emissions from a harbor sludge landfill in Germany, was made up of composite layers consisting of top soil with vegetation, sand, gravel, crushed and expanded clay pellets as well as a drainage layer. In order to study the effects of temperature variations, field samples were incubated in the lab at temperatures ranging from 3 to
45°C. Each sample was acclimatized to the required temperature over a period of 12 h after which a CH_4 concentration of 10% was amended to the soil. CH_4 emissions were monitored periodically, and results indicated an increase in the CH_4 oxidation rate with increasing temperature with an optimum temperature of 37°C for the biofilter material. Another set of incubation experiment was conducted using two cultures of Type II methanotrophs obtained from the biofilter medium, one was the Methylobacter sp. and the other was Rhodococcus erythropolis enriched at an incubation temperature of 10°C. These results showed that the incubations of pure cultures at different temperatures of 28 and 10°C lead to the formation of co-cultures such as Methylosinus sp. And Methylobacter sp. that have the both abilities to withstand temperature changes and contribute to CH_4 oxidation. Overall, a change in temperature resulted in a species shift rather than a change in adaptability of the existing microbial regime in the biofilter.

For the batch incubation studies under various water content and CH_4 and oxygen concentrations, the results obtained for the CH_4 oxidation rates agree well with observations reported in the literature (Gebert et al. 2003). The influence of changing salt concentrations on the CH_4 oxidation rate was studied using a pure culture of Methylosinus sp. and the biofilter medium. There was a decrease in CH_4 oxidation rate with increasing electrical conductivity (EC) values >6 mS in both the cases studied, although the rate of decrease in the pure culture was three times higher than that in the biofilter medium, which indicates a better ability for the methanotrophs in

the biofilter to adapt to dynamic environments. Overall, this study suggests that the methanotrophic counts in the top layers of the biofilter were several orders of magnitude higher than those values reported in the literature for rice paddies and LF cover soils even though the methane oxidizing capacity was not any higher than the values reported in the literature. This could be due to several limiting factors under conditions that favor dense growth of methanotrophs in the biofilter medium like excessive competition for available nutrients and greater osmotic pressure as moisture and EPS accumulate. Since expanded clay pellets provide favorable physical–chemical characteristics for the oxidation of methane due to increased porosity and a high share of pores along with high WHC, there was no negative impact due to desiccation of the filter medium. EPS formation was not a limitation in this study since the clay pellets do not shrink or degrade by themselves to cause clogs in the filter bed and the formation of EPS.

Another study of the biofilter at the harbor sludge landfill in Germany (Gebert and Groengroeft 2006) evaluated the sensitivity of the CH_4 oxidation rate as a function of dynamic atmospheric pressure changes. The atmospheric pressure changes that occur daily due to auto oscillation of air, temperature variations and barometric pressure changes all affect the CH_4 emissions from a landfill as well as cause changes in the gas profile along the cover depth. The influx of CH_4 will either decrease or increase in response to pressure changes that induce the advective transport of the landfill gases. The flux reversals observed in the biofilter demonstrated a significant increase in the aeration of the landfill soil profile, which can result in lower CH_4 production from the waste below due to suppressed methanogenesis since oxygen limits the activity of methanogens. Overall, the researchers suggest that a good biofilter design must account for diurnal changes in landfill gas pressures that can impact the CH_4 oxidation rates, which cause huge variations in daily CH_4 emission patterns. In a study by Gebert et al. (2011a), the CH_4

oxidation efficiencies obtained for laboratory soil and compost columns by a mass balance approach were compared to those values obtained from soil gas profiles at various depths by accounting for the probable discrepancy caused by soil/compost respiration, which can contribute to the production of CO2 in addition to CH_4 oxidation. Column studies were conducted in two separate stages with the first stage consisting of soil cover materials and the second consisting of compost amended with soil. Batch incubation experiments were conducted to determine the oxidation potential for the samples from the soil columns and 40 samples collected from a local landfill cover soil. The samples from the second set of column experiments containing compost amendments were used to determine the respiration potential of the various materials in incubation experiments conducted in the dark (dark respiration). The results obtained for the respiration studies indicated that the amount of CO2 produced by other sources (excluding the CH_4 oxidation process) were below 10% of the total CH_4 produced and, hence, was negligible. Overall, Gebert et al. (2011a) conclude their findings, based on certain assumptions in order to be applied to field-scale studies and column studies, with the main assumption that negligible soil respiration can result is more accurate measurement for CH_4 oxidation efficiency using soil gas profiles. This technique can be applied to any biocover or biowindow system that shows a stable CH_4 oxidation rate because the cover material has matured enough to fit into this assumption.

The use of aged refuse and aged sludge as biocover materials was evaluated in laboratory incubation experiments that used aged refuses of various maturity levels (9, 14 and 18 years) that were collected from Laogang Refuse Landfill, the largest MSW disposal site in China (Lou et al. 2011). Specifically, the fraction of aged refuse passing through a 4-mm mesh was used and the aged sludge was 5 years old. The optimum mixing ratio of aged refuse and aged sludge to achieve maximum CH_4 oxidation rates was first determined in the laboratory by testing seven different

mixtures. The maximum CH_4 oxidation rates were observed to be 78.7 and 66.9% for the aged refuse: aged sludge ratio of 7:3 and 6:4, respectively. The study continued, maintaining the mixing ratio at a constant value of 7:3. It showed that the CH_4 oxidation rate increased with increasing refuse age and attained a maximum value for the 14 years old refuse. Finally, the optimum conditions for impacting factors such as MC, Eh and OM were determined for 14-year-old refuse mixed with aged sludge at a ratio of 7:3. The optimum MC was achieved at 8–9%, which was much lower than usually reported values in the range of 20–30%, leading to the assumption that the biocover materials were more suitable to be applied under arid regions due to the ability to efficiently oxidize CH_4 even at low MC. In order to further investigate the effects of Eh on CH_4 oxidation rate, other factors previously tested were held constant at the optimum values obtained. For a mixing ratio of 7:3, the oxidation rate decreased with increasing Eh values and for the mixing ratio of 6:4, the oxidation rates increased with increasing Eh values from 104 to 108 mV beyond which the rate decreased. The CH_4 oxidation rate was 100% for the organic matter content in the range of 12.2–12.5%.

Another recent study compared the oxidation rates of four media namely, landfill cover soil, compost, and soil with compost in two mixing ratios of 1:1 (M11) and 3:1 (M31) by conducting laboratory column tests over 100 days (Rose et al. 2012). The landfill cover soil was classified as a ‘‘typical red yellow silt–clay Podzolic’’ and the compost was comprised of the organic matter fraction of MSW that was separated from the total waste load received at the subject landfill in Brazil. The laboratory column set up comprised of 60 cm long PVC column, which was 10 cm in diameter, and a mixture of CH_4 and air was passed into the column from the bottom at a flow rate of 150 ml/min, which resulted in an empty-bed contact time of 1.3 h. The results showed that the CH_4 oxidation rates obtained for the M11 and compost were higher with the compost being

the highest. The maximum CH_4 oxidation efficiency was between 93 and 97% for the substrates containing compost; for the soil column, the efficiency was much lower at 67%. At the end of the experimental period, MSW compost proved to be the best filter substrate with an oxidation rate of 990 g/m^3/day and an average efficiency value of 44%. The low values for efficiency were attributed to insufficient retention time for CH_4 and low dry densities of the filter materials. Table 2-6 provides a comparison on the effect of material dry densities and CH_4 retention times on the biofilter efficiency to oxidize methane in this study along with those values reported in previous studies.

Mature composts can exhibit a steady-state oxidation efficiency of 100% (Scheutz et al. 2009a, b). However, excessive oxygen consumption by methanotrophs during the microbial oxidation process can hurt the biocover performance due to a greater possibility of EPS formation and clogging of the pores, as observed by Wilshusen et al. (2004) in columns tests of different media. The capacity of aged refuse or old MSW from landfill dumps to oxidize CH_4 has been explored by several researchers. Zhang et al. (2012) incorporates the ability of other heterotrophs such as ammonia- oxidizing bacteria to co-oxidize CH_4 upon incubating aged refuse with livestock wastewater that was obtained from an anaerobic digester to stimulate the growth of microbes. Due to the similarity in the molecular structure of NH_4 and CH_4, the ammonia oxidizing bacteria can use CH_4 as a substrate for their microbial synthesis and convert it to CO2. Three different filter substrate materials were tested in this study: original mineralized refuse, incubated mineralized refuse and soil from a landfill cover. The CH_4 oxidation rate for the incubated aged refuse material was the highest for all the materials. Since the aged refuse was incubated with ammonia oxidizers, there were increased suspended solids in the refuse, which enhanced CH_4 adsorption in addition to promoting oxidation by heterotrophs.

TABLE 2-6: SUMMARY OF BIOCOVER FIELD STUDIES

Location	Cover type	Material Used	Cover Area (m2)	GDL, Cover layer (cm)	Monitoring Period (days)	CH_4 oxidation efficiency (%)	CH_4 emission reduction (%)	Reference
Fakse Landfill, Denmark	Biowindow	garden waste compost (4 yr.)	160	15, 100	≈ 450	41	28	Scheutz et al. 2011b
Leon County Landfill, Tallahassee, FL	Biocover Cell	Chipped Yard Waste (3 yr.)	57.76	10, 50	≈ 300	64	87	Stern et al. 2007
Outdoor Facility, Tallahassee, FL	Biofilter	Chipped Yard waste compost (4 yr.)	1.1	16, 58	86	63	-	Powelson et al. 2006
	Water-Spreading soil cover	Concrete sand & Fill sand	1.7	46, 46	86	64	-	
Leon Country Landfill, FL	Shallow Biocover	Fresh garden waste	576	15, 30	≈ 540	0 - 40	-	Bogner et al. 2010
	Deep Biocover			15, 60		20 - 70	-	
Saint-Nicéphore Landfill Quebec, Canada	PMOB 2	Compost: Sand (5:1)	26.8	10, 80	730	≈ 100	≈ 100	Roncato et al. 2012
	PMOB 3B	Compost: Sand (5:1) w/ gravel	26.8	90, 30	730	≈ 100	≈ 100	
Austrian Landfill	Lysimeter A	Sewage Sludge Compost	4	0.2, 1	≈ 210	≈ 100	≈ 100	Hrad et al. 2012
	Lysimeter B	Sand & sewage sludge compost	4	0.2, 1	≈ 210	≈ 100	≈ 100	
	Lysimeter C	Subsoil loess & top soil silt	4	0.2, 1	≈ 210	38	0 – 60	
	Lysimeter D	Subsoil loess	4	0.7, 0.5	≈ 210	3	0 – 20	
	Lysimeter E	Sand	4	0.2, 1	≈ 210	20	0 - 20	

Several studies have evaluated the impact of vegetation on compost cover in terms of its CH_4 oxidation rate (Bohn et al. 2011; Lamb et al. 2012) and one such study by Tanthachoon et al. (2008) demonstrated enhanced CH_4 uptake by methanotrophs due to the increased oxygen diffusion into the deeper zones of the cover through plant roots. This study also evaluated the effects of precipitation and dry conditions that prevail in tropical climates on the CH_4 oxidation rates using vegetated compost cover. The experimental set-up consisted of leaf compost and sandy loam soil packed to a height of 60 cm in100 cm high and 15 cm diameter columns and LFG was supplied at a constant flow rate of 4 ml/min. Sampling ports were driven across the length of the columns in 5 cm intervals. The columns were irrigated with rainwater and leachate separately in order to determine the effects on CH_4 oxidation rate. Leachate with a low BOD/COD ratio was chosen. In all, the intermittent addition of leachate favored methane oxidation rates in the case of compost columns better than in the sand columns due to the increased WHC and organic matter in the compost column bed. Under rainwater irrigation, the methane oxidation rate in the non-vegetated sand column was 11 mol CH_4/m^3 day for a period of 100 days, while under the presence of vegetated species, the oxidation rate in the compost column reached a high value of 12 mol CH_4/m^3 day over 330 days. The effect of leachate irrigation on the columns showed that the methane oxidation rates remained at 12 mol CH_4/m^3 day in the case of vegetated and non-vegetated columns for a period of 240 days. Under simulated dry conditions, the methane oxidation rate significantly decreased to 8 mol CH_4/m^3 day and had a shorter period of active oxidation (80 days).

A study by He et al. (2012) to determine the LFG production rate during the stabilization of waste in landfill indicated that the waste biocover material mixed with landfill cover soil had a comparatively higher rate of stabilization within a shorter duration of time than the conventional landfill cover soil when used alone. Additional information on the CH_4 oxidation activity in the

waste biocover and soil reactors indicated that there were more methanotrophs present at the bottom layers of the waste biocover, which resulted in higher potential for CH_4 oxidation. Wang et al. (2011) studied the potential for using waste biocover soil in place of conventional landfill cover soil by conducting extensive batch studies to determine the effects of influential factors on methane oxidation, such as moisture content, temperature and pH, in addition to oxygen and ammonia concentrations. Those results indicate that the CH_4 oxidation rate of waste biocover soil with a pH of 9.1 and a moisture content of 45% at an average particle size of 4 mm was the highest and the rate increased with the increase in CH_4 concentration up to 10% CH_4 (v/v). The highest oxidation capacity obtained from the Michaelis–Menten kinetics was 9.03 mol/g d.w./h and the Km value was 7.95 9 104 ppmv. The investigation of the effect of ammonium content present in the waste biocover soil found that the CH_4 oxidation activity was stimulated at values below 600 mg/kg of NH_4 and NO_3 whereas, it was inhibited at higher values.

The use of residuals generated from mechanically and biologically pretreated (MBT) waste was evaluated as a potential support medium in biocovers to oxidize the CH_4 (Einola et al. 2008). Two types of MBT residuals with 5 and 12 months of aerobic stabilization period were evaluated. An increase in the CH_4 oxidation potential was observed in the column experiments, run for 124 days, and the values ranged from\1.6 up to 104 lg CH_4/g dw/h at low temperature (5 ^{0}C). For a higher temperature (23°C), the CH_4 oxidation potential was 578 lg CH_4/g dw/h. During these experiments, researchers observed that there can be a high possibility for the MBT waste to produce leachates and the application of MBT waste as a potential CH_4 oxidizing medium must take this effect into consideration when designing the biocover.

Limited studies are reported that deal with full-scale implementation of biocovers for mitigating methane emissions at landfill sites (Humer and Lechner 1999; Barlaz et al. 2009; Stern et al. 2007;

Einola et al. 2009; Huber-Humer et al. 2009; Cabral and Jugnia 2010). Selected published field studies on various bio-based systems are summarized in Table 2-7. Humer and Lechner (1999) developed the first prototype biocover to undergo field testing at an Australina MSW landfill. The settling effects of compost were studied by using MSW compost that contained glass cullet, plastic parts and stones as primary structural materials and the results were compared against sewage sludge compost with wood as the principle structural material over a period of 3 years. The latter contained finer particles at the end of the study period (Huber-Humer 2004). A series of tests over several years led to the development of an efficient design. The researchers recommended a two-part cover system with 0.3–0.5 m coarse gravel layer covered by 1.2 m mature, well-structured compost. During the field trials, the biocover design exhibited good insulating property and the year-round CH_4 removal rate was 95–99% without regard to the season (Humer and Lechner 2001a). The biocover in Austria is monitored for 6 years (Huber-Humer et al. 2008). The flat top areas on the biocover were nearly 100% efficient in oxidizing CH_4, while some of the hot spots (sloped areas on the cover) were found to release CH_4 to the atmosphere especially when the gas extraction system was turned off. In order to check the quality of a biocover, CH_4 influx must be known; a complex measurement in the field. Hence, the researcher recommend that reference values can be determined from flux measurements on the site adjacent to the biocover, which can also capture temporal variations of CH_4 flux (Huber-Humer et al. 2008). Berger et al. (2005) observed that a multi-layer landfill cover system comprised of a gas distribution layer (30-cm porous small gravel) covered by a 10-cm sand layer that was in turn topped by a compost layer resulted in poor oxygen ingress during rain events and consequently negatively affected the performance of the cover.

TABLE 2-7: EFFECTS OF DRY DENSITY AND RETENTION TIME ON BIOFILTER EFFICIENCY

Reference	Dry density (g/cm^3)	Retention time (days)	Biofilter efficiency (%)	Methane oxidation rate (mol $CH_4/m^2/d$)
Park et al. 2002	1.61	0.8	83	14
		0.56	77	19
		0.32	71	23
Huber-Humer 2004	0.96	2.4	52	10.5
	1.08	2.5	98	14
De Visscher et al. 1999	1	1.6	67	18.1
Knightley et al. 1995	1	2.2	61	10.4
Powelson et al. 2006	1.4	2	58	26.5
	1.6		72	16.7
Berger et al. 2005	1.2	0.03	90	3.4
Kettunen et al. 2006	0.9	0.03	74	16
	1	0.03	97	9.8
Rose et al. 2012	0.92	1.3	20	-
	0.85		20	-
	0.75		20	-
	0.5		42	-

Jugnia et al. (2008) studied the effects of a mixed sand and compost biocover PMOB-1 (5 volumes of compost with 1 vol of sand) containing particles >12 mm and 80 cm thick on top of a 20 cm thick gas distribution layer and supplying biogas from a 3.5-year-old landfill waste. The compost came from sewage sludge and sludge from the paper and agricultural industries. Three experimental plots with dimensions of 2.75 m (W) by 9.75 m (L) were constructed during the summer 2006 and monitored for 4 months by inserting temperature, water content, and gas concentration probes at different depths in the cover cell. A weather station installed close by recorded the daily meteorological data, including precipitation, air temperature, wind speed, and barometric pressure. The CH_4 emissions, measured using a dynamic chamber method and soil cores, were collected from time to time from the top most part of the cover at four depths of 0–10, 10–20, 20–30, and 30–40 cm and analyzed in the laboratory within 24 h for pH and the particulate MMO (pmoA) gene using qPCR. Gas concentration profiles were plotted weekly by collecting six gas samples from different depths in the gas probes with that analysis performed in situ using an IR gas analyzer. During this study, the researchers observed dynamic changes in the barometric pressure, which was inversely correlated to the wind speed, and noted that the highest CH_4 emission (210 g/m^2//day) occurred during the lowest barometric pressure. Temperatures across the sampling profile varied between the summer and the fall months and the highest recorded temperatures occurred in the top 10 cm of the biocover. The methanotrophic oxidation process is an exothermic reaction and the top 10 cm of the biocover was found to be the most active zone of methane oxidation across time. This was supported by the results of the qPCR analysis, which showed that the pmoA gene abundance was ten times greater in the top 10 cm than at 10–20 cm depth. In the same above study, the oxygen concentration decreased with depth and was significantly affected during precipitation events. The blockage of oxygen diffusion beyond 40 cm

from the top became a challenge. Further, the CH_4 concentrations started out at 55% from the bottom of the biocover and significantly decreased towards the top layers leading to a lack of visible emissions during the first few months of summer operation. During the colder months, the microbial reduction of CH_4 from the bottom cover as it diffused to the top layers was significantly lowered, resulting in higher emissions. Although, the emissions were not as high as previously recorded by Humer and Lechner (2001b), the biocover performance was significantly affected by moisture content and oxygen diffusion. Another important observation relates to the developmental and growth period of methanotrophs that can effectively contribute to the CH_4 oxidation rates of the biocover. The lag phase was observed previously in the laboratory studies corresponded to 1 month at 19°C, whereas, a longer time period was required for the onset of methanotrophic activity in the field experiment (Jugnia et al. 2008).

In order to further investigate the relationship between the methanotrophic abundance with depth and the CH_4 oxidation rates of the PMOB-1, another study was conducted by Ait-Benichou et al. (2009). The methanotrophic count was determined using the most probable number (MPN) and those values obtained for the PMOB as a function of biocover depth were compared to those of a reference cell comprised of the existing clay cover at the landfill site. The pH, degree of saturation and the organic matter for the biocover and the reference cover was determined at various depths. The pH was higher at the deeper layers of the biocover and decreased at the top layers. They observed and confirmed findings by Hilger (1999) that the production of intermediate biochemical reaction products during microbial CH_4 oxidation and the formation of EPS decreased the pH of the soil environment. The reference cell, on the other hand, did not exhibit any kind of a pattern with respect to the pH values with depth and those values fluctuated randomly. This study spanned 2 years during which the degree of saturation (Sr) of the biocover substrate was higher

and more stable than that of the reference cell, which varied randomly with depth. This showed that the biocover substrate had a higher capacity to hold water, which favors methanotrophic oxidation. The organic matter content in the PMOB-1 was almost ten times greater than that of the reference cell, indicating that the PMOB-1 has a better capacity to oxidize methane by providing enough substrate for the methanotrophs to exist. The DNA sequencing results showed that the PMOB-1 contained extensive amounts of Type I methanotrophs and the methanotrophic count decreased as the depth from the top of the biocover increased where enough amounts of methane, oxygen and moisture prevailed.

Cabral and Jugnia (2010) constructed an experimental passive CH_4 oxidation biofilter (PMOB-2) on top of an existing landfill cover to study the effect of increasing the methane loading rate on methane emissions from May to November 2008. CH_4 loading ranged between 9.3 and 820 g CH_4/m^2//day. The active oxidation zone was established through gas profile samples and probes were inserted to determine MC, temperature and matric suction. The methanotrophic count was obtained at different biofilter depths for a better understanding of the CH_4 oxidation mechanism from the bottom towards the top surface of the biocover. Additionally, the precipitation effects on the degree of saturation were studied in order to characterize the physical–chemical mechanisms controlling movement of gases through the cover. The results indicated that the CH_4 removal efficiency was unaffected with increased CH_4 loading and the CH_4 removal rate increased with CH_4 influx. The maximum CH_4 removal rate was 804 g/m^2//day with nearly 100% oxidation observed throughout the study period. The methanotrophs were highly abundant near the surface and the CH_4 oxidation zone was established as between 0.6 and 0.8 m. The upper limit for the PMOB-2 to oxidize CH_4 was not reached even at the end of the study period when the landfill

management closed the biocover for winter. Overall, that substrate offered good conditions that facilitated methanotrophic growth.

In a more recent study, Roncato and Cabral (2012) analyzed the oxidation efficiencies of PMOB-2 and PMOB-3B from June to September 2007 using the stable isotope technique and mass balance equations under field as well as laboratory conditions. The structure and placement of PMOB-2 were the same as those described in Cabral and Jugnia (2010), but some changes were made to the cross section of PMOB-3B in that it was constructed with a thicker GDL (0.9 m) as opposed to that of PMOB-2 (0.4 m). In addition, the thickness of the substrate layer for PMOB-3B was reduced to 0.3 m from that of PMOB-2 (0.8 m). PMOB isotopic measurements were taken, along with static chamber measurements for both the biocovers and mass balance calculations, to determine the fraction of CH_4 oxidized in PMOB-3B since the influx and the efflux of CH_4 was known due to the controlled CH_4 supply in PMOB-3B. The researchers concluded that in a more realistic field environment, it is not possible to accurately estimate CH_4 oxidation rates based on the impact of individual factors such as water content, oxygen ingression, temperature, and CH_4 loading alone. Rather, a more reasonable conclusion must consider the interaction effects of all these factors. For example, although the PMOB-3B showed higher ingression of oxygen to deeper layers of the biocover, the CH_4 abatement not only occurred due to methanotrophic activity, but also due to the dilution effects with increased pore space and movement of gases within the cover since the CH_4 loading into the system was increased due to the increased thickness of the GDL. The temperature of the cover profile must be considered along with other factors that control CH_4 emissions in order to effectively determine the primary mechanism controlling the oxidation of CH_4 within the biocover layers. The CH_4 oxidation rates observed under laboratory conditions for PMOB 2 and 3B were 115 and 118 g CH_4/m^2//day, respectively. However, the CH_4 oxidation rates

observed under field setting for PMOB 2 and 3B were significantly higher than that of laboratory conditions with values ranging from 576 to 352 g CH_4/m^2//day, respectively. The researchers concluded that the reason behind this observation was the presence of plants on the cover material in the actual field setting.

2.7 Unresolved Issues/Challenges

Bio-based cover systems can be a promising alternative to traditional soil cover systems for methane mitigation from landfills. However, the literature exposes some key challenges to creating a bio-based cover or biocover that performs well. High input LFG can impede the diffusive ingress of oxygen and, thus, the media diffusivity and anticipated LFG load must be considered while sizing the biocover. Temperature can significantly affect the performance of a biocover, especially during the winter months when methanotrophic activity is suppressed under low temperatures. Another challenge involves the precautions taken to avoid desiccation of the cover materials during alternating wet and dry periods, which can be minimized by using materials that have a enough WHC. Moreover, the use of organic cover materials introduces a strong possibility of self-degradation of the materials, thus leading to the production of methane. Excessive formation of EPS due to increased methanotrophic activity under higher levels of ambient oxygen can result in the pores becoming clogged and the impedance of oxygen transport to deeper layers of the cover. In addition, the inability of compost-based materials to contribute to the adsorption of methane and possible occurrence of competitive inhibition of methanotrophic activity due to the presence of excessive nutrients in the organic materials makes them highly problematic and potentially ineffective for LFG mitigation. Maturity of the compost is one of the critical design considerations for an effective bio-based system (Scheutz et al.

2009b, 2011c) as it well-appreciated that the process of composting itself generates a large amount of greenhouse gas emissions. Since composts are a more seasonal material, its limited availability for field scale implementation year-round makes it a less preferred option among landfill owners and operators, thus necessitating further research to develop a more sustainable and effective biocover materials and bio-based covers that can further alleviate methane emissions from landfills.

2.8 Summary

Over the past few decades, extensive research has addressed the problem of the continual rise in the global anthropogenic methane emissions from landfills. Conventional LFG management systems include the use of gas collection wells and landfill soil cover systems. The use of gas extraction systems is technically and economically challenging to implement in old or abandoned landfill sites as well as in active landfills with low budget costs for operation and maintenance. The concept of methane oxidation in soil cover systems was explored by several researchers and was found to enhance the partial mitigation of methane emissions from landfills. Some laboratory and field scale studies determined the impact of key factors that affect methane oxidation rates such as soil moisture, porosity and permeability, temperature, methane loading rate, oxygen mixing ratio, EPS formation, and the role of vegetation on the cover layer. Several modeling studies looked at means to efficiently predict the field-scale performance of the cover materials and proposed design criteria to scale-up the laboratory results for a more practical field implementation.

Given the continual rise in the global methane levels and the fact that landfills are a prominent source for these emissions, the need to evaluate and develop a more efficient, cost-

effective technique paved the way for the evolution of bio-based systems. Several organic rich materials were explored for their use as landfill biocover materials and extensive laboratory and field-scale studies were conducted to establish an effective design approach to achieve high oxidation rates under field conditions. Thus, the use of bio-based systems to stimulate methane oxidation in landfill covers has become a promising technology with practical applications at existing landfills. The current biocover systems employ a wide variety of organic materials that include different types of composts and sewage sludge. With the advent of sustainability concepts integrated into engineering practice, it now becomes critical to develop biocover materials and cover systems that can reduce the carbon footprint of the landfill and promote the recycling and re-use of waste materials.

Overall, this review summarizes the various technical aspects of designing an effective landfill cover system along with approaches to assess its performance and model the methane oxidation rates. Additionally, this review also sheds light upon the challenges with currently employed CH_4 oxidation systems along with critical analysis of published case studies, which can pave way for future research and development in this field.

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3. PHYSICAL-CHEMICAL CHARACTERIZATION OF BIOCHARS

3.1 Introduction

The contents of this chapter has been previously published during the author's doctoral work in the form of three peer-reviewed conference papers which were co-authored by the doctoral committee chair and advisor, [**Sadasivam, B.Y.,** and Reddy, K.R. (2013). "Study of methane adsorption by biochar in landfill cover." *Proc., 106th Annual Conference & Exhibition, Air & Waste Management Association*, Chicago, IL, USA]; [**Sadasivam, B.Y.,** and Reddy, K.R. (2014). "Quantifying the effects of moisture content on methane adsorption capacity of biochars." Geotechnical Special Publication 241- Geoenvironmental Engineering, *Proc. of the Geo-Shanghai 2014*, Editors: Reddy, K.R. and Feng, S., American Society of Civil Engineers, Reston, VA, 191-200] and [**Sadasivam, B.Y.,** and Reddy, K.R. (2015). "Influence of physico-chemical properties of different biochars on landfill methane adsorption." IFCEE2015, San Antonio, TX, March 17-21, 2015]. Additionally, portions of this chapter pertaining to the physical-chemical and characterization of biochars have been orally presented by the author in the following technical conferences during the author's doctoral work, [**Sadasivam, B.Y.** and Reddy K.R.: "Methane Adsorption by Different Biochars," IBG meeting held at Illinois Sustainability Technology Center (ISTC), Champaign, IL on April 5th, 2013]; [**Sadasivam, B.Y** and Reddy K.R : "Use of Biochar in Landfills for Methane Mitigation," *Midwest Biochar Conference*, Champaign, IL, USA, June 2013]; [**Sadasivam, B.Y.**, and Reddy, K.R., "Methane Adsorption by Different Biochars," IBG meeting held at Illinois Sustainability Technology Center (ISTC), Champaign, IL on April 5th, 2013]; [**Sadasivam, B.Y.**, and Reddy, K.R., "Investigation of Biochar from Wood Pellets as a Sustainable Landfill Cover Material," SURF meeting held at University of Illinois at Chicago

between July 23rd – 26th 2013 in Chicago, Illinois] and [**Sadasivam, B.Y.**, and Reddy, K.R., "Influence of Physico-Chemical Properties of Different Biochars on Landfill Methane Adsorption," IBG meeting held at USDA Research Facility in Peoria, IL on November 15th, 2013]. This chapter was also previously published as a peer-reviewed journal paper by the author as part of this doctoral work [Yargicoglu, E.N., **Sadasivam, B.Y.**, Reddy, K.R., Spokas, K., 2015. "Physical and chemical characterization of waste wood derived biochars". *Waste Management* 36, 256-268]. The author of this doctoral thesis solely contributed to acquiring the various biochars from suitable vendors, conducting majority of the physical-chemical characterization testing in the laboratory, compiling and analyzing results, visual presentation materials such as figures and tables and writing several sections of the journal paper.

Recent innovations in environmental applications have focused on improving environmental accountability, either using more sustainable materials or better management practices, into project design and implementation. Biochar has been a widely researched material for its ability to be used in environmental management and soil improvement and has shown promise as a sorbent for some environmental contaminants, including heavy metals (Park et al., 2011; Mohan et al., 2011), polycyclic aromatic hydrocarbons (Chen et al., 2011, 2012), and other organic contaminants (Cao et al., 2009; Sun et al., 2011). Ongoing research indicates biochar may be a favorable landfill cover amendment for enhanced microbial methane oxidation due to its high internal microporosity, sorption properties, and stability in soil (Yaghoubi, 2011). Because biochar is often produced from waste biomass such as agricultural residues (e.g. corn stover, rice husks), scrap wood or other feedstocks (e.g. sewage sludge, poultry litter, dairy manure), biochar production and application is considered a sustainable process (Laird, 2008). Biochar amendment to soil is often deemed "carbon negative" as it can be considered as a mechanism to sequester organic carbon in vegetative

biomass that would otherwise be discarded from being degraded and released into the atmosphere as CO_2 (Spokas, 2010; Enders et al., 2012); thus, the organic carbon is moved to a more slowly cycling reservoir (biochar) potentially for centuries.

In this study, six biochars produced commercially using waste wood are characterized relative to a manufactured granular activated carbon (GAC) to provide further insight on the effects of production and post-production processes on relevant physicochemical properties of commercial, wood-derived biochars in order to assess their suitability for use in environmental applications.

3.2 Materials and Methods

Six different wood-derived biochars and granular activated carbon (GAC) were obtained from commercial vendors and selected for detailed physical-chemical characterization tests. Biochars were selected based on local availability and potential for use in large-scale applications; a visual image of each tested biochar is shown in Figure 3-1. Table 3-1 summarizes the feedstock sources, production processes and conditions, and type of post-treatment applied (if any) for each of the studied biochars. In addition to physical and chemical characterization, both the total and leachable PAH contents of biochars and GAC were determined in order to assess the total and leachable amounts of toxic constituents in the selected wood-derived biochars. All characterization tests were performed using each biochar obtained as received from the vendor unless otherwise stated.

TABLE 3-1: PRODUCTION CONDITIONS AND SOURCE MATERIALS OF BIOCHARS USED IN THIS STUDY

Sample ID	Feedstock	Treatment Process	Treatment Temp.	Residence Time	Post-Treatment
GAC	Coconut charcoal	*Proprietary information not available*			High-temperature steam activation
BS	Pine wood	Slow pyrolysis	350 – 600°C	6 hrs	Screened through 3mm mesh
CK	90% pine; 10% fir wood	Fast pyrolysis	> 500°C	< 1 hr	Activated with O_2
AW	Aged oak & hickory wood biochar	Pyrolysis – Missouri type concrete kiln	~500°C	NR	Mixed with proprietary inocula blend & sieved (1/4")
CE-WP1	Pinewood pellets	Gasification	~520°C	NR	Fine ash retained
CE-WP2				NR	Fine ash sieved
CE-AWP				NR	None (aged for 2 years under laboratory conditions)

In Addition to The Biochars Listed in this Table, Granular Activated Carbon (Gac) Obtained From Fisher Scientific Was Also Used. NR: Not Reported.

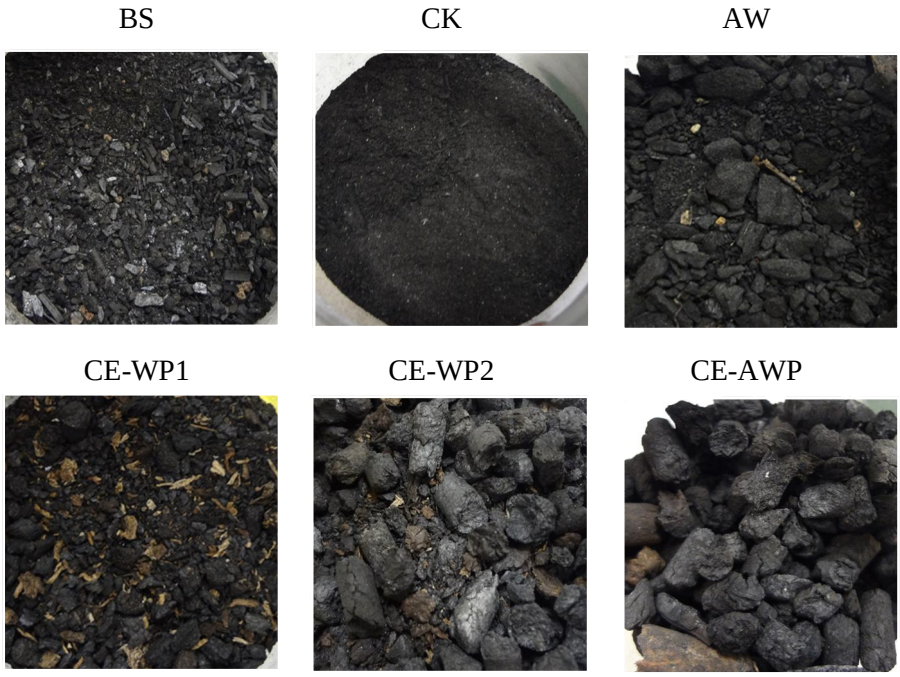


FIGURE 3-1: PHOTOGRAPHS OF BIOCHARS TESTED IN THIS STUDY

3.2.1 Particle size distribution, specific gravity and dry density

Specific gravity and particle size distributions of dry biochar samples were characterized according to ASTM D 854 and ASTM D 422, respectively. Maximum dry density was determined using the Harvard miniature compaction test setup (Humboldt Mfg. Co.) according to the suggested test method described by Wilson (1970). After weighing the empty Harvard miniature mold, it was filled with the dry biochar sample in three uniformly spaced layers with five compaction strokes per layer. Once filled, the biochar samples were leveled on the surface of the mold and the weight of the mold with biochar was noted. The maximum dry densities of the biochars were computed based on the weight of biochar compacted into the mold and the volume of the mold.

3.2.2 Hydraulic Properties

Prior to testing the biochar samples for field capacity, or water holding capacity (WHC), they were oven-dried overnight at 60°C to remove any residual absorbed water. The WHC of the biochars was determined by placing a known weight of biochar material in a ceramic Buchner funnel lined with filter paper (size P8; Fisherbrand). A known amount of deionized water was added to biochar slowly until the biochar was saturated and the water could drain by gravity from the biochar for approximately 3 hours. The final moisture content of the biochar was determined gravimetrically as per ASTM D2216. WHC was determined by calculating the moisture content of the saturated sample and the relative proportion of water passing through the biochar sample after correcting for the moisture absorbed by the filter paper. This procedure was also previously adopted by a study pertaining to biochar characterization and proved to be effective in quantifying the field capacity of biochars (Kinney et al., 2012). Hydraulic conductivity was determined via the constant-head test method as per ASTM D2434. For each biochar, 3 different constant head levels were used, and the results averaged to determine the hydraulic conductivity (k) of the material. Deionized water was used during the first trial so that leachate could be collected and analyzed for leachable contaminants, namely PAHs and heavy metals.

3.2.3 Surface area measurements

Surface areas were determined on dry biochar samples via N_2 adsorption at 77 K on a Surface Area Analyzer (Micromeritics ASAP 2020 BET). BET and Langmuir adsorption isotherms were generated to determine the single-point surface area.

3.2.4 SEM imaging and image analysis

Samples were first coated with 3 to 6 nm of Pt/Pd coating using a sputter coater (Cressington HR208) in order to minimize sample charging. Images were captured using a Hitachi S-3000N Variable Pressure Scanning Electron Microscope (SEM) operated in high vacuum mode with 2 to 10 kV accelerating voltage (voltage applied varied based on extent of sample charging) using a secondary electron detector. Images were taken at several magnifications ranging from x50 to x4000.

The micro-porosities of biochars and GAC were quantified using the image processing software Pores (Particles) and Cracks Analysis System (PCAS), which was developed and validated by Liu et al. (2011). The SEM images are imported into the software which then converts them into equivalent binary forms based on the grey-level threshold values (T) entered. The microporous regions in the binary images are distinguished by segmenting the image into black and white regions representing solid surfaces and void spaces, respectively. The average T values used for this study ranged from 107 – 138 for the biochars and GAC. Error analysis was conducted for individual biochars by varying the T values from T-4 to T+4 at two-step intervals. The minimum pore area (S_0) was set to a default value of 50 pixels and the division radius (r) was set to 2.1 pixels. The segmentation process for the SEM images was repeated for each threshold value prior to the auto analysis. The statistical parameters corresponding to a pre-set probability range number (n=7) was extracted from the software for the pore area range analyzed. The average porosity value is then displayed from the resulting tabular output along with other micropore characteristics corresponding to pore geometry.

3.2.5 Organic matter, ash, volatile matter and fixed carbon contents

Organic matter was determined according to ASTM D 2947 via loss on ignition (LOI) at 440°C. This test is typically applied to determine organic matter in soils, and thus may underestimate the actual organic content of charred materials due to the high recalcitrance of carbonaceous residues. Consequently, standard chemical analyses for wood charcoal as per ASTM D 1762-84 were also performed to determine the volatile matter, ash, and fixed carbon contents of air-dried biochar samples. Moisture content was determined gravimetrically as per ASTM D2216 prior to these tests.

3.2.6 pH, oxidation-reduction potential and electrical conductivity

Biochar samples (10 g) were soaked in 1:1 slurry of 0.01 M $CaCl_2$ solution for 2 hours prior to measurement of pH, ORP and EC (Orion720A Model pH meter) as per ASTM D4972. The pH meter was calibrated with standard pH buffers at pH 4, 7 and 10 prior to analysis. All analyses were performed in triplicate and the results averaged.

3.2.7 CHN elemental analysis

Samples were first air-dried at 60°C and placed into glass vials. At least two subsamples (2.0-3.0 mg each) from these sample vials were analyzed using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer operated in CHN mode. The CHN mode utilizes the Pregl-Dumas method in which samples are combusted in a pure O_2 atmosphere, and the resultant combustion gases are automatically measured and quantified to determine initial elemental concentrations of C, H and N. The reported values are averaged results from each set of duplicate samples.

3.2.8 Zeta potential measurements

Zeta potential (ZP) was determined for each sample in duplicate using a Zeta-Meter 3.0+ system (Zeta Meter Inc., VA). All samples were dried and passed through a No. 200 sieve prior to measurement. A solution of 0.05 g biochar in 50 ml deionized water (sample concentration of 1 g/L) was prepared in clean 50-ml vials. A small amount of the solution was placed into the sample well in the Zeta-Meter System. The velocity of particles moving towards a positively charged electrode is then measured to compute the ZP of each sample using the Zeta Meter. This measurement was taken 5-6 times per trial and averaged, with duplicate samples for each biochar tested.

3.3 Results

3.3.1 Particle size distributions

The percentage of particles greater than 4.75 mm and 0.075 mm, as well as the average and effective grain sizes (D_{50} and D_{10}, respectively), for each biochar type are shown in Table 3-2. Particle size distribution curves for biochars are presented in Figure 3-2. Based on visual interpretation of the particle size distribution curves, the percentage of fine particles (<0.075 mm) varies considerably among commercially-available biochars. As anticipated, the pelleted CE biochars typically had a lower fraction of small particles than the finer grained chars (i.e. CK, BS and AW). Though these biochars were produced via gasification, which tends to generate chars with smaller particles (Brewer et al. 2009), the pre-treatment pelleting (and in the case of CE-WP2, post-production sieving) removed many of the smaller particles, effectively changing the physical attributes of the biochar. This likely impacted the effective surface areas of the biochars, given

that finer-textured biochars typically had higher measurable surface areas as compared to the pelleted chars (Table 3-2).

TABLE 3-2: PHYSICAL PROPERTIES OF BIOCHARS AS DETERMINED FROM ANALYSIS OF GRAIN SIZE, DRY DENSITY, AND SPECIFIC GRAVITY

Biochar	% > 4.75 (mm)	% > 0.075 (mm)	D_{10} (mm)	D_{50} (mm)	Avg. Dry Density, ρ_d (g/cm^3)	Avg. Specific Gravity, G_s	Surface Area ($m^2\ g^{-1}$)
BS	0.0	90.8	0.09	0.71	0.73	1.36	40.63
CK	3.8	73.0	0.08	0.22	0.54	1.51	155.1
AW	6.6	90.1	0.33	0.89	0.48	1.19	5.41
CE-WP1	0.4	96.1	0.24	1.13	0.56	0.77	0.38
CE-WP2	13.9	85.2	1.29	3.15	0.52	0.59	0.10
CE-AWP	67.3	31.5	2.68	5.75	0.53	0.91	-
GAC	0.0	91.1	1.18	2.97	0.67	1.65	611.87

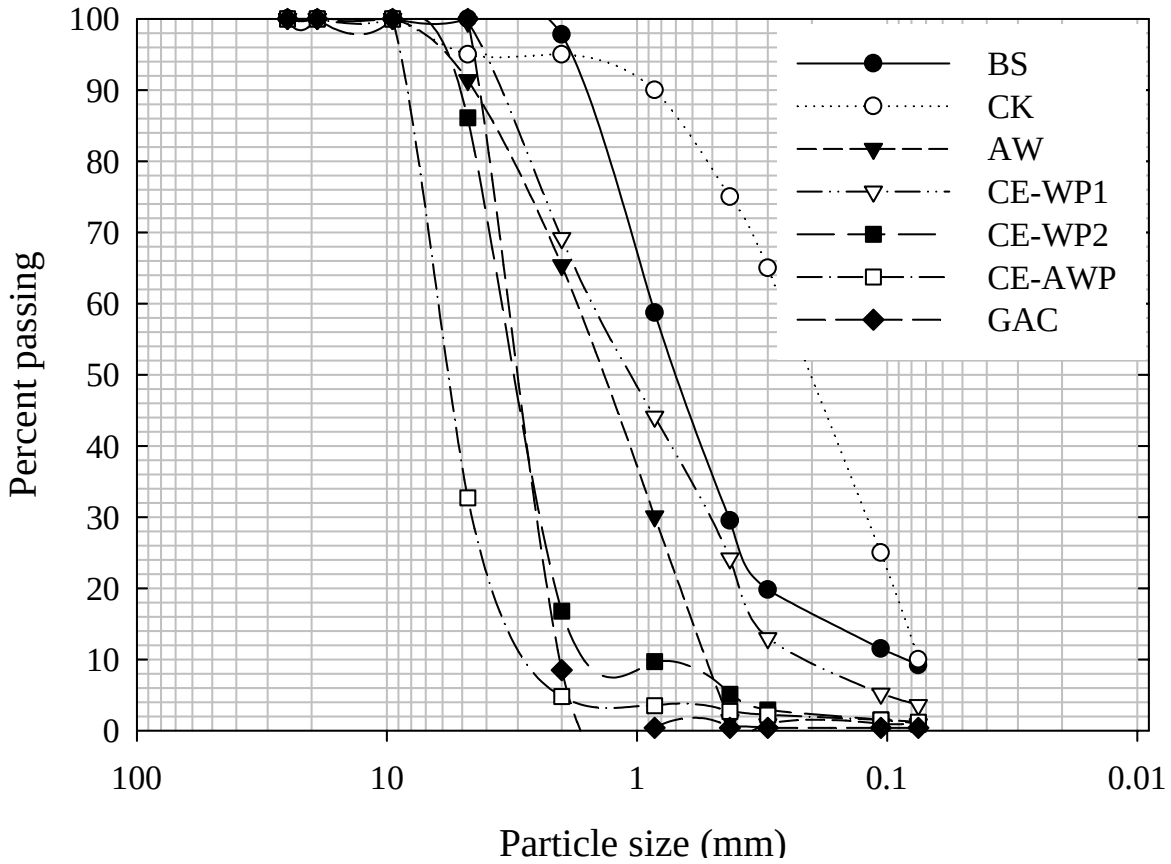


FIGURE 3-2: PARTICLE SIZE DISTRIBUTIONS OF TESTED BIOCHARS AND GAC

3.3.2 Dry density and specific gravity

For all tested biochars and GAC, the average dry bulk density values were less than 1 g cm^{-3} (Table 3-2). The low densities observed likely reflect the high internal porosities of biochars. Specific gravities of the biochars varied between 0.59 and 1.51 (Table 3-2), with the highest specific gravity belonging to the biochar with lowest H:C ratio (i.e. CK biochar). Since H:C can

be an indication of charring intensity (Ameloot et al., 2013), this was likely due to the concentration of heavier biomass components (e.g. ash, metals) due to greater extent of pyrolysis.

3.3.3 Surface area

Surface areas for the biochars were low relative to GAC, which had a surface area of 611.87 $m^2\ g^{-1}$ (Table 3-2). Single point surface areas for biochars ranged from 0.095 (CE-WP2 biochar) to 155.1 $m^2\ g^{-1}$ (CK biochar; refer to Table 3-2). The relatively low surface area values reported for the CE biochars are thought to be underestimates of the actual surface area due to difficulty in obtaining accurate measurements for the CE biochars. This may be attributed to the presence of pore constrictions smaller than 0.5 nm, which can lead to underestimates of surface area during N_2 adsorption, especially for coal and carbonaceous materials (De Jonge and Mittelmeijer-Hazeleger, 1996). Because of these limitations, these low surface area values are not considered to be entirely representative of the actual surface areas of the CE biochars.

3.3.4 SEM image analysis

SEM images were taken at several magnifications ranging from x50 to x4000; Figure 3-3 shows representative images of each of the biochars at x250 magnification. Visual inspection of these images illustrates the differences in microstructure among the chars, with distinct micropores observable, especially in the CK and BS biochars. The SEM images for all samples captured at a magnification of x2000 were used for PCAS analysis. Data on microporosity obtained from PCAS analyses for all biochars and GAC are shown in Figure 3-3. The results of error analysis using PCAS indicated that the error values corresponding to average porosity of samples were within the acceptable range of 5% (Liu et al. 2011). The average porosity of biochars and GAC range

from as low as 30% for AW up to 60% for GAC. The porosity values corresponding to CE-biochars ranged closely from 36 – 44%. The SEM image identification results for CE-WP2 and GAC are shown in Figures 3-5a and 3-5b, respectively. The porosity of GAC is higher than the wood-derived biochars tested for this study. CK biochar had the second highest porosity, with a value of approximately 55%. These results agree with previous studies which reported an increase in porosity and surface area of biochars with increasing treatment temperatures and activation (Brown et al., 2006; Zhang et al., 2004). Moreover, the presence of micropores in biochars makes it highly preferable for gas adsorption, which will also aid gas retention within a landfill cover.

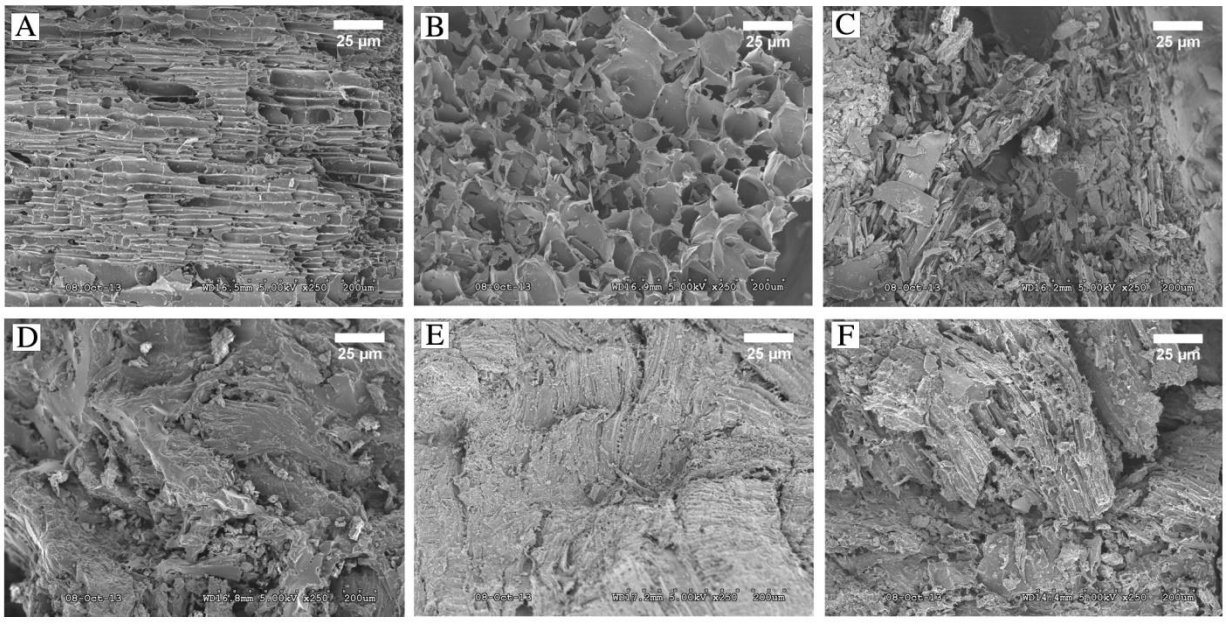


FIGURE 3-3: SEM IMAGES OF BIOCHARS TESTED IN THIS STUDY AT X250 MAGNIFICATION. A: BS, B: CK; C: AW; D: CE-WP1; E: CE-WP2; F: CE-AWP

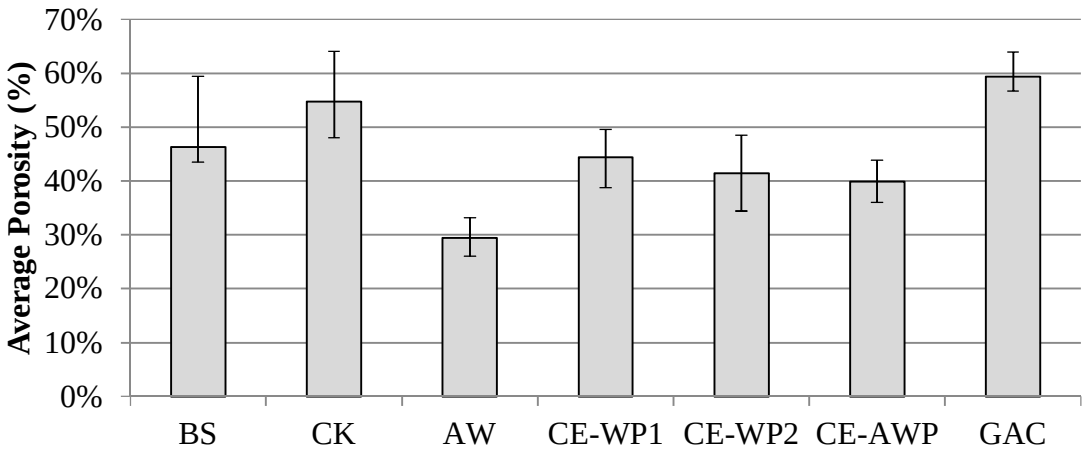
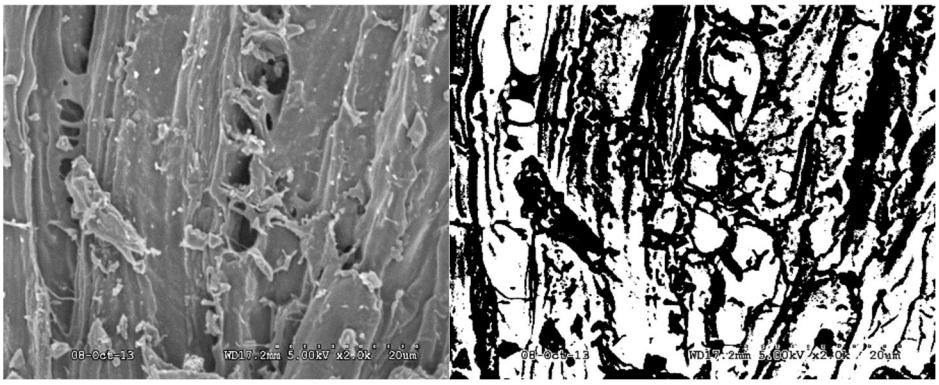


FIGURE 3-4: AVERAGE PORPOSITY OF BIOCHARS AND GAC FROM PCAS ANALYSIS

3-5a: CE-WP2



3-5b: GAC

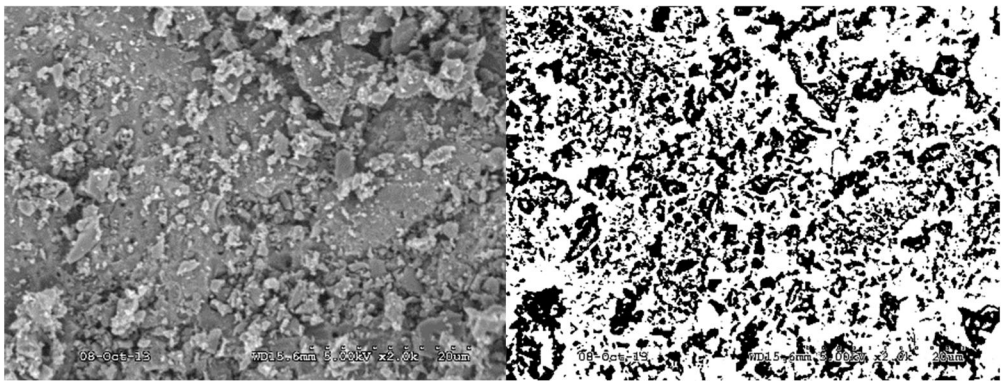


FIGURE 3-5: SEM IMAGE SEGMENTATION USING PCAS

3.3.5 Hydraulic properties

Hydraulic properties determined for each biochar and GAC include hydraulic conductivity and water-holding capacity (WHC), shown along with the initial moisture content of the samples as received from the vendors in Table 3-3. WHC of the tested biochars varied from 32.9 – 63.9% on a wet weight basis, or 50.6 – 179.4% on a dry weight basis, with the finer-grained biochars generally having higher WHC. This effect may be due to higher void ratios in finer grained biochars, in addition to stronger capillary forces among fine particles, and was especially notable in the increased WHC of the pinewood biochar with ash retained (CE-WP1) relative to the same type of pinewood biochar with the fine ash removed (CE-WP2), with WHC values of 58.7 and 32.9% on a wet mass basis, respectively. Hydraulic conductivities of the biochars are given in Table 3-3. As expected, finer-grained biochars also tended to have lower hydraulic conductivities, with the lowest values belonging to CK and AW (K_s values of 7.9×10^{-4} and 4.2×10^{-4}cm/s, respectively).

TABLE 3-3: HYDRAULIC PROPERTIES OF TESTED BIOCHARS

Sample	Moisture Content (%)	Water Holding Capacity		Hydraulic Conductivity, K_T (cm/s)
		% dry wt.	% total mass	
BS	0.33	120.6	54.7	1.7×10^{-3}
CK	5.66	179.4	63.9	7.9×10^{-4}
AW	66.2	113.8	50.0	4.2×10^{-4}
CE-WP1	1.38	142.4	58.7	1.1×10^{-3}
CE-WP2	2.15	50.6	32.9	3.9×10^{-3}
CE-AWP	1.98	80.8	44.5	2.7×10^{-2}
GAC	17.02	96.4	49.1	7.2×10^{-3}

Note: Moisture Content Is Reported As Received From The Vendor.

3.3.6 Organic matter, volatile matter, ash and fixed carbon contents

Gravimetric analysis of biochar is used to assess the relative fractions of fixed and labile organic matter, which can be represented by the volatile matter component. Ash content refers to the inorganic, non-combustible portion of biochar that remains after volatile matter is removed via heating at 950°C. Though originally intended for analysis of coal and charcoal, gravimetric analysis as per ASTM D1762 has been used by several researchers to investigate the chemical properties of biochars as the relative proportions of ash and volatile matter will impact both chemical and physical properties of the biochar (e.g. Spokas and Reicosky, 2009; Brewer et al., 2009; Lee et al., 2010; Keiluweit et al. 2010). Percentages of volatile matter, ash, and fixed and organic carbon are given in Table 3-4.

The CE biochars, which were all produced from the same feedstock type and pyrolysis technology, clustered together in terms of relative abundance of ash (1.5 - 4.6%), volatile matter (61.8 – 93.6%) and fixed carbon (33.2-47.8%). By contrast, biochars from other vendors (AW, BS, CK) all had distinct chemical compositions, reflecting the inherent variability in biochar chemistry that is reflective of feedstock and production conditions. Thus, these wood-derived biochars have relatively low ash content as compared to previously studied biochars derived from corn stover, which can have ash contents in the range of 54-74% (Spokas and Reicosky, 2009; Lee et al. 2010). Grasses have also been known to have relatively high ash contents (e.g. ~20%; Keiluweit et al. 2010), due to the lower abundance of lignin as compared to woody feedstocks. The fixed carbon content of GAC was found to be within the range observed for the biochars at ~18%, though the GAC had a higher volatile matter content (64%). The low ash content of GAC was like that observed in CE biochars at ~2.8% ash by weight.

TABLE 3-4: CHEMICAL PROPERTIES OF BIOCHARS AND GAC GAC INVESTIGATED

Property	BS	CK	AW	CE-WP1	CE-WP2	CE-AWP	GAC
LOI Organic Matter Content (%)	33.9	32.3	74.5	96.0	97.5	87.8	91.4
Volatile Matter Content (%)	28.0	28.1	74.1	61.8	62.7	55.4	64.2
Ash Content (%)	65.7	61.6	25.4	4.6	1.5	4.3	2.9
Fixed C Content (%)	4.6	3.7	ND	33.2	35.0	40.3	17.9
Elemental Analysis							
C (%)	53.2	23.5	51.9	70.7	74.0	78.1	76.5
H (%)	1.6	0.4	2.2	3.8	3.8	1.8	0.8
N (%)	0.4	0.01	0.4	0.3	0.3	0.4	0.2
Molar Ratios							
H:C	0.35	0.18	0.51	0.63	0.61	0.27	0.12
C:N	143.4	5513.9	151.9	290.7	293.9	261.5	426.6
pH	8.47	8.77	7.88	6.24	6.78	7.64	8.86
ORP	74.2	-116.1	-63.5	35.1	2.3	-48.7	-120.8
EC	0.04	0.007	0.14	4.15	1.1	0.54	0.01
Zeta Potential (mV)	-23.7	-15.8	-15.4	-25.6	-24.4	-18.6	-31.0
ΣPAHs (mg kg $^{-1}$)	16.9	83.0	0.68	BDL	BDL	BDL	BDL

BDL: Below Detection Limit. ND: Not Determined.

3.3.7 pH, ORP, EC and zeta potential

Table 3-4 presents pH, oxidation-reduction potential (ORP), electrical conductivity (EC), and zeta potential values of all biochars and GAC. Among the tested biochars, pH values ranged from slightly acidic to alkaline [pH=6.24 (CE-WP2) to 8.77 (CK)]. The pH of GAC was higher than all tested biochars at 8.86. Significant differences in ORP, a measure of redox activity, were also noted among the biochars. Only 2 of 6 commercial biochars, along with GAC, displayed negative ORP values, indicating a higher reductive potential (i.e. a tendency to become oxidized through loss of electrons via reduction of another compound). The EC of the solid biochars varied from

0.007 to 8.33 mS cm^{-1}, with higher EC values in the lower pH biochars (pH 6.24-6.78), which also corresponded to biochars with positive ORP values. Zeta potential values, which reflect surface charge of the material, were all negative for the tested biochars, varying from -25.6 (CE-WP1) to -15.4 mV (AW) for the biochars. Zeta potential of GAC was significantly more negative than all tested biochars (-31.0 mV), likely as a result of surface activation. A lower fraction of cationic metals may also contribute to the lower ZP of GAC relative to the biochars, considering that CK biochar was also activated, but had a ZP of only -15.8 mV as compared to -31.0 mV for GAC, in addition to a higher concentration of cationic metals.

3.3.8 Elemental composition

The elemental composition of solid biochars was assessed by measurement of C, H and N in the solid biochars as received from the vendors; percentages by weight of C, H and N for each dry biochar are given in Table 3-4. Overall, the chemical composition of tested biochars varied significantly, with C, H and N contents ranging from 23.5-78.1%, 0.35-3.8% and 0.005-0.4%, respectively. Molar ratios of H:C and C:N are also presented as they provide indications of the extent of biomass carbonization (Table 3-4). Chars with higher C:N and lower H:C ratios likely underwent greater thermal alteration due to the greater loss of H and N relative to C. Of the biochars included in this study, both the lowest H:C ratio and highest C:N ratio was observed in the CK biochar. As with other properties, these data suggest that a greater extent of carbonization occurred in this biochar. However, the elemental C content of CK biochar is relatively low at 23.5%, indicating the presence of a significant amount of inorganic minerals in the ash fraction of the char. A lower C content can also indicate more complete biomass combustion.

3.4 Discussion

3.4.1 Physical properties of biochars

Several differences in the physical properties of the tested biochars and GAC were apparent from visual observation alone, most notably whether biochars were in a loose, granular (AW, BS, CK) or pelleted form (CE-WP1, CE-WP2, CE-AWP). Generally, the pelleted biochars incorporated less of the finer ash particles (fine ash was separated from CE-WP2 biochar by sieving). These differences will impact how well biochar can be mixed into soils (demonstrated in an incubation study of biochar-amended soils by Zimmerman, 2010), as well as several key physical parameters including: specific surface area and surface charge, particle size distribution, porosity and thus also bulk density and specific gravity, water-holding capacity, and hydraulic conductivity. Considering the practicality for direct application to soil (e.g. for agriculture or soil remediation) pelleted biochars may be more favorable than fine-grained biochars due to lower dust generation during application to soils. Inhalation of charcoal dust can be a human health issue (Nadel, 1968; Kato et al., 2004). However, given the past utility of fine powders in environmental remediation, methods to reduce dust generation during application of fine powders have been developed to minimize this issue (e.g. application with a wet solution as slurry or high-pressure injection). Achieving homogenous mixing with pelleted biochars may be considerably more difficult than amending soil with a finer texture biochar. This can introduce spatial heterogeneity over small scales in a soil-biochar mixture, potentially creating pockets of anoxic and oxic conditions in the soil matrix.

The particle size distributions clearly impacted hydraulic properties, with the finer biochars having generally lower hydraulic conductivities due to smaller pore spaces. At the same time, higher water holding capacities were generally observed in finer biochars or those with fine ash

retained (i.e. CE-WP1). These properties are both considered favorable for soil improvement; however, higher ash content chars generally have lower fixed carbon contents and relatively high volatile matter contents, which would lower their resistance to biotic degradation and thus reduce their carbon sequestration potential (Brewer et al., 2011). There is also the hypothesis that metal oxides found in the ash fraction can react with the biochar to further accelerate its degradation (Huisman et al., 2012). As a result, high ash biochars likely have shorter lifetimes in natural soil systems due to higher degradation rates.

Given the relatively high hydraulic conductivities of some biochars, their use as filter media in environmental applications may be feasible depending upon the type of contamination and the required residence times. Other proposed uses of biochars for climate change mitigation, such as a landfill cover amendment, may require a certain low hydraulic conductivity to be maintained as otherwise it can pose a risk of excessive rainwater percolation and generation of leachate (Farquhar, 1989). An important consideration in biochar application in these scenarios will be the hydraulic conductivity of the biochar-soil mixture, both initially and over time as biochar is subject to ageing effects (e.g. surface oxidation).

3.4.2 Chemical properties of biochars

Overall, biochars made via pyrolysis exhibited a wide range of physical and chemical properties, and those produced via gasification (CE biochars) tended to have distinct properties from chars obtained from different vendors. As observed in previous studies, the fast pyrolysis biochars not only have finer textures due to more rapid conversion in a fast pyrolysis reactor, but also exhibited a higher degree of carbon enrichment than the slow pyrolysis or gasification biochars. Other properties, such as elevated pH and surface area, were also apparently related to

this rapid rate of carbonization, consistent with observations in prior biochar characterization studies (Bruun et al. 2011; Brewer et al., 2009, 2011).

The pH values of biochars with a greater extent of carbonization reflected by their relatively lower H:C ratios were slightly alkaline, with the highest pH values observed in the biochar with the greatest degree of carbonization (CK), consistent with prior reports documenting a liming effect as biomass is pyrolyzed (Cantrell et al., 2012). This contrasts with the CE biochars, which had pH values closer to 6.5 (ranging from pH 6.24 to 6.78). Again, it is observed that biochars from the same vendor cluster together, likely because the extent of biomass pyrolysis is controlling the development of alkaline pH due to the formation of insoluble salts (i.e. alkali metals), which are more typically more abundant in hardwood ash (Brewer et al., 2009). However, this also could suggest specific chemistries as a function of a pyrolysis reaction design, which has been observed for sorbed organics (Spokas et al., 2011). The highest pH values for commercial biochar are also associated with the highest elemental fractions of metals, such as K and P (i.e. CK and BS biochars), reinforcing the hypothesis that biochar pH and metal salt content are directly related and resultant from the degree of biomass carbonization.

Surface chemical properties of the biochars were also affected by the extent of thermal alteration, primarily because of enrichment in various ionic species, such as alkali metals, on the biochar surface as labile organic carbon and volatile matter are removed during pyrolysis (Keiluweit et al., 2010; Brewer et al., 2011). All biochars had negative zeta potential, indicating a negative surface charge for all tested samples. This is consistent with prior reports which document negative surface charge in biochar (e.g. Liang et al. 2006; Cheng et al. 2006, 2008; Mukherjee et al., 2011). This negative charge is the primary mechanism by which cationic nutrients are adsorbed and retained by the biochar, a process believed to lead to improved soil

fertility in biochar-amended soils (Glaser et al. 2001; Lehman et al. 2006). Thus, it would appear these evaluated biochars have favorable surface characteristics for application as an agricultural amendment, or for sorption of cationic nutrients and metals. Additionally, biochars with a higher portion of fine particles (AW, CK) typically had a higher (i.e. less negative) zeta potential than the pelleted CE biochars, except for BS biochar. Differences can also arise due to variations in the amount of sorbed cations (e.g. K^+, Ca^{2+}), which is a plausible explanation for the relatively higher (less negative) zeta potentials observed in those higher cations containing biochars.

The chemical compositions and properties of the biochars reflect both the chemical attributes of the source materials and the extent of thermal alteration of the original biomass. Moreover, differences in the relative amounts of volatile matter and ash also have implications for biotic and abiotic interactions in biochar-amended soil systems, namely the biochars' long-term stability and the extent of microbial utilization of the carbon in biochar (Spokas, 2010). Though not specifically addressed in this study, it is likely that the biochars with low fixed carbon (e.g. CK and BS) biodegrade more readily in soil (Zimmerman, 2010), thus requiring their more frequent application to maintain a targeted C content, for example. Moreover, because complete graphitization requires temperatures in excess of 1000°C, the biomass often is not completely or uniformly charred, leading to highly variable chemical properties within the same biochar batch (McBeath and Smernik, 2009; Spokas, 2010; Harvey et al., 2011). Incomplete combustion of feedstock biomass likely contributed to variations in biochar properties tested in this study, as evidence of incomplete charring was noted in some of the larger biochar particles (i.e. CE-WP1 and 2). Though the fast pyrolysis char (CK) included in this study had a high degree of thermal alteration, other researchers have noted that fast pyrolysis can lead to incomplete biomass combustion due to the very short residence times employed (Bruun et al. 2011). The significance of this issue should be evaluated

on a case-by-case basis as it can result in decreased stability in soil due to microbial degradation of readily bioavailable organic carbon, as well as affect the biochars' sorption properties.

3.5 Conclusions

In this study, physical and chemical properties of six different types of waste wood-derived biochars were characterized and results were compared with those of activated carbon and those of biochars reported in literature. Physical properties characterized included particle size distribution, dry density, specific gravity, surface area, hydraulic conductivity, and water-holding capacity. SEM imaging and image analysis were also conducted to characterize the physical properties of the biochar surfaces. Chemical properties tested included pH, ORP, EC, PAH and metal content, CHN elemental compositions, relative fractions of organic and fixed carbon, ash and volatile matter, and leachate properties. From these results, it is evident that biochar pH varied from 6.24 to 8.77 and was negatively correlated with H:C ratio, indicating the degree of carbonization of the biochar directly relates to its alkalinity. Biochar surface areas were inversely related to fixed carbon content, with the highest surface areas in biochars correlating with higher degree of carbonization (i.e. low fixed carbon content and H:C ratios). Surface porosity determined via SEM image analysis also followed a similar trend, with the highest porosity among biochars belonging to the biochar with the lowest amount of fixed C (CK biochar).

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4. ENGINEERING PROPERTIES OF WASTE-WOOD DERIVED BIOCHARS AND BIOCHAR-AMENDED SOILS

4.1 Introduction

The content of this chapter has been previously published by Sadasivam and Reddy (2015) during the author's doctoral work [**Sadasivam, B.Y.**, & Reddy, K.R. (2015). "Engineering properties of waste wood-derived biochars and biochar-amended soils. *International Journal of Geotechnical Engineering*, *9*(5), 521-535] and [**Sadasivam, B. Y.**, & Reddy, K. R. (2015). Shear strength of waste–wood biochar and biochar–amended soil used for sustainable landfill cover systems. *From fundamentals to applications in geotechnics*, 745-752].

Biochars are generated as a by-product during the thermo-chemical conversion of biomass (feedstock) into bio-fuel through pyrolysis or gasification process (Lehmann and Joseph, 2009). The physical-chemical characteristics of biochars are dictated by several factors such as, biomass conversion process, type of feedstock, residence time and temperature in the reactor and post-treatment processes such as activation (Yargicoglu et al., 2014). Due to the pyrogenic production conditions of biochars, they contain stabilized form of organic carbon compounds with a highly porous structure resulting in their potential to be used for a wide range of applications. In agronomy, biochar appears to increase soil fertility and minimize leaching of nutrients, thereby improving crop growth and production rates in coarse textured soils (Verheijen et al., 2010; Uzoma et al., 2011). Moreover, biochar is relatively stable in soil with mineralization rates that are slower than found in the original biomass (Spokas et al., 2010), which in turn makes biochar an attractive means to sequester carbon. There is evidence of a prominent increase in the wealth of biochar literature in response to the identified potential uses of biochar in various fields, such as

environmental remediation (Xie et al., 2014; Reddy et al. 2014a), agriculture, carbon sequestration, and greenhouse gas mitigation from soils (Verheijen et al., 2010; Gurwick et al., 2013; Liu et al., 2013).

Comprehensive review of literature in soil and bio-based cover systems proved the need to incorporate novel biocover materials to enhance methane mitigation in landfills (Sadasivam and Reddy, 2014a). Most recent research indicates that biochars have a high potential to mitigate the rising levels of anthropogenic methane emissions from landfills by increasing the methanotrophic population and promoting higher rates of methane oxidation when used as a soil amendment in bio-based cover systems (Reddy et al., 2014b). Biochar amended soil can promote the growth of methanotrophic community by way of increasing oxygen diffusion into the soil and can hence act as a sink to atmospheric methane (Chan and Parkin, 2000; Tate et al., 2007; Werner et al., 2007). The highly porous structure of biochars can conveniently house methanotrophs, the major drivers for methane oxidation to occur in landfills. The methane adsorption capacity and the gas diffusivity of different wood-based biochars were quantified and found to be several orders of magnitude higher than that of landfill cover soil (Sadasivam and Reddy, 2014b; 2014c) thereby, resulting in enhanced methane adsorption when amended to cover soil.

In order to make well-informed decisions relating to the field-scale design and implementation of biochars in engineered systems such as landfill biocovers or reactive barriers, it is critical to understand the engineering properties of the materials during and after construction under expected field loading conditions. The addition of biochars to soil resulted in an overall improvement of soil physical properties and mechanical stability due to the formation of macro-aggregates over time which, consequently result in an increased inter-particle cohesion and improved resistance to slaking (Sun and Lu, 2014). Extensive database on biochar properties has been compiled by

University of California, Davis and is available online. This database includes mainly the chemical properties such as elemental composition and toxicity characteristics and to a certain extent, the physical properties such as specific surface area. Limited information is available on the strength and mechanical properties of biochars (Baveye, 2014) and their effects on landfill cover slope stability when amended to soil. Compressibility and shear strength are critical engineering properties that define the behavior of materials under a specified range of compressive and shearing loads. Compressibility relates to the settlement characteristics of the landfill cover system during and after placement of the cover materials. Differential settlement can occur in landfill cover soils which cause cracking and eventually weaken the strength and integrity of the cover system in addition to causing advective (pressure-induced) transport of landfill gases which are emitted into the atmosphere through the cracks. Shear strength parameters namely, cohesion and friction angle, are used to compute the stability of landfill cover slopes.

The objectives of this study are to: (1) evaluate the compressibility characteristics of biochars and biochar-amended soils and quantify the constrained modulus, (2) determine the shear strength parameters of biochars and biochar-amended soils and evaluate the stability of cover slopes and, (3) determine the effects of physical-chemical properties of biochars on their constrained modulus and shear strength parameters.

4.2 Materials and Methods

Seven different types of biochars derived from woody feedstock were acquired from commercial vendors in 5-gallon buckets and stored in air-tight containers. The biochars were air-dried and the fraction of biochars that passed through #10 sieve (2 mm opening) and retained on #20 sieve (0.84 mm opening) were used for the compressibility and shear strength testing.

Information pertaining to feedstock, production processes, treatment conditions and post-treatment processes for the biochars as provided by their respective vendors are listed in Table 3-1. The cover soil was obtained from the stockpile near an active landfill in DeKalb County, IL. The cover soil was sieved using a 2-mm mesh and the fraction of soil passing the sieve was homogenized and powdered to eliminate any clumps and stored in air-tight glass jars at room temperature (25^0C) prior to usage for compressibility and shear strength testing. Photographs of all the biochars as obtained from the vendors and the homogenized landfill cover soil are shown in Figure 4-1.

FIGURE 4-1: PHOTOGRAPHS OF BIOCHARS AND LANDFILL COVER SOIL

4.2.1 Physico-Chemical Characterization Testing

Specific gravity of biochars and soil were determined in accordance with ASTM D 854. The biochars and soil were characterized for dry density using the Harvard miniature compaction test setup (Humboldt Mfg. Co.) in accordance with the method described by Wilson (1970).

Porosity of biochars and soil were quantified using an image processing software, Pores (Particles) and Cracks Analysis System (PCAS), which was developed and validated by Liu et al. (2011). Scanning Electron Microscope (SEM) images of biochars and soil captured at a magnification of 2000x were used to quantify the porosity using PCAS software. The water holding capacity of materials were calculated in accordance to the method proposed by Kinney et al. (2012). According to this method, the moisture content values of the materials after saturating them completely and allowing for gravity drainage to occur for a minimum of 3 hours, corresponds to their respective field capacity values.

Organic matter content was quantified using the loss-on-ignition (LOI) at 440^{o}C according to ASTM D2947. To determine the pH of biochars and soil, 10g of the material was soaked in 10 ml of 0.01 M $CaCl_2$ solution for 2 hours prior to measurement using the pH meter (Orion 720A Model pH Meter). The pH meter was checked for accuracy by performing a 3-point calibration using pH buffers corresponding to 4, 7 and 10 pH values prior to taking measurements. All the physico-chemical characterization tests were conducted on air-dried biochars obtained as-is from the vendors and on air-dried sample of cover soil that was sieved to particle size less than 2 mm and homogenized. Further details on the physico-chemical characterization procedures for biochars used in this study are discussed in Yargicoglu et al. (2014).

4.2.2 Compressibility Testing

The purpose of conducting compressibility tests is to compute the constrained modulus of biochars and biochar-amended soils so that their settlement characteristics of landfill covers can be ascertained. The protocol for testing the compressibility of biochars, soil, and biochar-amended soils were in accordance with that of ASTM D 2435. The compressibility of seven different wood-

based biochars were evaluated under two levels of moisture content (dry and 25% Water Holding Capacity, WHC) and that of biochar-amended soils were evaluated for four selected biochars (CE-WP1, CE-WP2, CE-AWP and CE-WC) amended to soil at amendment ratios of 0, 2, 5 and 10% on a dry weight basis in the presence (25% WHC) and absence of moisture (dry conditions). A total of 14 tests were conducted on biochars and 26 tests were conducted on biochar-amended soils. Compressibility tests were performed on the air-dried and sieved fraction of biochars with particle sizes ranging from 0.8 – 2 mm. Test samples were placed in a cylindrical consolidation ring in two consecutive and equal-thickness layers by providing light tamping after placement of each layer. The consolidation ring was 4.2 cm in diameter and 6.4 cm in height. The samples placed in the consolidation ring were then subjected to sequential loading (0.1 – 100 kPa) that encompass the expected field loading conditions incurred from the self-weight of a typical landfill cover material (10 – 40 kPa) and heavy equipment during the cover construction (Khoshand and Fall, 2014). After application of each vertical load, the corresponding displacement readings from the dial gauge were noted after allowing enough time for the vertical displacement to reach a constant value. The axial strain (ε, %) obtained for each sample is then plotted against the normal stress (σ, kPa) and the inverse of the slope of this graph given by, $\frac{\Delta\sigma}{\Delta\varepsilon}$ corresponds to the constrained modulus, M (kPa) of the material. The axial strain response for different biochars obtained from this study corresponds to the primary compression.

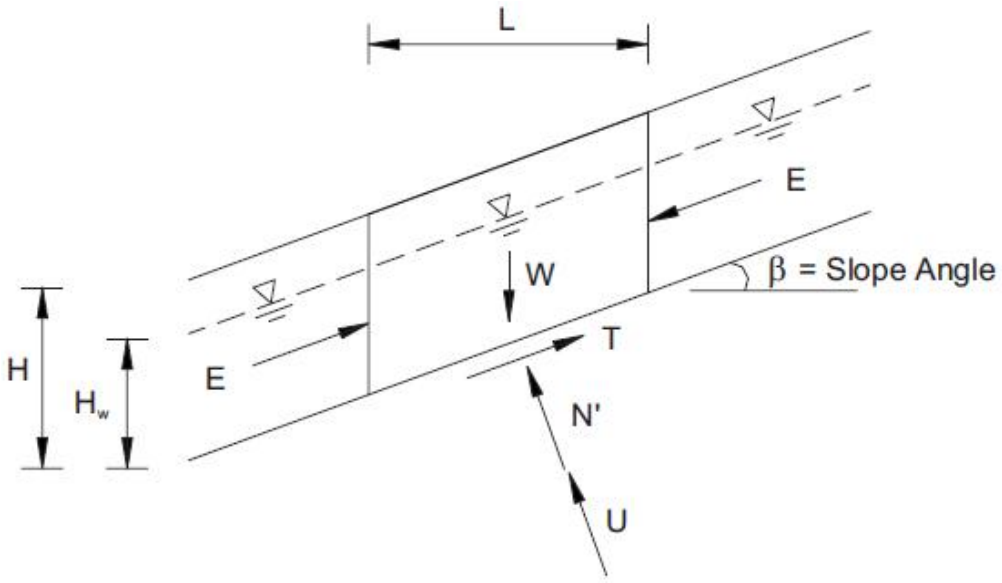
4.2.3 Shear Strength Testing

The shear strength parameters, cohesion (c', kPa) and friction angle (φ', degrees) are critical properties of cover materials that are required to evaluate the stability of landfill cover slopes. Direct shear tests were conducted in accordance with the method described in ASTM D

3080 on seven different wood-based biochars under dry conditions and on biochars amended to cover soil at 0 and 10% amendment ratios in the presence of 15% moisture content on a dry weight basis (d.w.). Powdered soil and air-dried, sieved biochar samples with particle size ranging from 0.8 – 2 mm are used for all the shear strength tests. The samples were placed in a cylindrical shear box in 2 consecutive layers by providing light tamping after placement of each layer. The packing density of the samples were then calculated and recorded for each test (Table 4-3). The shear box was placed into the direct shear testing instrument fitted with a vertical and a horizontal loading frame. Each sample was subjected to three different normal stresses (24, 48 and 96 kPa) and under each normal stress, shear loading was applied at a constant displacement rate of 0.025 inches/min. The sample was allowed to consolidate for a minimum of 1 hour under each normal stress prior to the application of shear load. The horizontal displacement of sample is then recorded over time until the sample undergoes a shear displacement of up to 0.25 inch with the diameter of the sample being 2.5 inches (i.e., 10% displacement with respect to the sample diameter). A total of 21 tests were conducted for biochars under dry conditions and 24 tests for all 10% biochar-amended soils at 15% moisture content (d.w.). The maximum shear stress value corresponding to each normal stress applied is obtained from the direct shear test data. Mohr-Coulomb failure envelope is plotted from the graph of maximum shear stress (kPa) versus normal stress (kPa). The slope of this best-fit line corresponds to frictional angle (φ', degrees) and the intercept of the line corresponds to cohesion (c', kPa). Thus, the shear strength parameters are computed for all the biochars and biochar-amended soils under the specified test conditions.

4.2.4 Slope Stability Analysis

The shear parameters (c' and φ') computed from direct shear test results are used to perform the infinite slope stability analysis to investigate and compare the stability of a homogeneous layer of landfill cover material comprising either soil or biochar-amended soil. The infinite slope analysis was conducted based on the assumption that failure occurs as a result of the movement of cover material in parallel direction to the slope and that the forces causing the movement, weight of the materials and the resisting forces correspond to strength of the cover materials (Sharma and Reddy, 2004). Infinite slope stability analysis was performed based on the slope geometry, water levels and formulations shown in Figure 4-2. The factor of safety for the cover slopes are computed by assuming three different slope scenarios (2H:1V, 2.5H:1V and 3H:1V) at different ratios of the height of water table (H_w) to the total height of the landfill cover (H) ranging from 0 - 1. The thickness of the landfill cover is assumed to be 1m and the unit weight of soil and biochar-amended soils are computed from the measured values of dry density.



$$FS = A\frac{\tan\varphi'}{\tan\beta} + B\frac{c'}{\gamma H}$$

$$A = 1 - \frac{\gamma_w H_w}{\gamma H Cos^2\beta}$$

$$B = \frac{1}{Cos^2\beta \tan\beta}$$

Φ' and c' = Shear parameters
β = Cover slope angle
γ and γ_w = unit weight of cover material and water
H = Height of cover soil
H_w = Height of water table

FIGURE 4-2: INFINITE SLOPE STABILITY ANALYSIS OF BIOCHAR-AMENDED LANDFILL COVER SOIL

4.3 Results

4.3.1 Physico-Chemical Characterization Testing

The physico-chemical properties of biochars and cover soil are listed in Table 4-1. Cover soil was classified to be 'silty clay' type (USCS classification – CL) with 30.8% clay, 27.8% silt and 41.4% sand. The porosity values of biochars range from 0.30 – 0.55 and soil has the least porosity of 0.25. On the other hand, soil has the highest value for specific gravity (2.6) and dry density (1.89 g/cm^3). The density of biochars are well below 1 g/cm^3 and the specific gravity values for biochars are also much lower compared to soil ranging from 0.6 – 1.5. The WHC of biochars are significantly higher ranging from 0.51 – 1.79 compared to that of soil which has a value of 0.21. The organic matter content of soil (8×10^{-3}) is three orders of magnitude lower than that of all biochars. The pH of BS, CK and AW biochars are clearly basic with values of 8.5, 9.0 and 7.9, respectively. The pH of all CE- biochars ranges from being slightly acidic to slightly basic (6.2 to 7.6). The pH of cover soil is around neutral with a value of 7.3.

TABLE 4-1: PHYSICO-CHEMICAL PROPERTIES OF BIOCHARS AND SOIL

Property	BS	CK	AW	CE-WP1	CE-WP2	CE-AWP	CE-WC	Soil
Porosity (fraction)	0.46	0.55	0.30	0.44	0.41	0.40	0.36	0.25
Specific gravity	1.4	1.5	1.2	0.8	0.6	0.9	0.9	2.6
Dry density (g/cc)	0.73	0.54	0.48	0.56	0.52	0.53	0.38	1.89
Water holding capacity (fraction)	1.21	1.79	1.14	1.42	0.51	0.81	0.74	0.21
Organic Content (fraction)	0.30	0.31	0.76	0.96	0.97	0.82	0.91	8×10^{-3}
pH	8.5	9.0	7.9	6.2	6.8	7.6	7.1	7.3

4.3.2 Compressibility Testing

The axial strain (%) response and the corresponding values of constrained moduli (MPa) for biochars and soil at dry and 25% WHC under normal stress values ranging from 0.1 – 100 kPa are shown in Figure 4-3. The compressibility of biochars under dry conditions are comparatively higher than that of soil. The axial strains for biochars range between 1.8 and 8.3% under dry conditions and between 1.6 and 5.2% at 25% WHC. The axial strain of cover soil at 25% WHC (2.5%) is slightly higher than the strain under dry conditions (1.1%).

Biochars and soil exhibit maximum values for constrained moduli under the highest applied normal stress values at dry and wet conditions. The maximum values for the constrained moduli of dry biochars range approximately between 2 and 7 MPa, whereas, that of dry soil is 14 MPa. Under 25% WHC, CE-AWP exhibited the maximum value for constrained modulus (≈7 MPa) which was followed by soil (≈4 MPa). There was little to no difference in the maximum values of constrained moduli for biochars between dry and wet conditions whereas, that of soil notably decreased in the presence of moisture.

The axial strains and corresponding constrained moduli of four selected biochar amended soils at 2, 5 and 10% biochar to soil amendment ratios under dry and 25% WHC are presented in Figures 4-4 through 4-7. All the biochar-amended soils exhibited the maximum values of constrained moduli under the highest applied normal stress range (40 – 100 kPa) at dry and wet conditions. The maximum constrained moduli of biochar-amended soils decreased as the biochar to soil amendment ratios increased from 2% (w/w) to 10% (w/w) under dry and 25% WHC.

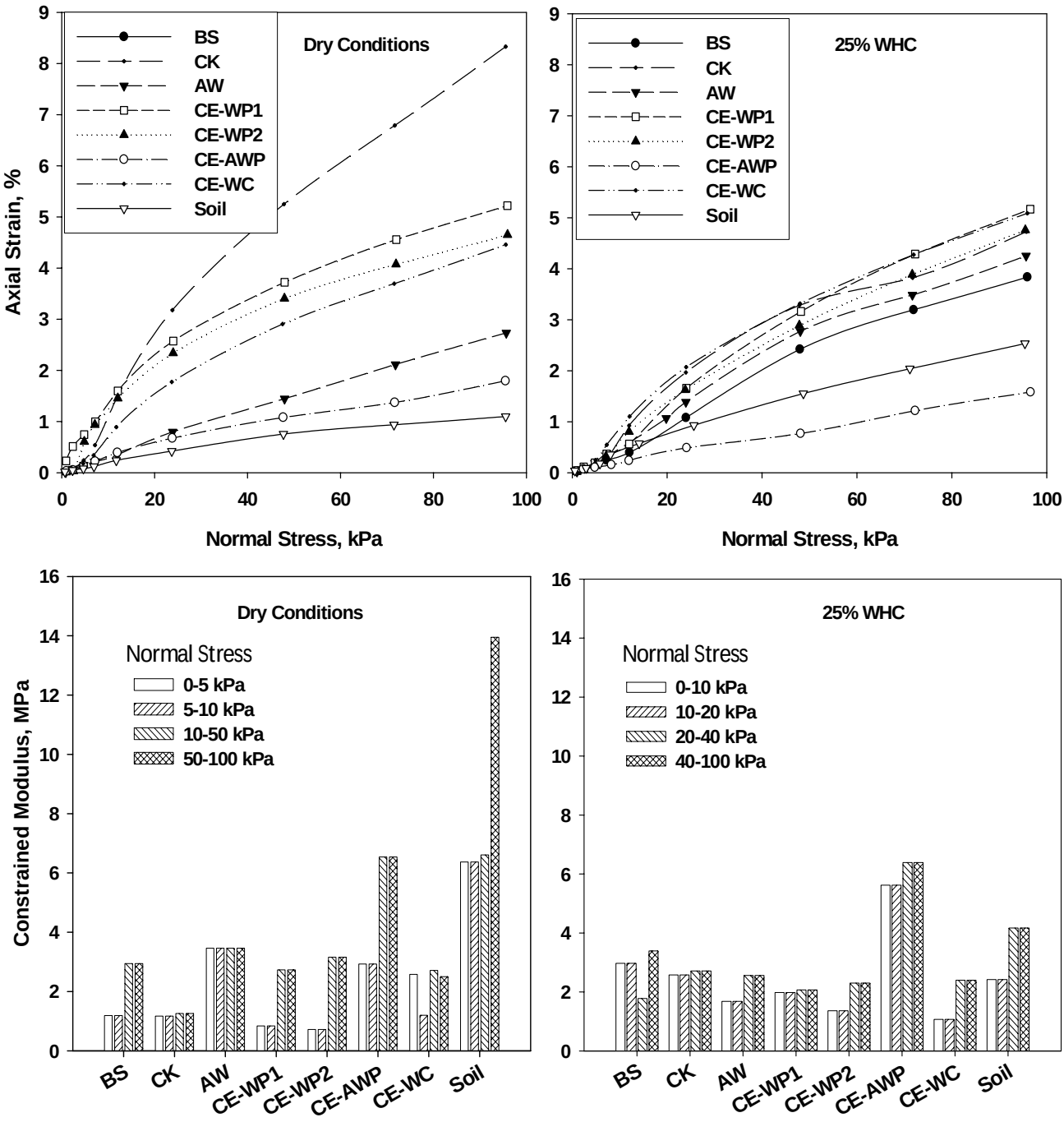


FIGURE 4-3: AXIAL STRAIN RESPONSE AND CONSTRAINED MODULI FOR BIOCHARS AND SOIL UNDER DRY AND 15% WHC CONDITIONS

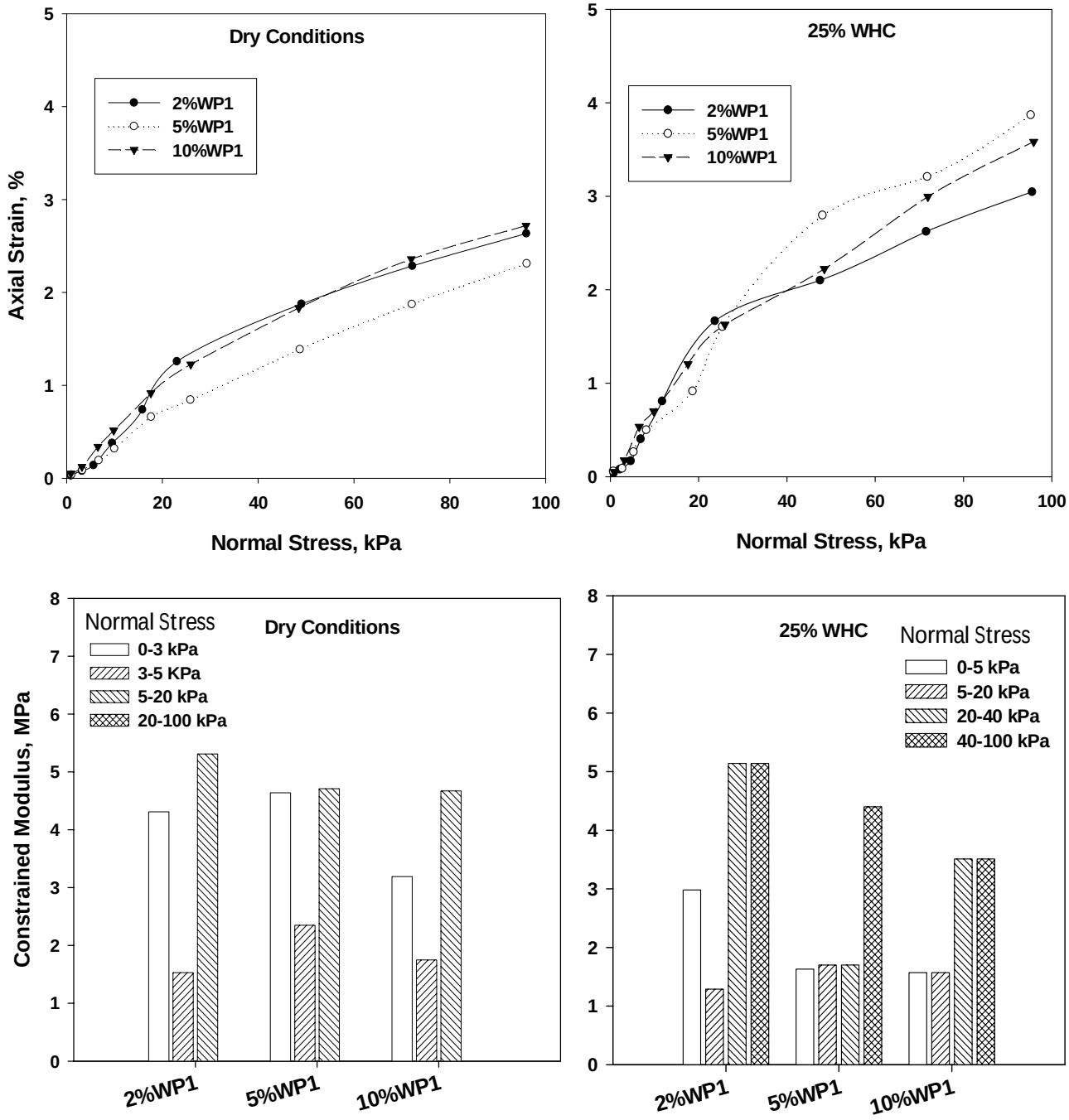


FIGURE 4-4: AXIAL STRAIN RESPONSE AND CONSTRAINED MODULI FOR BIOCHAR CE-WP1 AMENDED SOIL

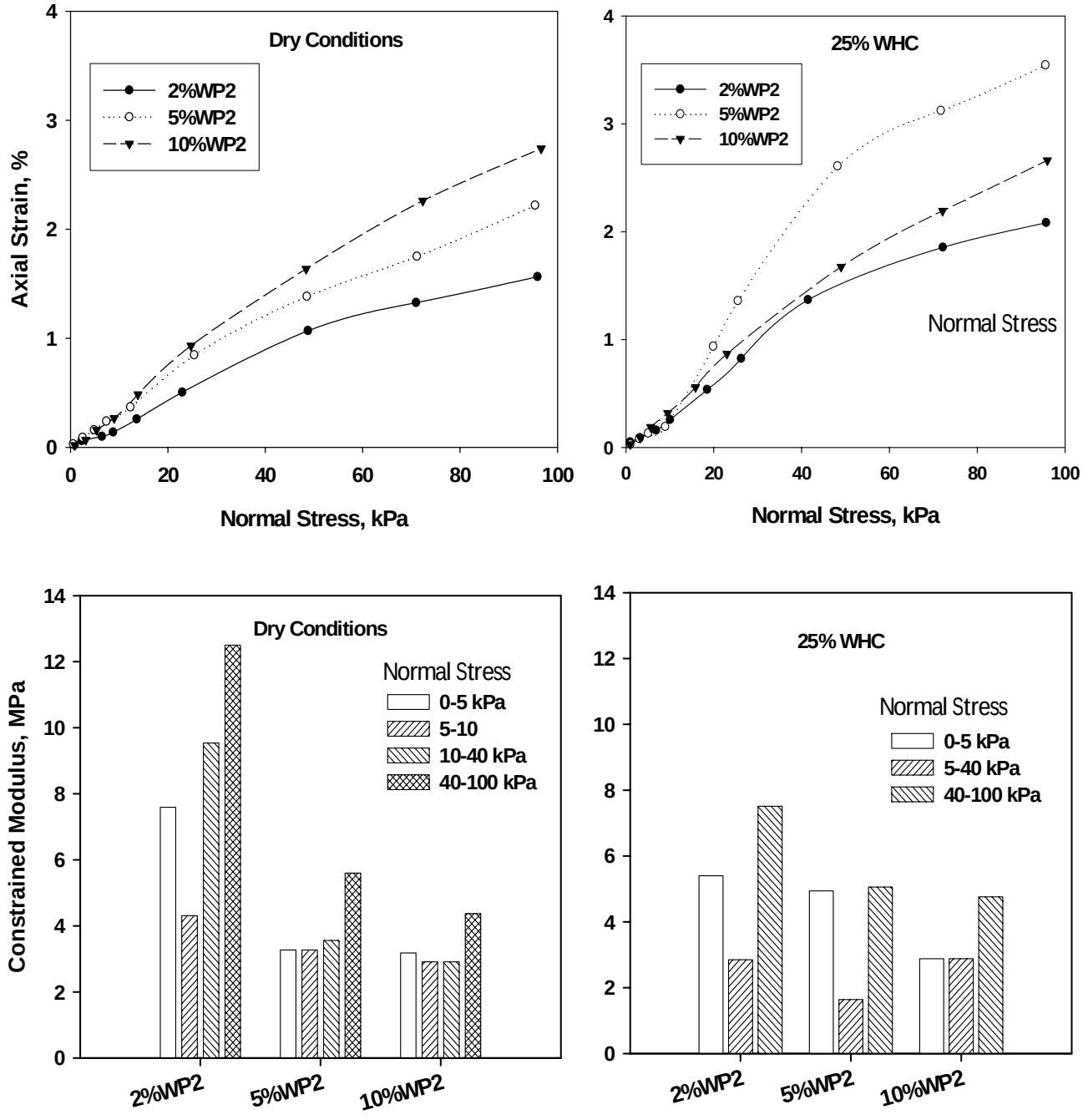


FIGURE 4-5: AXIAL STRAIN RESPONSE AND CONSTRAINED MODULI FOR BIOCHAR CE-WP2 AMENDED SOIL

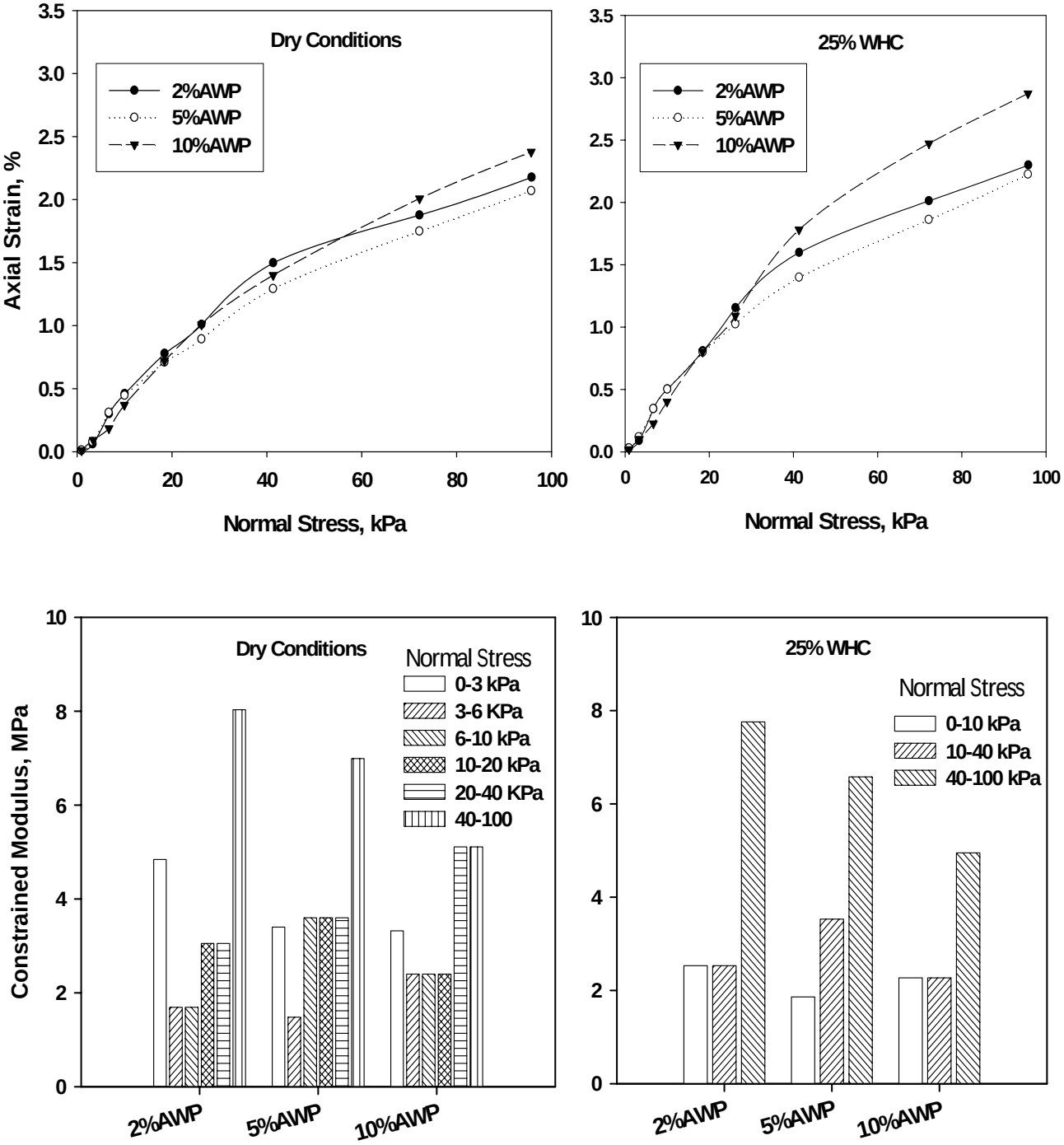


FIGURE 4-6: AXIAL STRAIN RESPONSE AND CONSTRAINED MODULI FOR BIOCHAR CE-AWP AMENDED SOIL

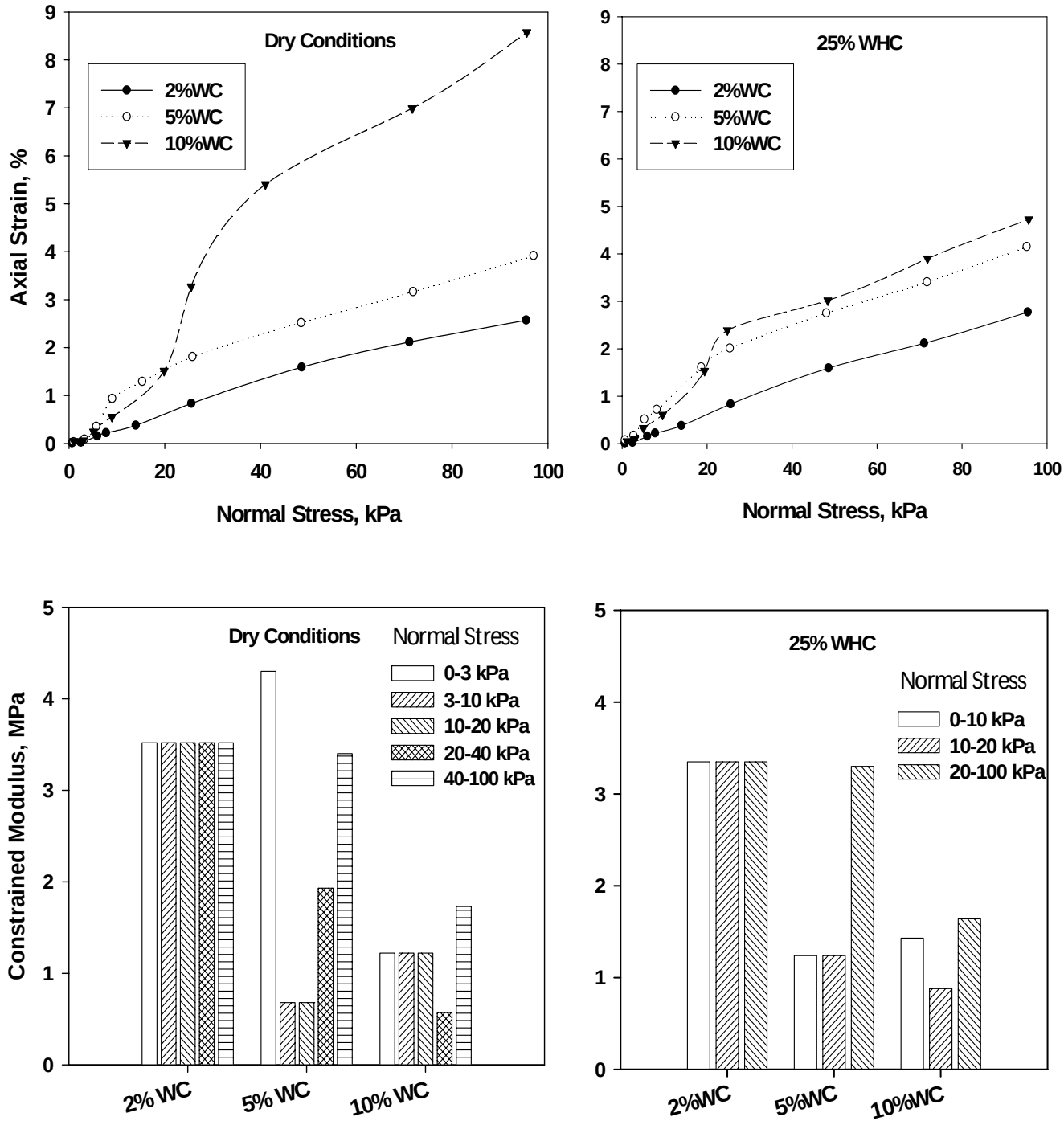


FIGURE 4-7: AXIAL STRAIN RESPONSE AND CONSTRAINED MODULI FOR BIOCHAR CE-WC AMENDED SOIL

CE-WC amended soils exhibited the maximum levels of axial strain and correspondingly, the least levels of constrained moduli (1.5 – 4.5 MPa) compared to other types of biochar-amended soils (Figure 4-7). 2% CE-WP2 amended soil underwent the least axial strain under dry conditions and exhibited the highest value of constrained modulus (13 MPa) among all biochar-amended soils but, its constrained modulus value decreased to 7.5 MPa in the presence of moisture (Figure 4-5). On the other hand, there were no noticeable differences between the maximum constrained moduli values of CE-AWP amended biochars under dry and wet conditions which ranged between 5 – 8 MPa (Figure 4-6).

The lowest (critical) values of constrained moduli of soil, biochars and biochar-amended soils at dry and 25% WHC under the expected field loading conditions of 10 – 50 kPa (Rajesh and Viswanadham, 2011) are shown in Figure 4-7. The critical constrained modulus of soil at dry conditions is approximately 6.5 MPa and reduces considerably to 2 MPa under wet conditions (25% WHC). Among the four selected biochars tested to study the compressibility behavior of biochar-amended soil, CE-AWP exhibited the maximum value of constrained modulus (≈7 MPa) at dry and wet conditions under expected field loading range (Figure 4-8). CE-WC amended soils exhibited the least values for critical constrained moduli under dry and wet scenarios at 10% amendment ratio (w/w) compared to other biochar-amended soils.

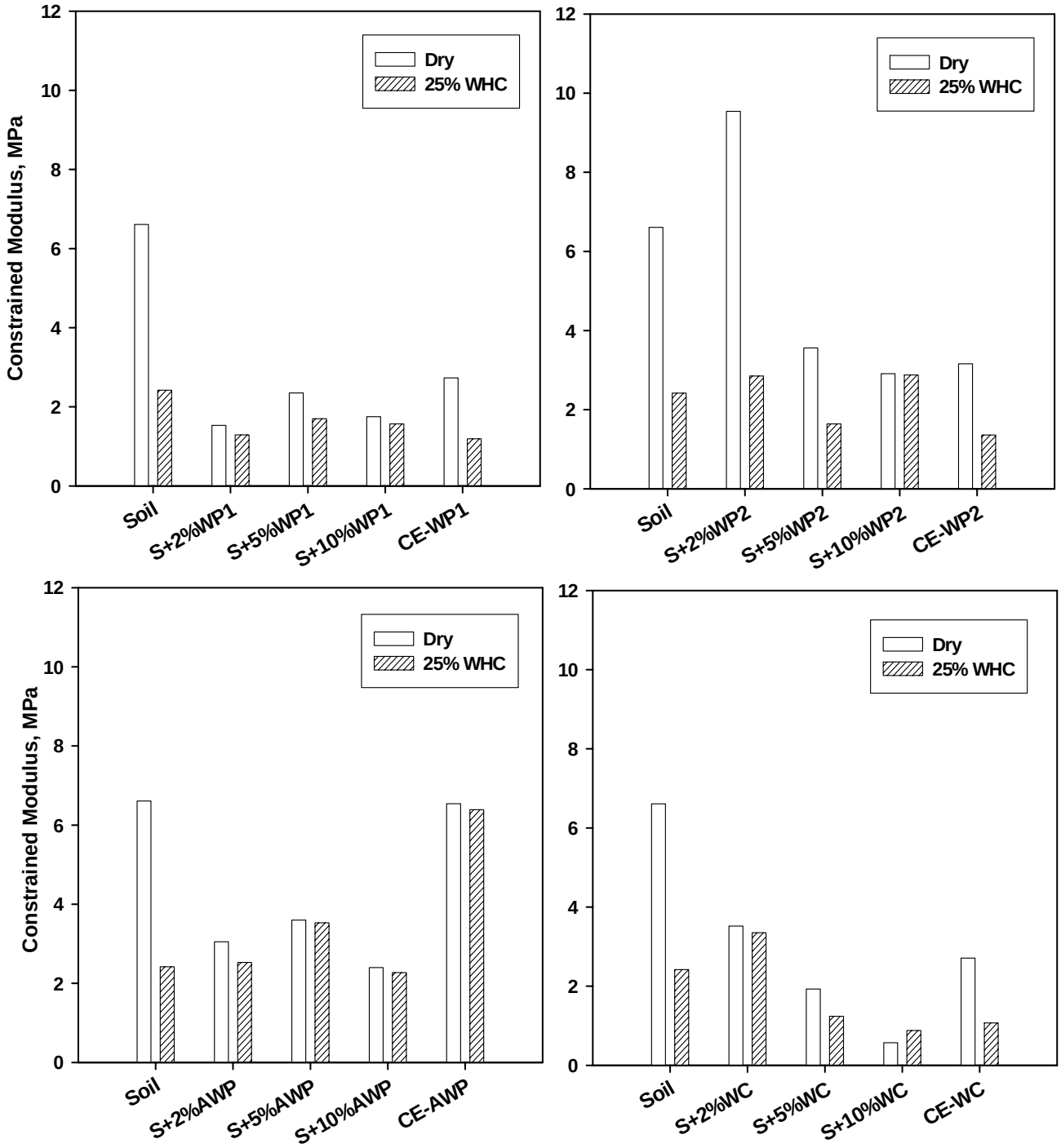


FIGURE 4-8: EFFECTS OF MOISTURE AND BIOCHAR-AMENDMENT RATIO ON CRITICAL CONSTRAINED MODULI AT NORMAL STRESSES RANGING FROM 10-5- KPA

4.3.3 Shear Strength Testing

Figure 4-9 shows the typical direct shear test results under three different applied normal stresses (24, 48 and 96 kPa) for soil at dry and 15% MC, CE-WP2 under dry condition, and 10% CE-WP2 amended soil at 15% MC. Similar graphs of shear stress versus horizontal deformation are obtained from direct shear data corresponding to all other tested materials. From the direct shear data, the maximum shear stress value corresponding to each normal stress is read and used to plot the Mohr-Coulomb failure envelope for each material as shown in Figure 4-10. The direct shear parameters (cohesion, c' and friction angle, φ') computed from the slopes and intercepts of the best fit lines corresponding to each test material are shown in Figure 4-10. Summary of shear strength parameters for biochars and biochar-amended soils are presented in Table 4-2.

The φ' values of all biochars under dry conditions range between 29.8^o and 39^o and their corresponding cohesion values range between 12.4 kPa and 27.1 kPa. Biochars have considerably higher cohesion under dry conditions compared to soil at 15% MC (dw). Moist soil had a c' value of 6.3 kPa and a φ' value of 28.3^o. Biochar-amended soils had greater cohesion (except for CK) and higher friction angle (except for BS) compared to soil under wet conditions. The cohesion values for biochar-amended soils were consistently lower than that of the biochars except in the case of AW-amended soil which exhibited a value of 31.3 kPa, almost twice the value of dry AW biochar (16.6 kPa). The friction angle of biochar-amended soils was mostly higher than those values corresponding to the dry biochars with the exceptions of BS and CE-WP2 biochars. Overall, the addition of biochars to cover soil increased the shear strength parameters of the cover soil.

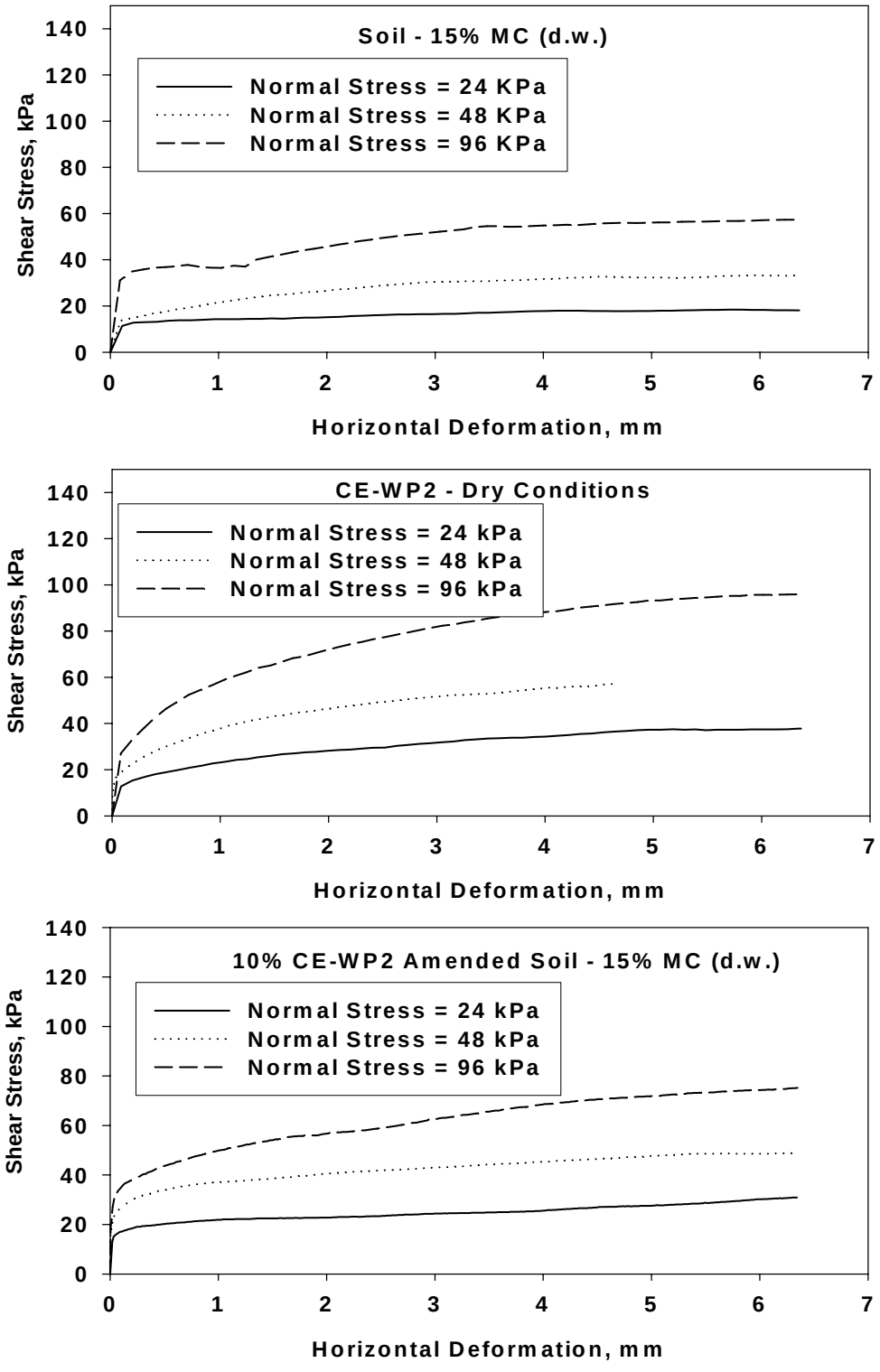


FIGURE 4-9: TYPICAL SHEAR STRESS VERSUS HORIZONTAL DEFORMATION CURVES AT VARYING NORMAL STRESSES FOR SOIL

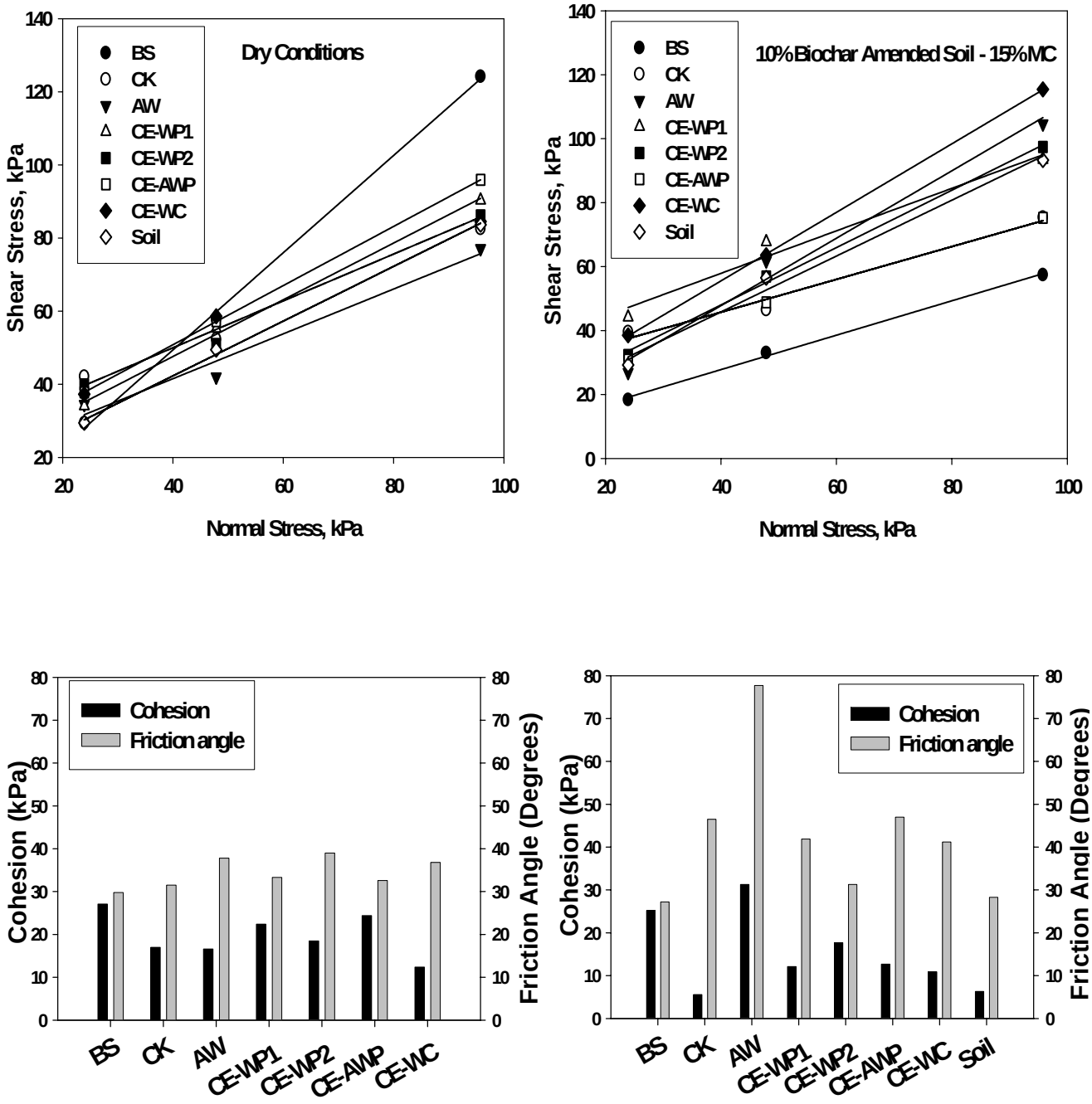


FIGURE 4-10: FAILURE ENVELOPES AND SHEAR STRENGTH PARAMETERS FOR BIOCHARS AND BIOCHAR-AMENDED SOILS

TABLE 4-2: SUMMARY OF SHEAR STRENGTH PARAMETERS FOR SOIL, BIOCHARS AND 10% BIOCHAR-AMENDED SOILS

Biochar Type	Dry Biochar			10% Biochar Amended Soil – 15% MC (dw)		
	Friction angle (deg)	Cohesion (kPa)	Unit Weight (KNm^{-3})	Friction angle (deg)	Cohesion (kPa)	Unit Weight (KNm^{-3})
BS	29.8	27.1	5.0	27.2	25.2	16.1
CK	31.5	17.0	2.0	46.5	5.6	11.7
AW	37.8	16.6	4.7	77.7	31.3	15.6
CE-WP1	33.3	22.4	4.2	41.9	12.1	17.0
CE-WP2	39.0	18.5	3.8	31.3	17.7	15.7
CE-AWP	32.6	24.4	3.5	47.0	12.7	16.7
CE-WC	36.8	12.4	2.3	41.2	10.9	12.9
Soil	--	--	--	28.3	6.3	18.5

4.3.4 Slope Stability Analysis

The computed factors of safety (FS) for soil and four selected 10% biochar-amended soils at three different slope angles are shown in Figure 4-11. The federal requirement for the design of final cover systems specifies a minimum acceptable FS value of 1.5 for static slope stability analysis using the two-dimensional limit equilibrium method (USEPA, 2004). Thus, a FS value of 1.5 needs to be met throughout the design life of the final cover systems under normal operating conditions (i.e., without accounting for seismic or live loading). All biochar-amended soils have a FS value greater than 1.5 and hence meet the design criteria for ensuring sufficient stability of

cover slopes under all the three slope angles (Figure 4-11). The lowest value for the FS of soil is 1.3 and occurs at the steepest slope (2H:1V) when $H_w/H = 1$. Though, the FS value under this condition is less than 1.5, it is still greater than 1.2 which is considered sufficient for meeting the stability criteria based on the assumption that the complete saturation of the cover system is considered to be a short-term loading condition and that the cover system would soon be restored to the expected, long-term loading conditions. The safety factors for 2H:1V slope for 10% biochar amended soils under fully saturated conditions range from 2.4 – 3.3, almost twice as much as the FS values for soil under these conditions.

The 10% WP2 amended soil exhibited the highest FS values at all the three slope angles under fully saturated conditions with values ranging from 3.3 at 2H:1V slope to 4.6 at 3H:1V slope. Similarly, at all the three slope angles, 10% WC amended soils exhibited the lowest values of FS under fully saturated condition, ranging between 2.4 at 2H:1V slope to 3.5 at 3H:1V slope. The safety factors for soil and biochar-amended soils increased with decreasing slope angles irrespective of the level of water table within the cover system. Overall, the FS values of all biochar-amended soils are at least twice as much as that of soil at all the slope angles and at varying levels of water table within the cover layer.

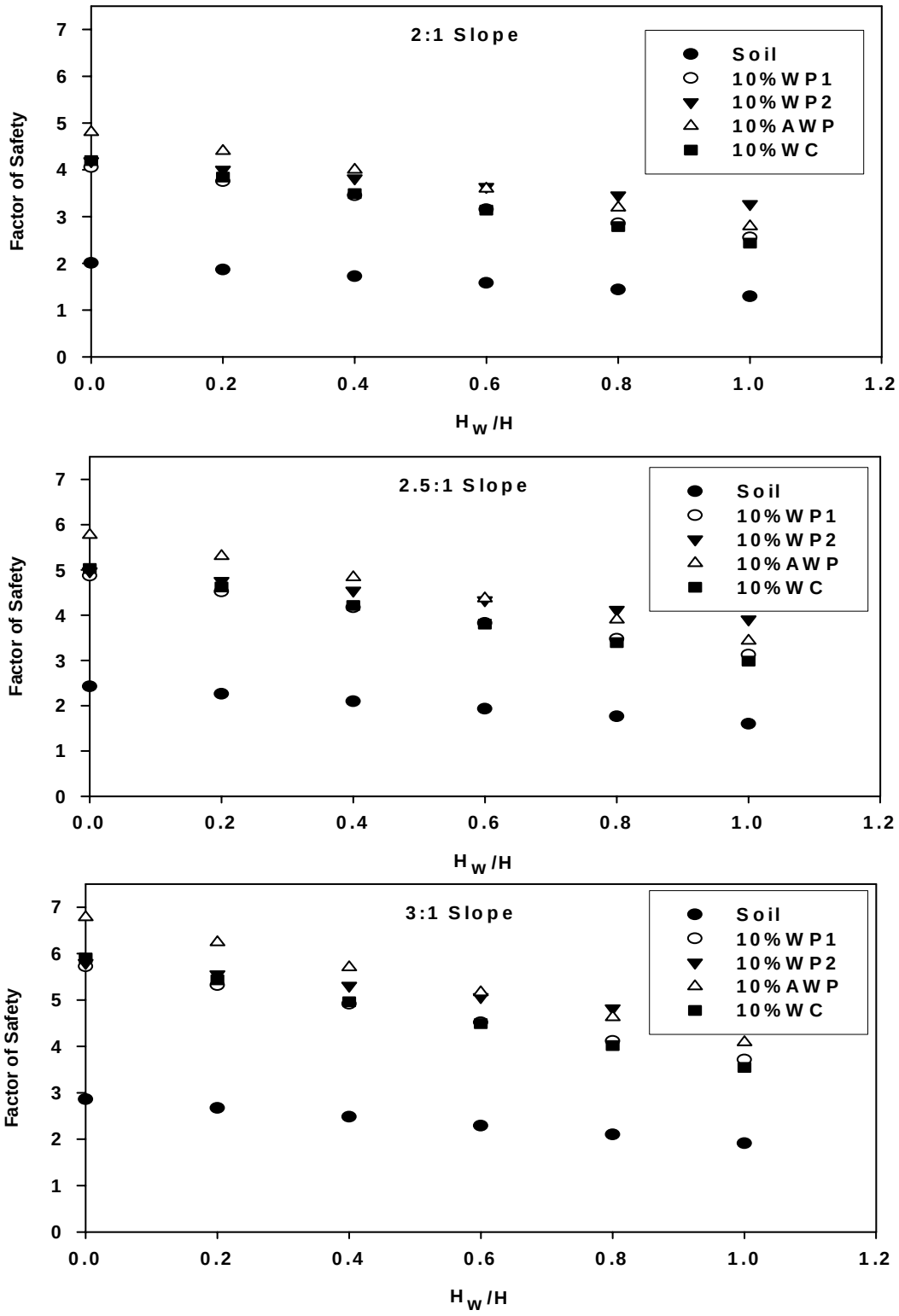


FIGURE 4-11: EFFECT OF 10% BIOCHAR AMENDMENT TO SOIL ON STABILITY OF COVER SLOPES

4.4 Discussion

4.4.1 Compressibility Testing

Results from this study indicate that dry biochars had higher values for axial strain (%) and lower values for maximum constrained modulus (M_{max}) compared to that of dry soil under normal stresses ranging from 0.1 – 100 kPa. This implies that biochars had greater ability to undergo compression resulting in much larger settlements when used as a landfill cover material. The probable reason for this being, biochars have higher porosity and lower density compared to cover soil (Table 4-1), making them more susceptible to undergoing particle rearrangement and densification upon application of vertical pressures. For a landfill cover of certain initial height, H, the cover settlement (ΔH) can be computed using the constrained modulus (M) of the cover material for the expected vertical loading ($\Delta\sigma$) conditions as shown in Eqn. (4-1).

$$\Delta H = \frac{\Delta\sigma \times H}{M} \tag{4-1}$$

The settlement of landfill cover is thus, inversely proportional to the constrained modulus of the cover material. Upon knowing the constrained modulus and the Poisson's ratio (ν) for any given material, its Young's modulus (E) can be calculated using Eqn. (4-2).

$$E = \frac{M(1+\nu)(1-2\nu)}{1-\nu} \tag{4-2}$$

The poisson's ratio values for the biochars were not determined in this study and there is no data published in literature for Poisson's ratio of biochars. However, the Poisson's ratio values for low density pyrolitic carbons range from 0.21 to 0.49 (Price and Kaae, 1969) and based on this information, the Young's Modulus values for biochars can be determined to obtain a rough estimate. Although, it has to be noted that the Poisson's ratio for biochars can vary widely depending on their density and porosity.

The compressibility of woody biochars ranged from 1 to 8 MPa under dry and wet conditions and these results agree with reported values of compressibility for biochars produced from plant-based biomass (Echterhof and Pfeifer, 2014). The application of uniaxial, compressive loads on biochars and soil result in a denser packing of the material by reducing the void ratio and promoting better inter-particle locking which subsequently increases the material's stiffness. Particle rearrangement causing densification of loose, granular materials occurs upon the application of compressive loads as a result of overcoming the inter-particle friction, thereby, forcing the particles to slip along the surfaces and rotate to settle into available pore spaces (Chuhan et al., 2003). The inter-particle bonding due to the formation of solid bridges between particles was reported to be much higher at higher compaction pressures and there was significant reduction in the porosity of materials under such conditions (Bazargan et al., 2014). This phenomenon could explain the reason behind the high constrained moduli values observed for soil, biochars and biochar-amended soils at vertical stresses ranging from 50 – 100 kPa.

The changes in the constrained modulus for biochars under dry and wet conditions as inferred from the corresponding changes in the slopes of the axial strain versus stress curves (Figure 4-3) indicate that the constrained moduli increased with increasing normal stresses for certain materials (dry BS, dry CE-WP1, CE-WP2, CE-AWP, wet CE-WC and soil). The constrained moduli values exhibited mixed trends (decreasing as well as increasing patterns) for certain materials (dry CE-WC and wet BS) whereas, it was constant throughout the applied vertical stress range for the remainder of materials (CK, dry AW and wet CE-WP1). The compressive behavior of biochars, soil and biochar-amended soils are represented by the plots of axial strain versus effective vertical stress and the shape of these curves are controlled by the nature of particle rearrangement that occurs when the material is subjected to compressive loads. In general, both,

locking and unlocking mechanisms between particles cause changes in the compressibility of materials. Some critical unlocking mechanisms that result in an overall reduction in the strength of materials are due to inter-particle slippage and the crushing of the particles due to particle damage from the applied loads. If the material undergoes particle re-arrangement due to locking mechanisms within a certain range of applied vertical stresses, then the constrained modulus of the material increases with increasing vertical stress for that loading range. Similarly, the constrained modulus of the materials decreases if unlocking mechanisms dominate the particle rearrangement under a range of loading conditions. However, if simultaneous locking and unlocking mechanisms occur for a certain loading condition, then the constrained modulus of the material remains constant for that range of vertical stress (Mersi and Vardhanabhuti, 2009).

Amending biochars to soil mostly resulted in an increase in the compressibility of soils, thereby reducing the constrained modulus values (Figure 4-8). This could be attributed to the reduction in the density and simultaneous increase in the porosity of soil with increasing amounts of biochar-amendments. Reduction in the soil strength and penetration resistance with increasing biochar amendment percentages has been reported in the literature and was attributed to the reduction in soil bulk density and increase in porosity and water holding capacity (Chan et al., 2007; Busscher et al., 2010). The type of biochar amended to soil influenced the compressibility behavior which can be attributed to the variations in the physical-chemical properties among the biochars tested. In general, biochars with high carbon content and low ash content are of higher quality as they exhibit better strength and stability (Echterhof and Pfeifer, 2014). CE-WP2 biochar had the lowest ash content (1.5% d.w.) among all biochars and CE-WP1 had relatively higher ash content (4.6% d.w.) among all the CE-biochars. CE-AWP biochar had relatively higher fixed carbon content (40.3% d.w.) and elemental carbon content (78.1% d.w.) (Yargicoglu et al., 2014).

The morphological characteristics of biochars analyzed from SEM imaging show that all the woody biochars vary distinctly amongst each other with respect to pore structure (shape and size) and pore size distributions (Yargicoglu et al. 2014) thereby, causing noticeable variations in the compressibility behavior.

The presence of moisture in the pores of biochars and biochar-amended soils decreases the void ratio of the materials thereby, affecting their compressibility behavior. The addition of water to biochars resulted in an initial increase in the constrained modulus values for vertical stresses ranging from 0.1 – 20 kPa and beyond this stress range, there was no noticeable changes in constrained moduli values between dry and wet biochars (Figure 4-3). The initial rise in compressive strength of biochars with addition of water was previously reported by Bazargan et al. (2014) and the reason behind this was attributed to the increased bonding and bridging between biochar particles in the presence of moisture because of enhanced van der waal's forces. Overall, the compressibility behavior and the constrained moduli of biochars are controlled by their physical properties such as porosity and water holding capacity (Figure 4-12). Constrained moduli of biochars appear to decrease with increasing porosity and water holding capacity. This implies that physical properties of biochars play a critical role in controlling the overall strength and settlement behavior. Thus, careful pre-screening of biochars are necessary prior to field-scale application in engineered systems.

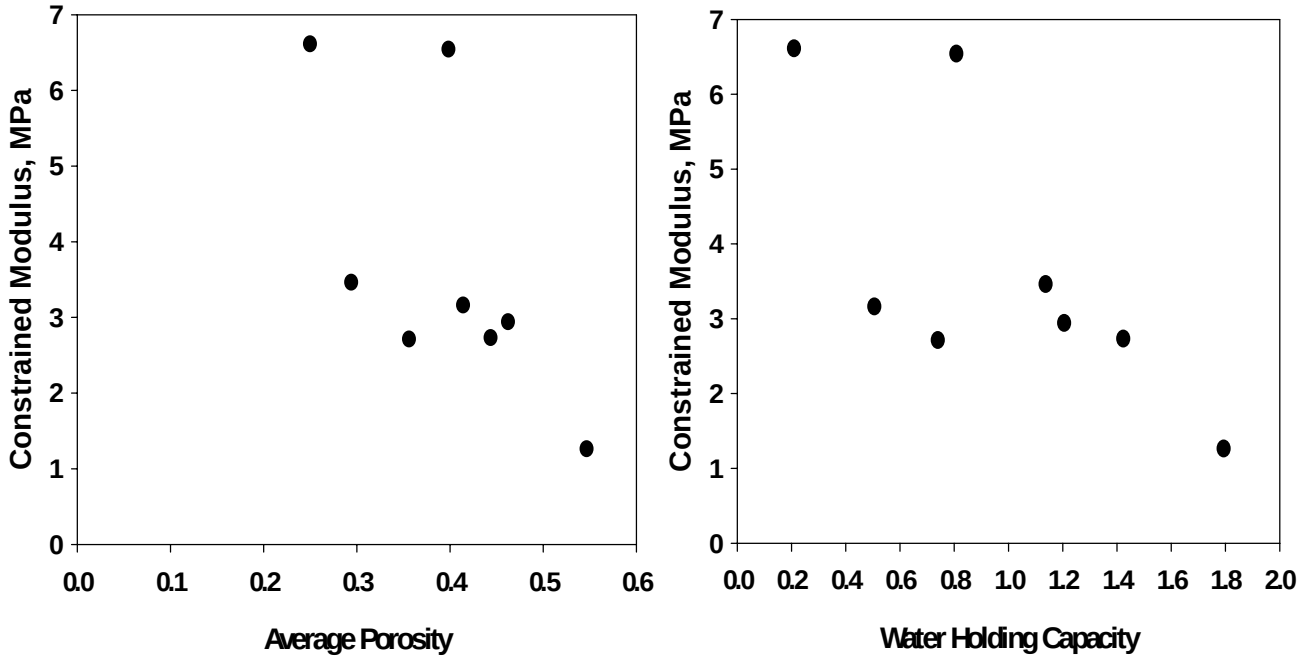


FIGURE 4-12: EFFECT OF POROSITY AND WATER HOLDING CAPACITY ON CRITICAL CONSTRAINED MODULUS AT NORMAL STRESS RANGING FROM 10 – 50 KPA

4.4.2 Shear Strength Testing

Among the strength parameters, cohesion is the stress-independent component of shear strength and is controlled by factors such as cementation or bonding and the extent of electrostatic forces of attraction between the particles. The cohesion component of shear strength can be further subdivided into 'true' and 'apparent' cohesion. 'Apparent' cohesion is contributed by the capillary forces that keep the particles agglomerated as a result of surface roughness and, mechanical interlocking and this can be eventually lost due to drying of soils and particle re-arrangement. On the other hand, 'true' cohesion which occurs due to the electrostatic and electromagnetic forces of attraction between particles remain effective and keep the particle bound to each other even after

drying (Bazargan et al., 2014). Friction angle is a stress-dependent component of shear strength which is controlled by the factors affecting the frictional resistance between the particles.

Direct shear test results implied that the shear strength of soil can be considerably improved by amending certain types of woody biochars. The feedstock and production conditions impacted the shear strength parameters of the biochars since all the biochars exhibited a certain degree of variation among their cohesion and friction angle values (Table 4-2). However, the strength parameters of BS, CK and AW biochars exhibited relatively higher variations compared to all the CE-biochars. This could be due to possible, similar production processes and treatment conditions for all CE-Biochars since they were obtained from the same vendor (Yargicoglu et al., 2014). BS, CK and AW biochars had relatively higher ash contents compared to CE-biochars which consequently lowered their carbon contents compared to all the CE-biochars (Yargicoglu et al., 2014). The presence of ash content in biochars was reported to negatively affect their strength and stability. On the other hand, biochars with higher carbon content were preferred for use in the generation of bio-energy due to their greater strength (Echterhor and Pfiefer, 2014). Shear strength of AW biochar was much higher compared to other biochars and this could be due to several reasons. AW biochar was made from aged oak and hickory wood using a conventional pyrolysis technique which employs the Missouri-type concrete kilns. The AW biochar had been stock-piled for over 50 years and was marketed as an agricultural amendment with specially inoculated strains of bacteria and fungi which makes the characteristics of this biochar highly unique compared to other biochars (Yargicoglu et al., 2014) that were relatively fresh (2 – 3 years old).

Soil amended with 10% CE-biochars in the presence of 15% moisture exhibited decreased cohesion and increased friction angle compared to that of dry biochars (Table 4-2). This decrease in cohesion could be attributed to the formation of clay-carbon complexes in the case of biochar-

amended soils as opposed to C-C bonding which occurs in the case of biochars. The formation of clay-C complexes could have reduced the attraction forces that promote the bonding through inter-locking mechanisms between the biochar-amended soil particles, consequently lowering the cohesion values (Zong et al., 2014). The shear strength parameters of soil are considerably increased with the amendment of 10% CE-biochars by weight. Aggregate formation in biochar-amended soils, under moist conditions were more pronounced compared to that of moist soil, thereby, increasing the particle diameter and thickness by promoting the binding of clay-minerals with carbon (Sun and Lu, 2013). This was found to occur when soil was amended with biochars having high carbon contents since the hydrophobicity of aggregates were more pronounced for these material mixes which, consequently increased the cohesion values of soil (Sun and Lu, 2013). The addition of 15% of moisture to soil (by weight) considerably increased the cohesion and remarkably decreased the angle of internal friction for the soil. Previous studies have shown that the separation distance between the clay particles increase due to added moisture and that the van der Walls forces are prominent for separation distance less than 2.5 nm, beyond which the electrostatic forces of attraction between the particles decrease, thereby, resulting in a dispersed structure at higher moisture contents which, in turn, results in a drop in cohesion (Al-Shayea, 2001). In the same study, it was reported that the friction angle reduced because of increasing water content in soil due to increased lubrication which causes the particles to slip and slide.

Cohesion values for different wood-based biochars tested in this study were found to be positively correlated to the physical properties of biochars such as their porosity and dry density (Figure 4-13). The increase in cohesion due to increased biochar porosities could be due to the fact that the highly porous biochars underwent extensive particle re-arrangement under the applied vertical loads which resulted in better interlocking and settlement of smaller particles within the

void spaces thereby, resulting in better inter-particle bonding. Figure 4-14 illustrates the effect of physico-chemical properties of biochars on their internal friction angle. The friction angle of biochars decreased with increasing porosities and this could be due to the reduction in the internal roughness of the biochar particles which subsequently lowers the resistance against slipping (Schöpfer et al., 2009). Biochar with higher porosities could be more susceptible to crushing and undergoing particle damage thereby, promoting unlocking mechanisms resulting in lower friction angles. The friction angle of biochars also decreased with increasing water holding capacity and this could be due to the fact that biochar porosity and water holding capacity were positively correlated. Similarly, friction angle decreased with increasing dry density and specific gravity of biochars whereas, cohesion was found to increase with increasing density of biochars. Denser materials are more brittle and are not easily subjected to particle rearrangement which could result in incomplete filling of inter-particle void spaces upon the application of vertical loads, thereby, increasing the probability of particle movement and slippage. The friction angle of biochars increased with increasing organic content and a similar trend was reported for soils (Bate et al., 2014; Zhang et al., 2005). The presence of organic carbon in biochars promoted inter-aggregate binding, thereby, increasing the frictional resistance against inter-particle collapse and slip failures. The frictional angle of biochars reduced at higher pH values and could be attributed to the changes in the surface chemistry of biochars. At higher pH, biochar surfaces are more negatively charged which could have resulted in the formation of metal precipitates and these precipitates can increase the probability of aggregate formation, thereby, resulting in a decreased frictional resistance.

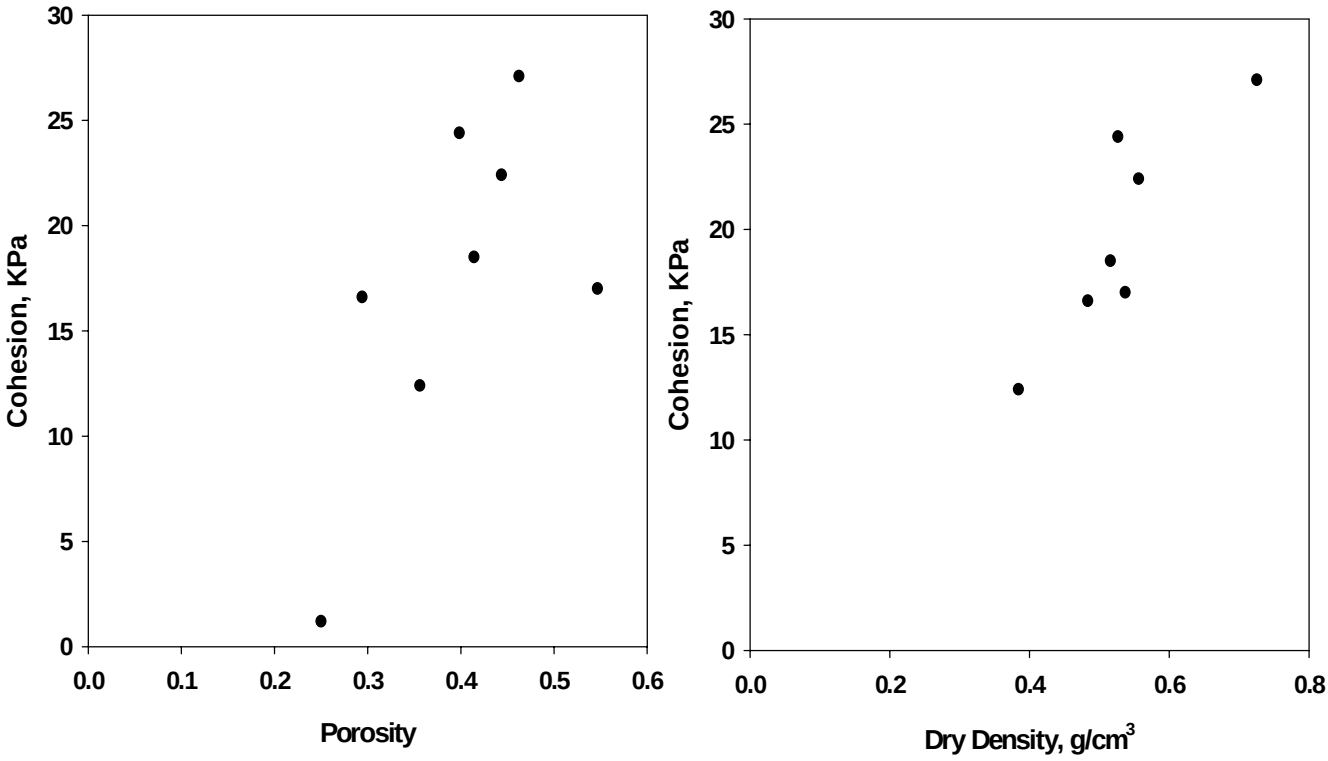


FIGURE 4-13: EFFECT OF PHYSICAL PROPERTIES OF BIOCHARS ON COHESION

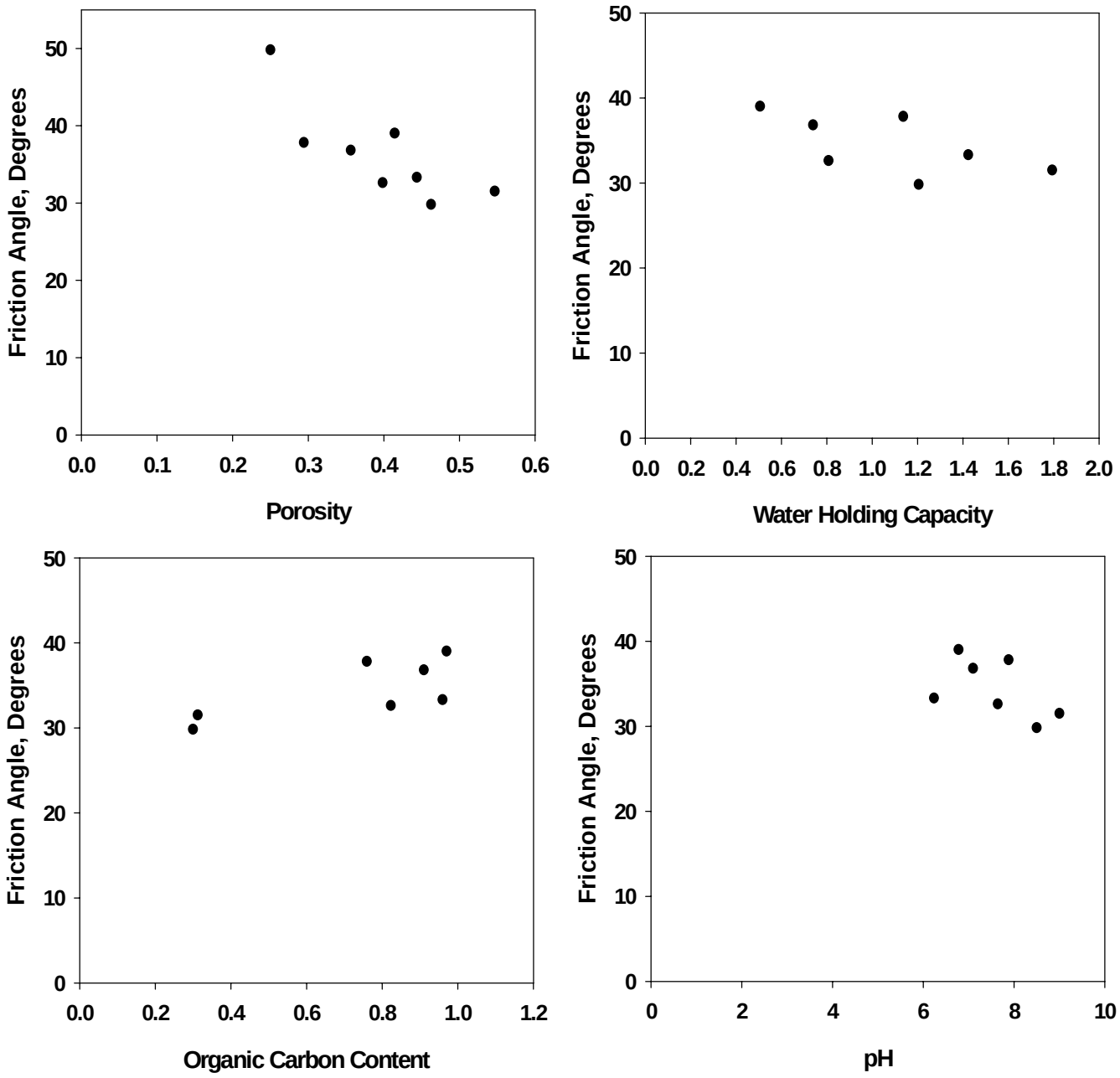


FIGURE 4-14: EFFECT OF PHYSICAL-CHEMICAL PROPERTIES OF BIOCHARS ON THEIR FRICTION ANGLE

4.4.3 Slope Stability Analysis

The natural presence/ absence of water within the landfill cover system due to seasonal shifts in the localized weather patterns is among the major factors controlling the overall stability of landfill cover slopes. The worse-case scenario for slope stability analysis is when $H_w/H = 1$, wherein, the entire cover system is saturated with rain water, resulting in higher possibility of slope failure. Slope stability analyses indicate that, irrespective of the level of water within the cover system, use of soil resulted in much lower factor of safety in comparison to biochar-amended soils and this could be attributed to the higher shear strength parameters observed for biochar-amended soils as discussed in section 4.2. Under dynamic field conditions, the shear strength of cover materials is expected to reduce by a factor of about 15 – 25% due to erosion and scouring as a result of internal seepage (Khoshand et al., 2014). To account for this, a higher safety factor, ranging from 1.5 – 2 is required to be met for ensuring long-term stability of the cover system. Biochar-amended soils exhibited high FS values (2.4 – 3.3) even under the worse-case scenario ($H_w/H = 1$) implying that steeper landfill cover slopes can be designed without compromising on the long-term cover slope stability.

4.5 Conclusions

This study evaluated the engineering properties of seven different types of waste wood-derived biochars and biochar-amended soils under dry and moist conditions. The effects of physico-chemical properties of biochars on their compressibility and shear strength were evaluated and discussed in detail. The feasibility of biochar-amended soils to be used in engineered landfill cover systems was evaluated from the perspective of cover slope stability. Based on the findings from this study, the following conclusions can be derived:

- Biochar amendment to soil increases the porosity, water holding capacity and organic matter and decreases the density and specific gravity of soil which consequently improves the overall soil physical quality.
- Biochars and biochar-amended soils exhibit higher axial strains as they are more compressible compared to soil. The maximum constrained moduli values of biochars for vertical stresses ranging from 50 – 100 kPa are considerably lower than that of soil under dry conditions and almost equal to that of soil under wet conditions.
- The amendment of biochars to soil decreases the maximum constrained moduli values of soil with increasing percentages of biochar-amendment.
- The critical constrained moduli of biochars between normal stresses ranging from 10 – 50 kPa decrease due to decreasing porosity and water holding capacity.
- The shear strength of moist soil was considerably enhanced by the addition of biochars. The cohesion values of dry biochars were much higher than the cohesion values of dry as well as moist soil, whereas, the friction angle of dry biochars were lower than that of dry soil and higher than that of moist soil. Amendment of selected biochar types to soil at 10% amendment ratio, in the presence of 15% moisture, resulted in a decrease of cohesion and increase of frictional angle as compared to dry biochars.
- Cohesion of biochars increased with increasing biochar porosity and dry density. Frictional angle of biochars decreased with decreasing porosity, WHC and, pH, whereas, it increased with increasing organic matter.
- The factor of safety for stability of cover slopes was increased by about two times by amending biochars to cover soil under drained conditions.

Overall, the results from this study provide valuable information pertaining to the compressibility characteristics and stability aspects of waste wood-derived biochars during and after placement/ construction of the engineered systems. The study results can be used to address the existing knowledge gaps in literature pertaining to the engineering properties of biochars and biochar-amended soils which are critical aspects to be taken into consideration prior to the design and field-scale application of engineered systems.

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5. ADSORPTION AND TRANSPORT OF METHANE IN BIOCHARS

5.1 Introduction

The content of this chapter has been previously published during the author's doctoral work [**Sadasivam, B.Y.**, & Reddy, K.R. (2015). "Adsorption and transport of methane in biochars derived from waste wood." *Waste management, 43, 218-229*]; [**Sadasivam, B. Y.**, & Reddy, K. R. (2014). "Quantifying the effects of moisture content on transport and adsorption of methane through biochar in landfills". *Geoenvironmental Engineering*, pp. 191-200] and [**Sadasivam, B.Y.**, & Reddy, K.R. (2015). "Influence of physico-chemical properties of different biochars on landfill methane adsorption." *IFCEE, pp. 2647-2656*].

Methane mitigation can be achieved by a combination of adsorption and biochemical oxidation in landfill cover systems. To date, extensive research conducted in this field highlights the importance of employing organic rich biocover materials to improve the microbial methane oxidation capacity of landfill cover systems (Park et al. 2004; Stern et al. 2007; Nikiema et al. 2007; Huber-Humer et al. 2008; Huber-Humer et al. 2009; Pederson et al. 2011; Scheutz et al. 2011; Roncato et al. 2012). However, researchers have not yet explored the process of methane adsorption within landfill cover systems that can also contribute to methane mitigation. The combined effects of both adsorption and microbial oxidation of methane need to be quantified upon employing a suitable biocover material that can facilitate both processes (Sadasivam and Reddy 2014a).

Although the addition of organic rich compost amendments to landfill cover soils can enhance the microbial methane oxidation capacity of the cover, exo-polymeric substances can form within the cover system over time that clog the pores and hinder the diffusion of gases (Wilheusen et al.

2004; Hilger et al. 2000; Powelson et al. 2006). Thus, using a biocover material with a relatively higher porosity and enhanced gas transport properties can minimize the consequences of EPS formation within the cover system. In order to design an efficient biocover system for methane mitigation, a stable biocover material also needs to be selected such that the material has a high porosity with the capability to enhance methane adsorption capacity as well as favor the growth of methanotrophs to promote microbial methane oxidation.

Biochar is an organic rich material derived from wood, manure or plant biomass through pyrolysis under limited oxygen environments (Lehmann and Joseph, 2009). The choice of waste biomass conversion process and treatment conditions is dependent upon the desired end-product, which includes biofuel for energy (Lehmann, 2007) and biochar for the purpose of environmental management (Lal 2004; Lehmann and Joseph 2009). The physical and chemical characteristics of biochars are dictated by the pyrolysis conditions, such as temperature and residence time (Lua et al. 2004; Boateng 2007; Xie et al. 2015). The porosity and specific surface area of biochars are dependent upon the highest treatment temperature (Brown et al. 2006) and post-treatment processes, such as activation (Zhang et al. 2004). Generally, the biochar surface area increases with a rise in treatment temperatures and the process of chemical activation tends to increase the microporosity of biochars. Some chemical activation methods used for enhancing the surface area of biochars include steam activation using KOH (Ippolito et al. 2012) and phosphoric acid impregnation (Lin et al. 2012). The presence of micropores in the biochars makes it highly preferable for gas adsorption (Billemont et al. 2013). When used as a soil amendment, biochars have a high potential to increase the sorption ability of soils, mainly due to their pyrogenic production process (Sadasivam and Reddy 2014b). Several studies have compared the sorption properties of pyrogenic and non-pyrogenic or fresh biomass and found that the sorption ability of

pyrogenic substances, such as biochars, is a couple of orders of magnitude higher than that of fresh biomass (Baring et al. 2002; Huang et al. 2003; Nguyen et al. 2004). The highly porous structure of biochars can facilitate the effective colonization of methanotrophic communities, which are major drivers for methane oxidation to occur in landfills. Moreover, biochars have a high organic content and are stable in the soils for a long period of time, which increases its suitability for use as a soil amendment in environmental management.

The amendment of biochars to cover soil increases the shear strength of the cover soil and, consequently, results in higher safety factors for the slope stability of landfill covers (Sadasivam and Reddy 2014c). Preliminary results indicate that methane adsorption by biochars enhances the methane oxidation efficiency of biochar-amended soils in long-term column experiments (Reddy et al. 2014). Since sorption of methane onto biochars was found to significantly affect the methane transport through biochar-amended cover systems (Xie et al. 2013), it is important to quantify the extent of methane mitigation contributed solely by adsorption and evaluate the effects of varying environmental conditions on the CH_4 sorption capacities. The primary focus of this paper is to quantify and analyze the effects of varying levels of exposed CH_4 concentrations, moisture content and temperature on the methane adsorption and transport characteristics of several different biochars derived from waste wood and compare those results with that of a more conventional adsorbent, such as GAC. The results from this study can help researchers identify the potential use of biochar-based biocover amendments to landfill soil with the view of achieving cost-effective, sustained methane mitigation.

5.2 Materials and Methods

5.2.1 Biochars and GAC

Seven types of hardwood biochars were obtained from commercial vendors in 5-gallon buckets and stored in air-tight containers prior to use. The biochars were produced through varying treatment processes and production conditions (Sadasivam and Reddy 2015). GAC was obtained from Fisher Scientific for use in the methane adsorption studies. Detailed physical and chemical characteristics of these biochars and GAC are presented by Yargicoglu et al. (2015). Prior to use, the biochars were autoclaved in a Napco® model 8000-DSE autoclave at 121°C for 30 min for two consecutive days (Bennett et al. 2003) to minimize the microbial interference on adsorption. Biochars were sealed in sterilized glass containers at 22 °C for 24 hours between autoclave treatments (Carter et al. 2007).

5.2.2 Batch Adsorption Testing

Batch adsorption tests were conducted to determine the methane adsorption capacity of the biochars and GAC under different levels of moisture content, temperature and exposed methane concentrations. The materials were used as obtained from the vendors (As-is) without being subjected to physical-chemical pretreatment except for sterilization. Five grams of biochar samples were placed inside 250g amber glass bottles and sealed with long sleeved rubber stoppers. Then, predetermined amounts of air in the headspace were replaced with synthetic landfill gas (50% CH_4 and 50% CO_2) to achieve headspace CH_4 concentrations of 2, 5, 8, 10, 15, and 20% (v/v). The control test units were also set up similar to the sample test units, but without adding the biochar to determine the initial CH_4 headspace concentration (v/v) achieved for each experimental set.

In order to determine the effects of moisture content on methane adsorption, test units were set up following the aforementioned procedure, but with the addition of measured volumes of de-ionized water using a calibrated pipette to achieve moisture levels of 25, and 75% with respect to the corresponding water holding capacity (WHC) based on dry weight basis (Yargicoglu et al. 2015). To study the effects of moisture content on the adsorption of CH_4 onto the biochars and GAC, the temperature in all the test units was maintained at 295K and the CH_4 gas pressure within the test units ranged from 0.15 to 1 kPa. To simulate the effects of increasing temperature on methane adsorption, as expected to occur under field conditions, a hydrometer water bath (Model H - 4239A, Humboldt Co., Arlington Heights, IL) was used to maintain preselected constant temperature conditions (25 ^{0}C, 35 ^{0}C and 45 ^{0}C) within the test units. All the test units (including the controls) were placed in a water bath and allowed to acclimate to those preset temperature levels. A thermometer was used to ensure that appropriate temperature conditions existed prior to the start of the tests. The concentrations of CH_4 in the headspace of all the adsorption test units were increased until the material's maximum adsorption capacity was achieved. Gas samples were collected and analyzed as described in section 2.4 at different intervals until the equilibrium headspace CH_4 concentrations were achieved.

5.2.3 Column Adsorption Testing

The column adsorption tests were conducted to assess the combined transport and adsorption characteristics of CH_4 through biochars and GAC. These tests were conducted using a Kontes brand Chromaflex® glass chromatography column (420870) measuring 2.5 cm in diameter and 30 cm in length. The glass column set-up and the fittings were sterilized following the aforementioned procedure used for biochars to avoid possible microbial interference in the test results. The tests

were conducted under three influent methane flow rates of 7.3, 5.4 and 3.1 ml min^{-1} and three moisture levels of 0%, 25% and 75% of the corresponding WHC. This resulted in theoretical gas retention times of approximately 48, 36 and 11.8 minutes for a feed flowrate of 3.1 ml min^{-1} under dry, 25% and 75% WHC, respectively. For a feed flowrate of 5.4 ml min^{-1}, the theoretical gas retention times under dry, 25% and 75% WHC were approximately, 27, 20 and 7 minutes, respectively. At the highest feed flowrate used in this study (7.3 ml min^{-1}), the retention times for dry, 25% and 75% WHC were approximately 20, 15 and 5 minutes, respectively.

The columns were fitted with a bed support mesh screen, PTFE tubing, end connections, and screw caps. Flow meters (GF-8330-1001, Gilmont Instruments) were installed at both ends of the column to control the influent methane gas flow rates and monitor the effluent flow rate (Figure 5-1). The columns were filled with wood pellet biochar in two 15 cm thick layers with light tamping after the placement of each layer. For the tests conducted at moisture levels of 25% and 75% of the corresponding WHC, a biochar stock was prepared with a known mass by adding a known volume of de-ionized water and used to fill the column, as mentioned previously. For each test, a gas mixture comprising 5% CH_4 (v/v), 5% CO_2 (v/v) and 90% N_2 (v/v) was introduced through the column bottom at a pre-selected constant flow rate and the effluent flow rates were recorded during each sampling event. It should be noted that the maximum methane concentration of 50% CH_4 (v/v) in LFG was not used in this study as it will result in instantaneous breakthrough due to the selected high inflow rate and small-scale column set-up. The feed flowrate could not be reduced any further due to the sensitivity of the flow meters used. Nevertheless, the use of low methane concentration (5% CH_4 v/v) and high flow rate allowed quantifying the transport of CH_4 in the column set-up. Gas samples were collected from the effluent sampling port at different time intervals until the breakthrough condition was established.

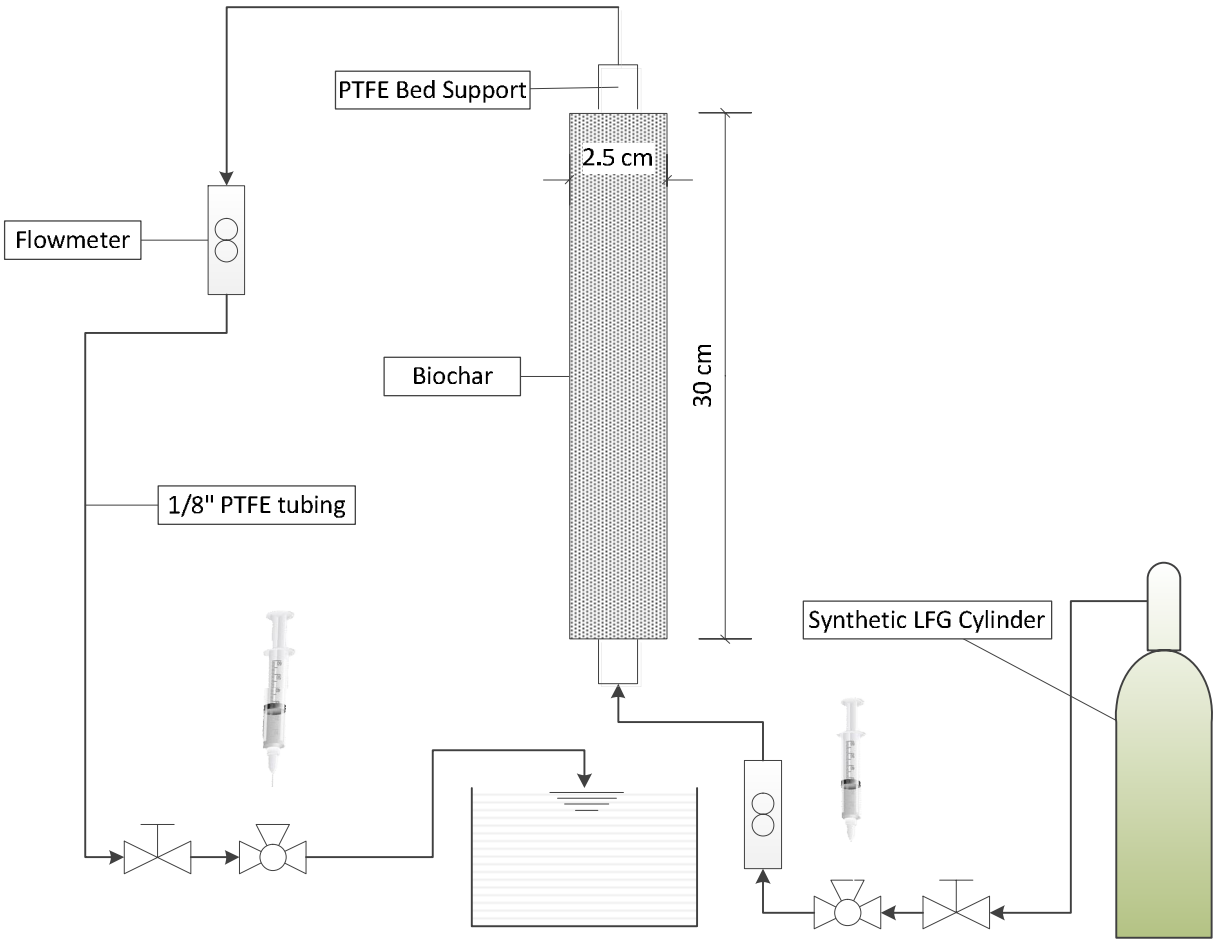

FIGURE 5-1: COLUMN ADSORPTION TEST SET-UP

5.2.4 Gas Sampling and Analysis

All the gas samples were collected using a BD 10 ml louver lock syringe and non-coring needle fitted with a two-way plastic stop-cock. The sampling syringe, needle and stop-cock were sterilized to avoid bacterial contamination of the test units and the samples. Gas samples were then stored in evacuated 5 ml glass vials and analyzed within 4 hours from the time of collection using HP 6890 GC with FID and GS-Carbon Plot column. Prior to analyzing the gas samples, the GC

was calibrated using ultra high purity methane standards (0.1, 1, 5 and 25% CH_4 v/v obtained from Airgas) and a calibration curve was prepared to interpret the CH_4 concentrations of the samples.

5.2.5 Statistical Analysis

Batch adsorption tests and column adsorption tests were conducted in triplicate. Statistical Analysis System (SAS®) software (version 9.3) was used to perform the statistical analysis of the results to determine if the results were statistically different. Analysis of Variance (ANOVA) procedures were used to determine the significant differences between the data sets. All the statistical analyses assumed that the error is normally distributed and relatively constant at all treatment levels. The assumptions were then validated using the Proc univariate procedure and the null hypothesis was tested for means at an alpha level of 0.05.

5.2.6 Batch Adsorption Modeling

Based on the batch adsorption test results, adsorption kinetic parameters were obtained from the methane adsorbed at various time intervals using the plots of linear forms of Lagergren first-order and second-order models, as shown in Eqns. (5-1) and (5-2), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5-1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \tag{5-2}$$

where q_t (mL/kg) is the amount of methane adsorbed at time t (min), k_1 (min^{-1}) is the rate constant of Lagergren first-order adsorption, k_2 ($kg.mL^{-1}min^{-1}$) is the rate constant of pseudo-second order adsorption, and q_e (mL/kg) is the amount of CH_4 adsorbed per mass of the material at equilibrium.

Linear forms of Langmuir and Freundlich adsorption isotherm models, as shown in Eqns. (5-3) and (5-4), were also used to model the adsorption equilibrium data obtained from batch adsorption tests:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{C_e} \tag{5-3}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5-4}$$

where C_e is the equilibrium concentration of the gas (kPa), q_e is the amount of CH_4 adsorbed per mass of the material (mol kg^{-1}), Q^0 is the mole amount of gas adsorbed per unit weight of adsorbent (mol kg^{-1}), b is a constant related to the affinity of binding sites (kPa^{-1}), and K_F and n are Freundlich constants related to adsorption capacity (mol kg^{-1}) and adsorption intensity (unit less), respectively. Q° and b are the Langmuir model parameters that were calculated from the slope and intercept of the straight lines of the plot of $1/q_e$ versus $1/C_e$, whereas, K_F and n are the Freundlich model parameters, which were determined from the linear plot of log q_e versus log C_e.

5.2.7 Column Adsorption and Transport Modeling

For modeling the transport of CH_4 through biochar columns, the linear sorption coefficient (K_d) is calculated from the corresponding batch sorption experiments conducted on the biochars at low exposed CH_4 concentartions (< 8% CH_4 v/v). The linear and non-kinetic sorption is assumed for the column tests; however, the nonlinear and kinetic sorption may be approriate to consider in the field scale cover systems. The one-dimensional advection-dispersion transport retarded by linear sorption is given by Eqn. (5-5):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\partial S}{\partial t} \tag{5-5}$$

where C = solute concentration (mol m^{-3}), t = time (min), D = hydrodynamic dispersion (m^2 min^{-1}), ν = average linear velocity (m min^{-1}), and x = distance in the direction of flow (m).

$\frac{\partial S}{\partial t}$ is assumed to be the adsorption isotherm. In the case of linear sorption, this is given by Eqn. (5-6) below,

$$\frac{\partial S}{\partial t} = \frac{\rho_b}{\eta}\frac{\partial (K_d C)}{\partial t} \quad (5\text{-}6)$$

Eqn. (5-6) can be recognized as shown in Eqn. (5-7), below,

$$\frac{\partial C}{\partial t}\left(1 + \frac{\rho_b}{\eta} K_d\right) = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \quad (5\text{-}7)$$

where

$$R = 1 + \frac{\rho_b}{\eta} K_d \quad (5\text{-}8)$$

where R = retardation factor, unitless; ρ_b = bulk density of adsorbent, (Kg m^{-3}), K_d = solid water distribution ratio, (m^3 Kg^{-1}), and η = total porosity of the adsorbent, unitless. It should be noted that there is a possibility that a small fraction of methane is transferred from the gas phase to the liquid phase instead of directly sorbing to the biochar surface from the gas phase. However, the sorption of methane in gas phase directly onto the pore spaces of biochar was assumed to be more predominant than dissolution in this case since the solubility of methane in water is very low, with a value of 0.03 mL CH_4/ mL H_2O at STP (Yamamoto et al. 1976).

The following initial and boundary conditions are assumed for the column experiments for this study:

$$C(x, 0) = 5\%\ (v/v) \text{ for } x \geq 0$$

$$C(0, t) = C_0 \text{ for } t \geq 0$$

$$C(\infty, t) = 5\%\ (v/v) \text{ for } t \geq 0$$

The solution to the advection-dispersion equation (5-7) is given as:

$$C = \frac{C_0}{2}\left[erfc\left(\frac{L-v\prime t}{2\sqrt{D\prime t}}\right) + \exp\left(\frac{v\prime L}{D\prime}\right) erfc\left(\frac{L+v\prime t}{2\sqrt{D\prime t}}\right)\right. \quad (5\text{-}9)$$

where ν' = ν/R and D' = D/R.

The solution in Eqn. (5-9) assumes that equilibrium exists between the solute concentration and adsorbed phase surface concentration and that the relationship is linear. The transport of methane through the adsorbent is modeled assuming that the lateral dispersion of the gas is negligible while accounting for linear dispersion, only. The methane breakthrough curves were modeled using MATLAB to compute the dispersion coefficients for the biochars and GAC.

5.3 Results

5.3.1 Batch Adsorption Tests

Batch adsorption tests were conducted on biochars and GAC to determine the effects of exposed levels of CH_4 concentrations, moisture content and temperature on the CH_4 adsorption kinetics and isotherm parameters. Equilibrium conditions within all the batch adsorption test units were achieved at the end of two hours from the initiation of the tests. The linear form of a pseudo-second-order kinetic model appeared to fit all the adsorption test data better and with much higher R^2 values (ranging from 0.95 - 0.99) than the linear form of first-order kinetic model. The second-order kinetic model parameters, q_e (mol Kg^{-1}), which corresponds to the equilibrium adsorption capacity, and k_2 (kg mol^{-1} min^{-1}), which corresponds to the rate of CH_4 adsorption for the biochars and GAC under varying headspace CH_4 concentrations and moisture content, are presented in Figures 5-2 and 5-3, respectively. Figure 5-4 compares the maximum adsorption capacities of biochars and GAC under different moisture conditions. Similar results for the effects of temperature on the q_e (mol Kg^{-1}) and k_2 (kg mol^{-1} min^{-1}) values are presented in Figures 5-5, 5-6 and 5-7. The equilibrium adsorption capacity significantly (α=0.05) decreased with a decrease in

the initial headspace CH_4 concentrations under varying levels of moisture and with temperature ($p < 0.0001$). The rate of CH_4 adsorption (k_2) onto the biochars and GAC was not correlated to the initial headspace CH_4 concentrations under all the levels of moisture and temperature. However, the rate constant decreased with an increase in the levels of moisture content and temperature in all of the materials tested.

The isotherm modeling parameters for the biochars under varying levels of moisture content and temperature are listed in Tables 5-1 and 5-2, respectively. The best-fit isotherm model for all of the biochars, under each condition tested, is determined based on whichever model produced the better fit for the adsorption data (or higher R^2 value). The Langmuir isotherm model best represented the adsorption characteristics of methane onto BS, AW, CE-WP1, CE-AWP, CE-WC, and GAC under the 'As-is' conditions at 25^0C, while the Freundlich model better fits the adsorption data for CK and CE-WP2. The modeled maximum adsorption capacity of biochars ranged from 0.05 to 0.9 mol Kg^{-1}; the AW biochar had the least methane adsorption capacity and the CK biochar had the highest (Table 5-1). The modeled maximum methane adsorption capacity of GAC was found to be much higher than that of the biochars under dry condition, with a value of 3.21 mol Kg^{-1} (Table 5-2). However, the presence of moisture in the GAC hindered the methane adsorption process to a greater extent, resulting in a much higher loss of adsorption sites as compared to the biochars (Figure 5-4). A significant (α=0.05) reduction in the extent of the modeled maximum methane adsorption capacity onto the biochars and GAC occurred with increasing moisture levels (Figure 5-4), with a P value less than 0.0001. The rate of methane adsorption and the maximum adsorption capacity of biochars significantly ($P < 0.0001$) decreased with an increase in temperature (Figure 5-7). The extent of the reduction in the adsorption capacity of biochars was more sensitive to the presence of moisture than elevated temperature levels.

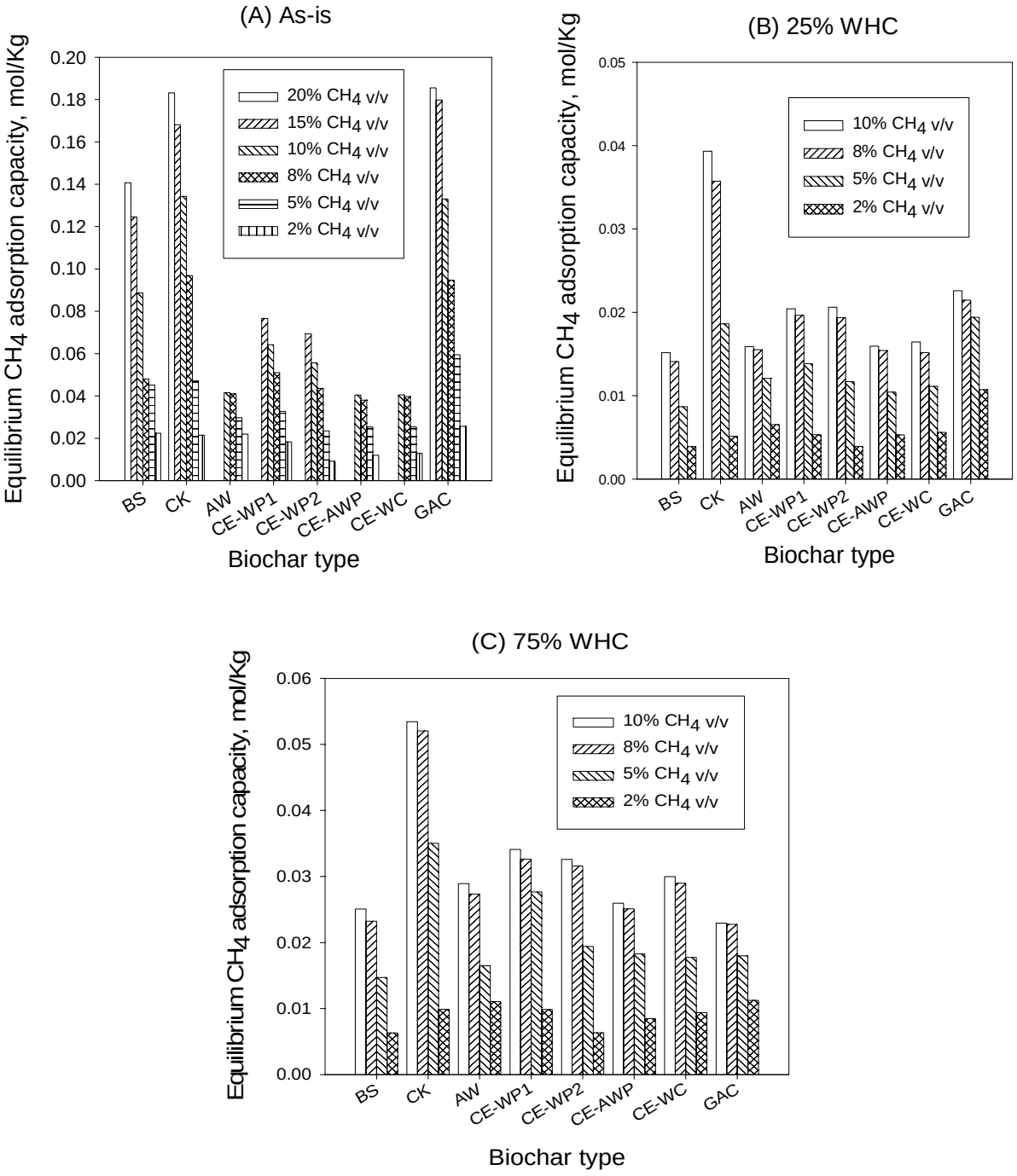

FIGURE 5-2: EFFECT OF MOISTURE ON EQUILIBRIUM CH_4 ADSORPTION ONTO BIOCHARS

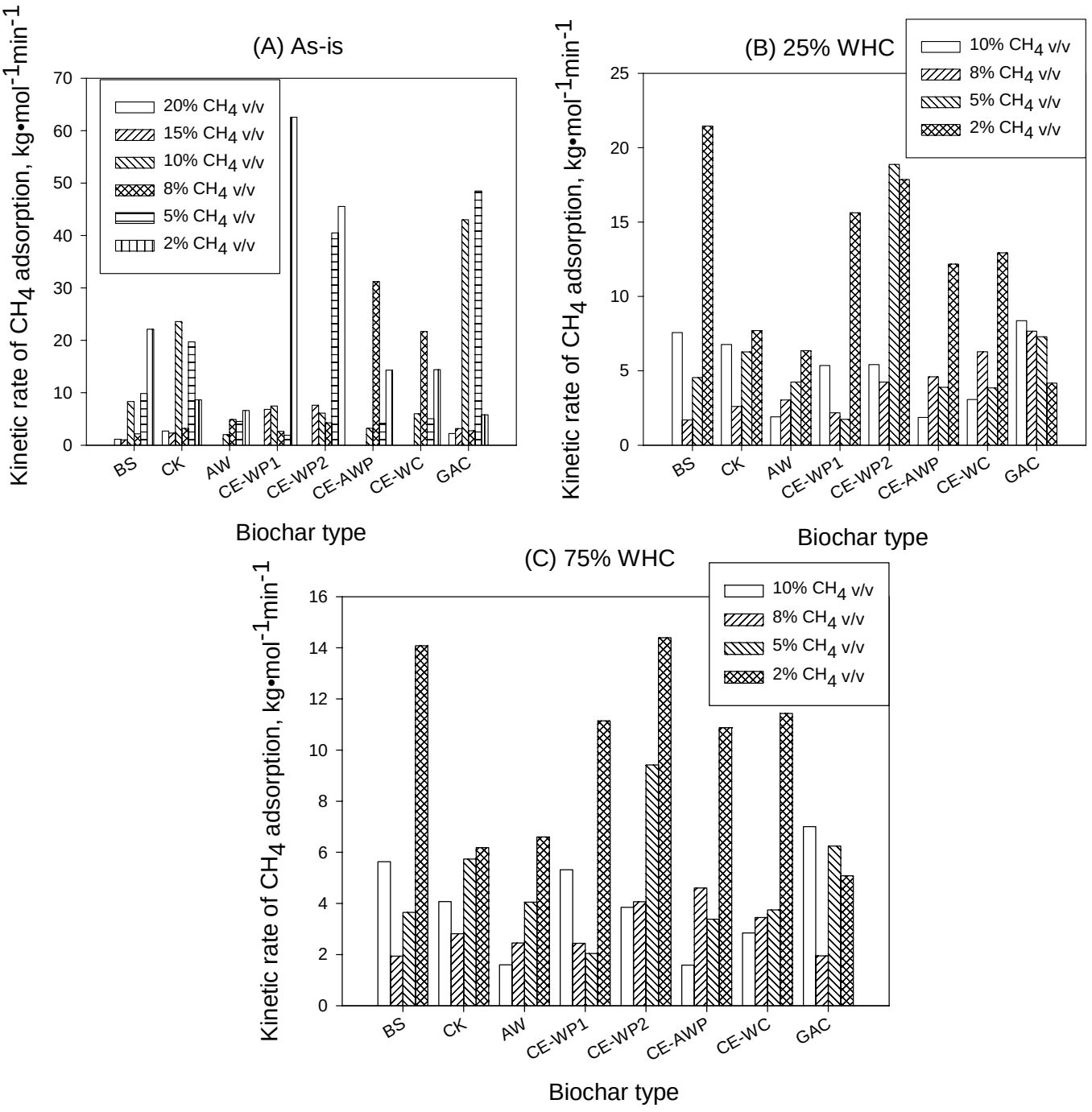

FIGURE 5-3: EFFECT OF MOISTURE ON KINETIC RATE OF CH_4 ADSORPTION ONTO BIOCHARS

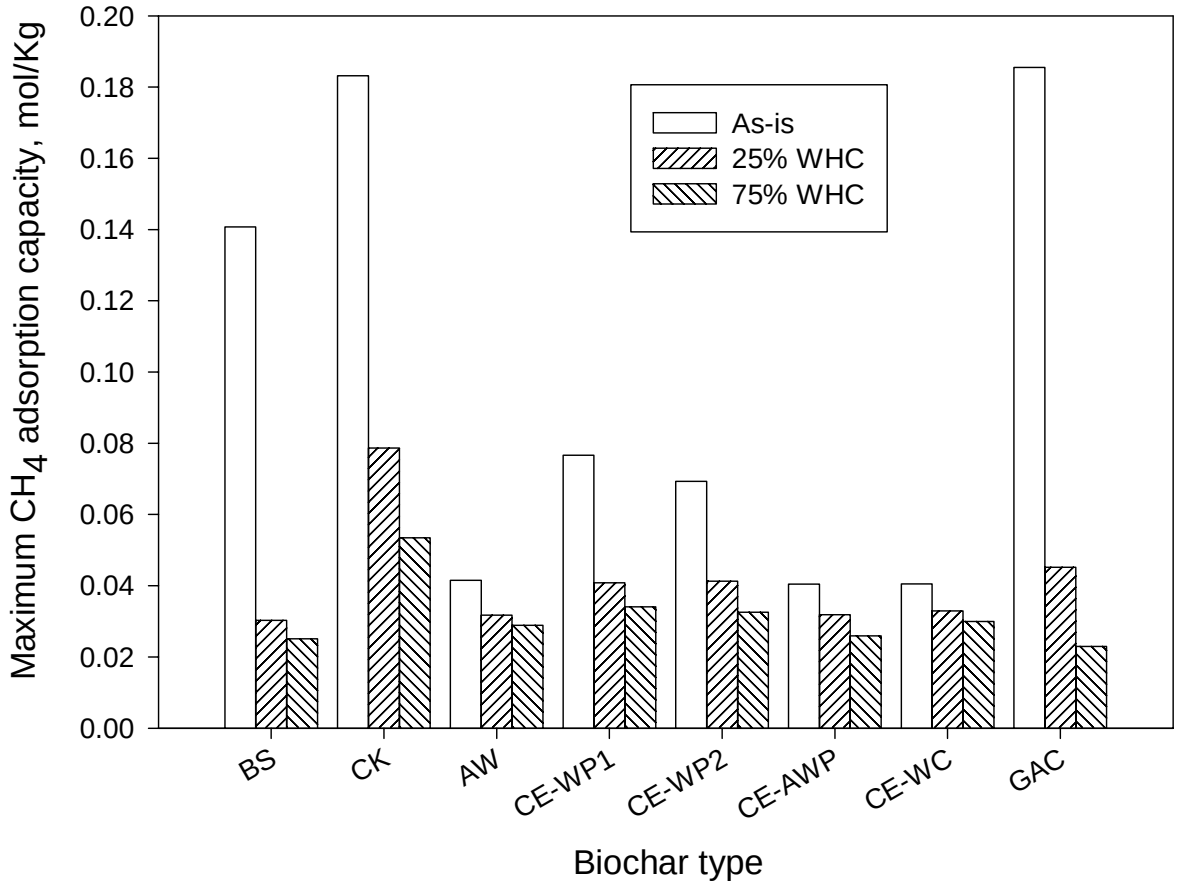

FIGURE 5-4: EFFECT OF MOISTURE ON MAXIMUM CH_4 ADSORPTION CAPACITY OF BIOCHARS

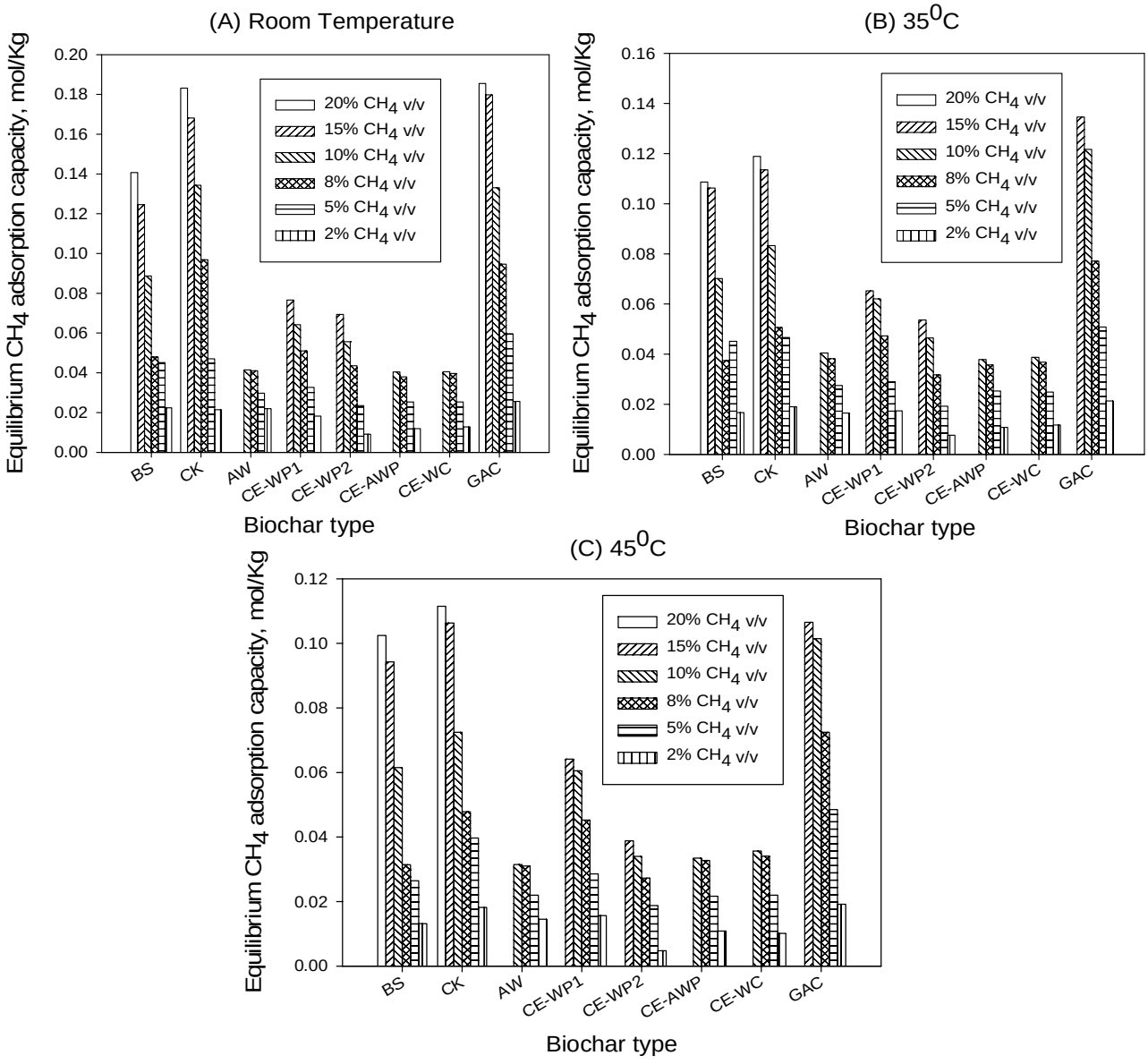

FIGURE 5-5: EFFECT OF TEMPERATURE ON EQUILIBRIUM CH_4 ADSORPTION OF BIOCHARS

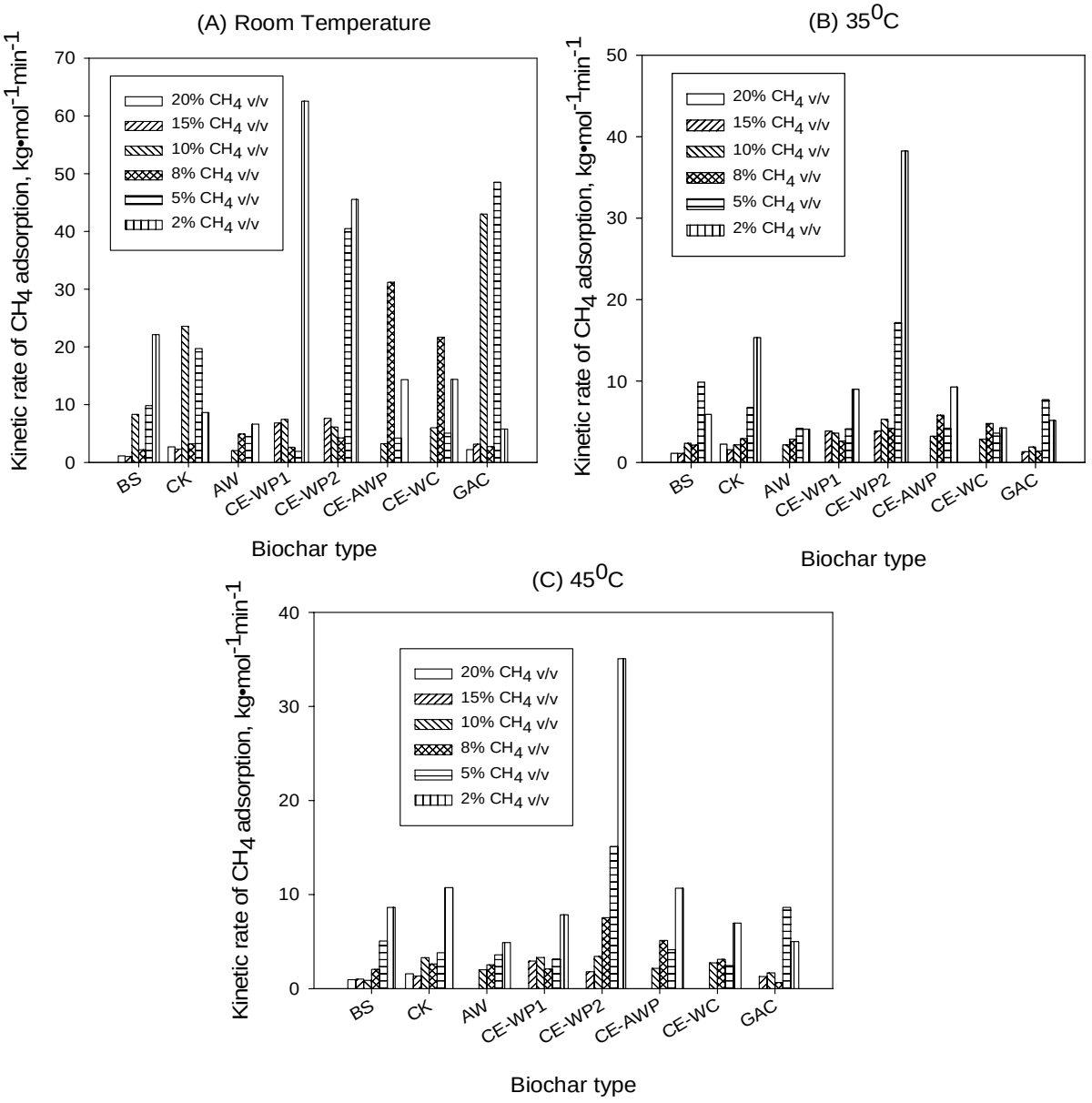

FIGURE 5-6: EFFECT OF TEMPERATURE ON KINETIC RATE OF CH_4 ADSORPTION ONTO BIOCHARS

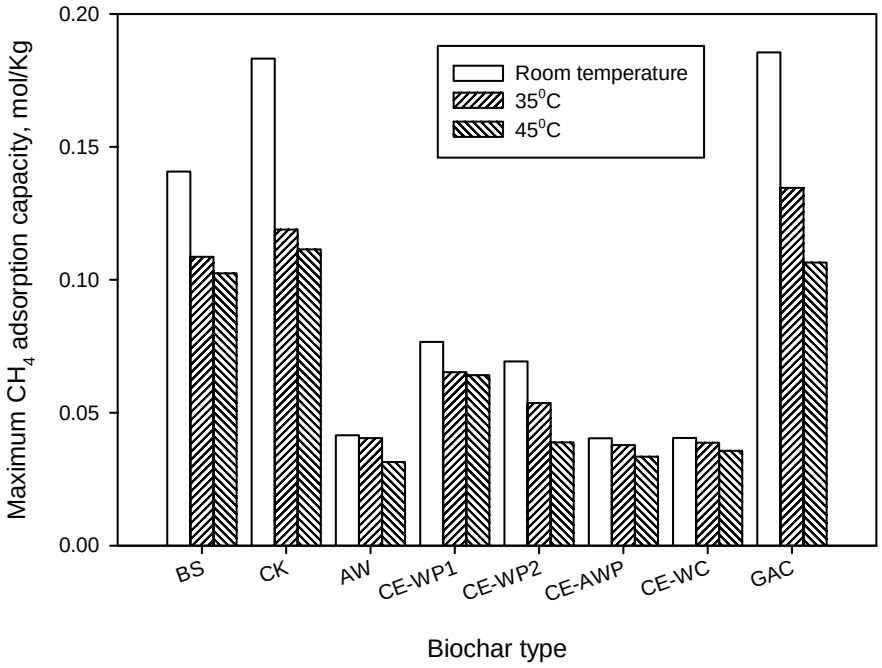

FIGURE 5-7: TEMPERATURE EFFECT ON MAXIMUM CH_4 ADSORPTION CAPACITY OF BIOCHARS

TABLE 5-1: EFFECT OF MOISTURE CONTENT ON ADSORPTION ISOTHERM PARAMETERS FOR BIOCHARS AND GAC

Material	Langmuir Model Parameters			Freundlich Model Parameters		
	Q^0 (mol/Kg)	b	R^2	K_F (mol/Kg)	n	R^2
Dry Condition						
BS	0.55	0.59	0.99	0.22	1.20	0.96
CK	--	--	--	0.87	0.76	0.94
AW	0.05	9.49	0.98	0.06	2.62	0.94
CE-WP1	0.21	1.14	0.96	0.17	1.09	0.95
CE-WP2	--	--	--	0.14	0.92	0.97
CE-AWP	0.13	1.27	1.0	0.09	1.25	0.99
CE-WC	0.10	1.9	0.99	0.09	1.33	0.98
GAC	3.21	0.04	0.99	--	--	--
25% WHC						
BS	0.12	0.75	1.0	0.06	1.19	0.99
CK	--	--	--	0.46	0.66	0.95
AW	0.05	4.02	1.0	0.05	1.86	0.97
CE-WP1	0.11	0.40	1.0	0.09	1.13	0.98
CE-WP2	--	--	--	0.11	0.95	0.97
CE-AWP	0.07	1.88	0.99	0.06	1.42	0.98
CE-WC	0.06	2.83	1.0	0.06	1.58	0.99
GAC	0.06	2.49	0.99	--	--	--
75% WHC						
BS	0.13	0.54	1.0	0.05	1.16	0.98
CK	--	--	--	0.17	0.91	0.91
AW	0.05	3.20	1.0	0.05	1.68	0.99
CE-WP1	--	--	--	0.07	1.25	0.99
CE-WP2	--	--	--	0.10	0.89	0.98
CE-AWP	0.08	1.25	0.98	0.05	1.41	0.92
CE-WC	0.07	1.78	1.0	0.05	1.42	0.97
GAC	0.03	2.48	0.99	--	--	--

TABLE 5-2: EFFECT OF TEMPERATURE ON ADSORPTION ISOTHERM PARAMETERS FOR BIOCHARS AND GAC

Material	Langmuir Model Parameters			Freundlich Model Parameters		
	Q^0 (mol/Kg)	b	R^2	K_F (mol/Kg)	n	R^2
			Room temperature			
BS	0.55	0.59	0.99	0.22	1.20	0.96
CK	--	--	--	0.87	0.76	0.94
AW	0.05	9.49	0.98	0.06	2.62	0.94
CE-WP1	0.21	1.14	0.96	0.17	1.09	0.95
CE-WP2	--	--	--	0.14	0.92	0.97
CE-AWP	0.13	1.27	1.0	0.09	1.25	0.99
CE-WC	0.10	1.9	0.99	0.09	1.33	0.98
GAC	3.21	0.04	0.99	--	--	--
			35^0C			
BS	0.35	0.78	1.0	0.18	1.16	0.99
CK	0.28	1.25	1.0	0.18	1.32	0.98
AW	0.05	6.71	0.99	0.06	1.98	0.99
CE-WP1	0.08	2.0	0.95	0.10	1.57	0.94
CE-WP2	--	--	--	0.10	0.98	0.97
CE-AWP	0.10	1.65	1.0	0.08	1.33	0.98
CE-WC	0.09	2.14	1.0	0.08	1.37	0.99
GAC	2.22	0.05	1.0	--	--	--
			45^0C			
BS	0.22	0.84	0.97	0.15	1.03	0.97
CK	0.20	1.67	0.99	0.16	1.31	0.99
AW	0.04	8.52	0.97	0.05	2.26	0.98
CE-WP1	0.09	2.88	0.97	0.10	1.46	0.96
CE-WP2	--	--	--	0.08	0.83	0.91
CE-AWP	0.06	2.93	0.99	0.06	1.50	0.98
CE-WC	0.08	1.87	1.0	0.07	1.50	0.98
GAC	0.80	0.12	1.0	--	--	--

5.3.2 Column Adsorption Tests

The effects of the methane inflow rates and moisture content on the adsorption capacity of biochars and GAC are presented in Figure 5-8. The adsorption capacity in this study is expressed as the difference in the cumulative volume of methane entering and exiting the column per known quantity of the biochar within that column. In the presence of moisture, the methane adsorption capacity significantly ($\alpha = 0.05$) decreased for all biochars and GAC (Figure 5-8). The decrease in adsorption capacity was more pronounced for GAC in the presence of water molecules as compared to the biochars (Figure 5-8). An increase in inhibition in the CH_4 adsorption capacity was observed due to an increase in the amount of water present in the biochar and GAC (Figures 5-8b, 8c).

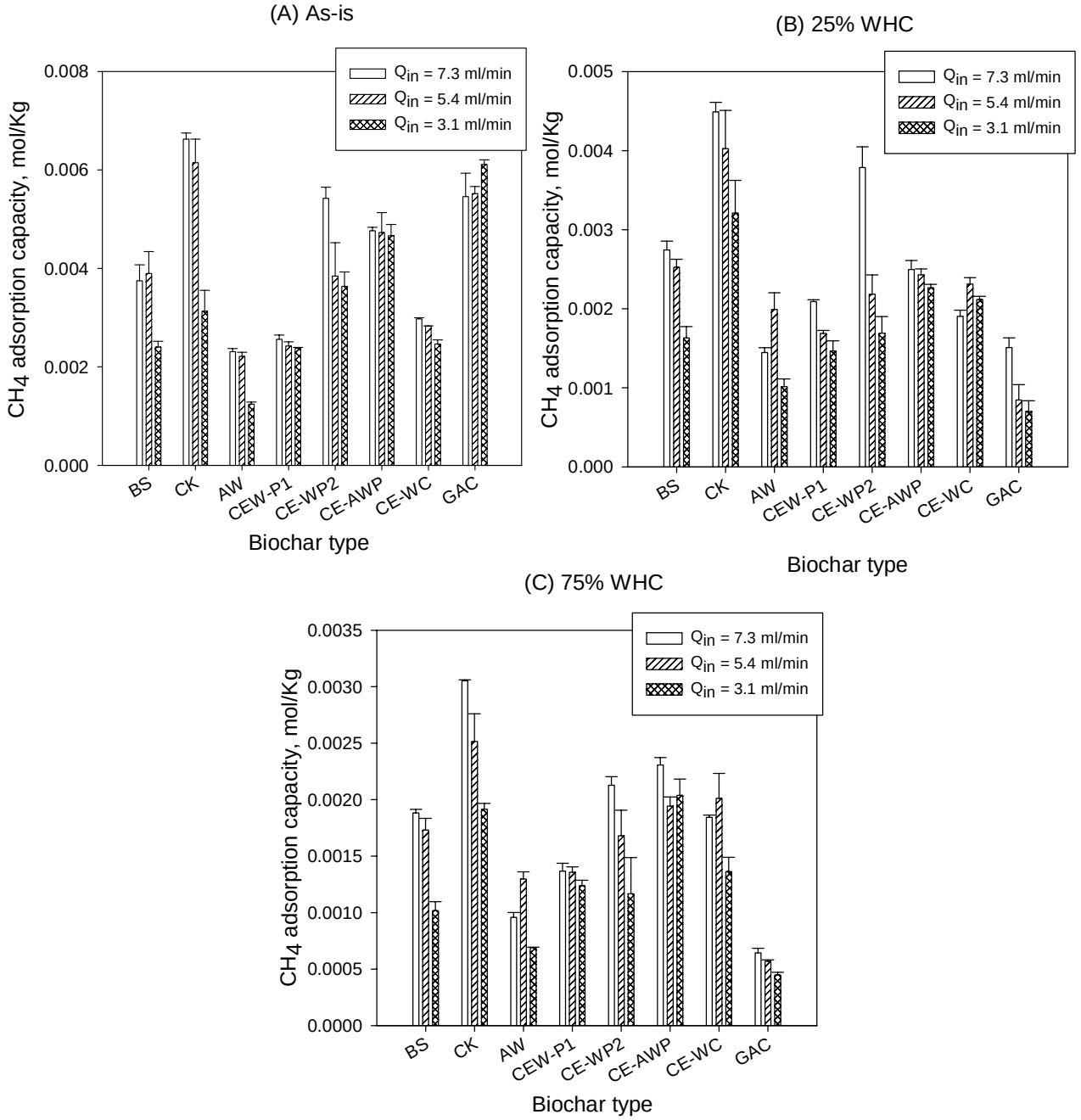

FIGURE 5-8: EFFECT OF CH_4 INFLOW RATE AND MOISTURE ON CH_4 ADSORPTION ONTO BIOCHARS

5.3.3 Column Adsorption and Transport Modeling

The transport and adsorption characteristics of CH_4 through the columns packed with biochars and GAC were modeled using the 1-D advection-dispersion equation (Eq. 9) in order to predict the breakthrough curves under varying moisture levels. This model assumes linear adsorption coefficients (K_d) as inflow gas with low methane concentration was used in the column experiments. The values of K_d were calculated using the batch adsorption tests conducted at low CH_4 concentration range alone. It should be noted that nonlinear adsorption should be accounted for when modeling the full-scale cover systems. With all the other parameters for modeling the breakthrough curves using Eq. 9 known, only the dispersion coefficients were varied until the model data matched the experimental data. The computed dispersion coefficients are listed in Table 5-3 along with the other transport and adsorption modeling parameters. Examples of the comparison between the experimental and modeled breakthrough curves for BS biochar are presented in Figure 5-9 under varying moisture levels. Similar comparisons were observed for all other biochars and GAC. The R^2 values representing the goodness of fit between the experimental and modeled data for the corresponding dispersion coefficients ranged from 0.94 – 0.99 (Table 5-3). The dispersion coefficients for biochars ranged from 0.08 – 0.29 m^2 min^{-1} (1.3 x 10^{-3} – 4.8 x 10^{-3} m^2 s^{-1}) and were found to decrease as the levels of moisture content within the packed columns increased (Table 5-3). The retardation factors for biochars under dry conditions were much higher compared to those values under wet conditions (Table 5-3). Retardation factors quantified in this study are indicative of the ability of biochars to adsorb and retain the methane within the cover system prior to breakthrough. Higher retardation factors imply that a longer time is required to achieve breakthrough in the cover system.

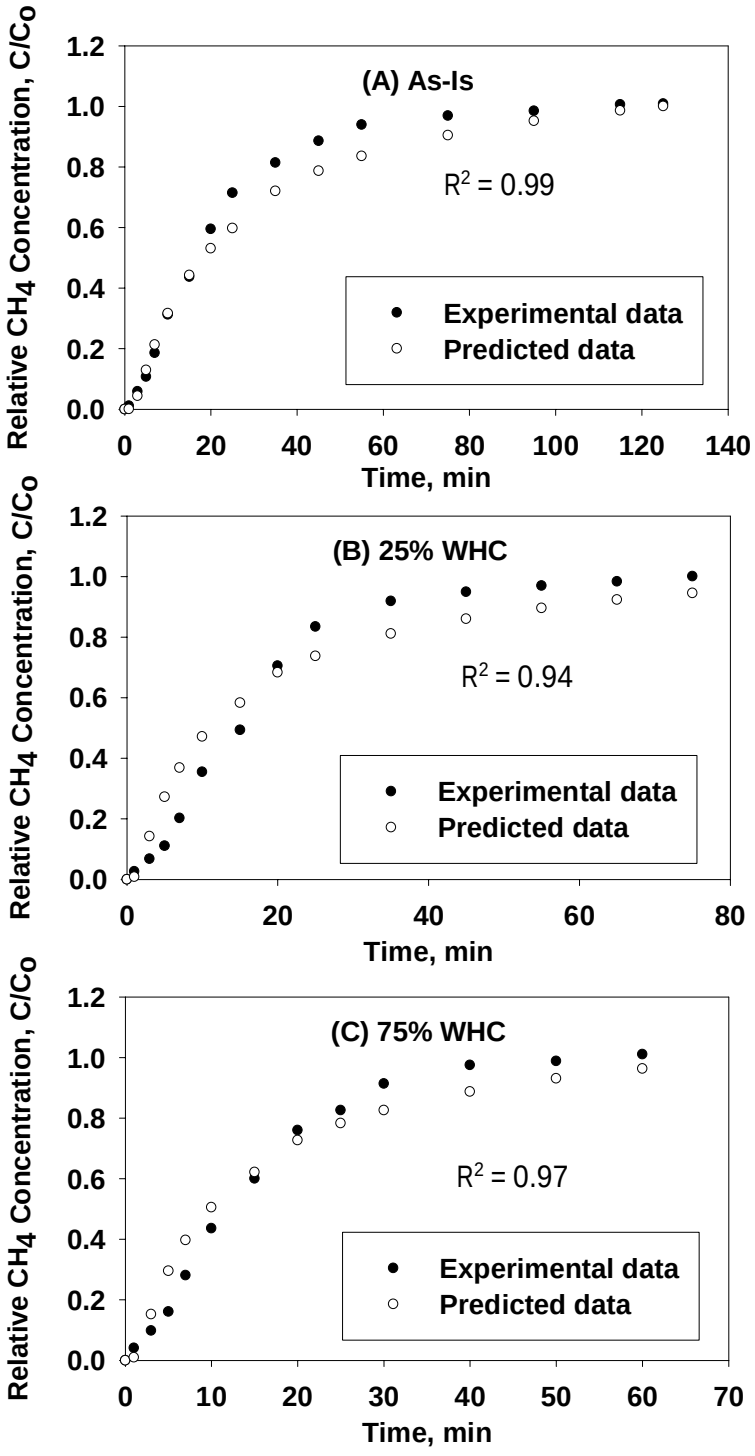

FIGURE 5-9: EFFECT OF MOISTURE ON CH_4 BREAKTHROUGH CURVES FOR BIOCHAR, BS

TABLE 5-3: SUMMARY OF COLUMN ADSORPTION MODELING PARAMETERS FOR BIOCHARS AND GAC

Material	D (m^2/min)	K_D (m^3/Kg)	η (%)	ρ_{bulk} (Kg/m^3)	R^2	Retardation Factor
Dry Conditions						
BS	0.18	0.033	46.3	725.5	0.99	52.7
CK	0.29	0.063	54.7	537.2	0.98	62.9
AW	0.19	0.012	29.4	483.5	0.96	20.7
CE-WP1	0.28	0.022	44.4	556.5	0.94	28.6
CE-WP2	0.20	0.017	41.0	516.0	0.99	22.4
CE-AWP	0.19	0.014	39.9	526.6	0.95	19.5
CE-WC	0.23	0.015	35.6	384.3	0.96	17.2
GAC	0.10	0.04	59.0	667.0	0.97	46.2
25%WHC						
BS	0.10	0.009	46.3	725.5	0.96	15.1
CK	0.12	0.028	54.7	537.2	0.99	28.5
AW	0.18	0.011	29.4	483.5	0.96	19.1
CE-WP1	0.26	0.013	44.4	556.5	0.96	17.3
CE-WP2	0.18	0.014	41.0	516.0	0.98	18.6
CE-AWP	0.16	0.010	39.9	526.6	0.96	14.2
CE-WC	0.20	0.011	35.6	384.3	0.92	12.9
GAC	0.10	0.011	59.0	667.0	0.98	13.4
75%WHC						
BS	0.08	0.007	46.3	725.5	0.97	12.0
CK	0.11	0.021	54.7	537.2	0.99	21.6
AW	0.17	0.009	29.4	483.5	0.96	15.8
CE-WP1	0.24	0.01	44.4	556.5	0.94	13.5
CE-WP2	0.14	0.011	41.0	516.0	0.97	14.8
CE-AWP	0.13	0.009	39.9	526.6	0.96	12.9
CE-WC	0.17	0.010	35.6	384.3	0.97	11.8
GAC	0.085	0.0074	59.0	667.0	0.97	9.4

5.4 Discussion

5.4.1 Adsorption Characteristics

Lagergren's second-order model best represents the adsorption kinetic data for the biochars and GAC. Similar results were observed in a recent study that looked into the adsorption kinetics of methane onto activated carbon (Luo et al. 2011). The parameters of the pseudo-second-order kinetic model are used to determine the extent of molecular exchange at the interface between the adsorbate in the gas phase and the adsorbent. From the adsorption kinetic data presented in Figures 5-1 and 5-2, it is evident that the amount of methane adsorbed onto the materials at equilibrium increases as the initial headspace CH_4 concentrations increase irrespective of the level of moisture content and temperature prevalent within the test units. This could be attributed to an increased amount of methane molecules readily available for adsorption onto the biochar and GAC surfaces at higher headspace concentrations that promotes elevated amounts of CH_4 adsorbed at equilibrium. For all the biochars and GAC, the values obtained for second-order kinetic model parameter q_e (mol Kg^{-1}) under all test conditions were found to increase consistently with the increasing initial headspace CH_4 concentration until all the adsorption sites were exhausted and the materials could no longer adsorb further CH_4 irrespective of increasing the levels initial headspace CH_4 concentration (Figures 5-2 and 5-5).

Figures 5-3 and 5-6 show that the second-order kinetic parameter, k_2 (k mol^{-1} $min^{-}1$), which corresponds to the rate of CH_4 adsorption, was not correlated to the initial headspace CH_4 concentrations for the biochars and GAC under any of the conditions tested. The second-order model fit for the adsorption kinetics data for all the materials indicates that at any given time the adsorption process is indicative of the available surface sites on the adsorbents rather than the gas-phase methane concentration (Liu 2008). This theory indicates that the rate of methane adsorption

onto the biochars and GAC is independent of the headspace CH_4 concentration, and this is a possible reason that there is no correlation between k_2 and CH_4 concentrations in any tests.

The adsorption capacity of biochars (As-is under relatively dry condition) were found to be correlated to the physical and chemical properties, such as total porosity, surface area, effective particle size, elemental and fixed carbon contents and initial moisture content (Sadasivam and Reddy 2015). Among all the biochars tested, AW had the lowest (0.05 mol CH_4 Kg^{-1} biochar) and CK had the highest (0.87 mol CH_4 Kg^{-1} biochar) adsorption capacity. Similarly, GAC exhibited highest potential for methane adsorption under dry conditions (3.21 mol CH_4 Kg^{-1}) in comparison to all the biochars tested. The order of CH_4 adsorption capacity onto biochars was found to be CK > BS > CE-WP1 > CE-WP2 > CE-AWP > AW > WC (Sadasivam and Reddy 2015).

5.4.2 Effects of Moisture on Adsorption

Several studies have examined the effects of moisture content on the adsorption of methane onto coal (Levy et al. 1997; Bustin et al. 1998) and activated carbon (Zhou et al. 2002; Farzad et al. 2007). From these studies, it is evident that the presence of moisture decreases the amount of methane adsorbed onto pyrogenic substances within the temperature and pressure ranges used in this study. The decreasing trend in the equilibrium adsorption capacity and kinetic rate of methane adsorption onto the biochars and GAC with increasing moisture is in accordance with the second-order kinetic model assumption that the extent of adsorption only depends on the available surface sites (Liu 2008). Moreover, a water molecule has a diameter of 0.306 nm as compared to a methane molecule with a diameter of 0.38 nm, which makes it harder for methane to penetrate through the biochar pores in the presence of moisture (Zhou et al. 2002), lowering the values of q_e and k_2 in

the presence of moisture as opposed to those values observed for the kinetic parameters under dry conditions.

From Figure 5-4, it is quite evident that moisture has comparatively less effect on the extent of the reduction in methane adsorption onto all CE-biochars, BS and AW. On the contrary, the effect of moisture on CH_4 adsorption onto GAC and CK was more pronounced with a significant difference in maximum CH_4 adsorbed under dry and wet conditions (Figure 5-4). The adsorption of water molecules onto the surface of activated carbons was higher than that of non-activated carbons (Brennan et al. 2002). In the case of non-activated carbon, the molecular interactions between carbon and water are relatively weaker as compared to interactions between two water molecules, while in the case of activated carbons, more uptake of water onto its surface structure occurred due to the presence of oxygenated surface sites or, in other words, activated sites (Brennan et al. 2002). This phenomenon could be the reason behind the more pronounced decrease in methane adsorption capacity for GAC and CK in the presence of moisture as compared to that of other non-activated biochars.

5.4.3 Effects of Temperature on Adsorption

An increase in temperature lowered the CH_4 adsorption capacity and kinetic rate of CH_4 adsorption onto biochars and GAC (Figure 5-6). One of the reasons for this trend could be attributed to the exothermic nature of the adsorption process wherein heat is released (Ning et al. 2012; Bagheri et al. 2011). Additionally, the decrease in micropore width on the adsorbent's surface as a result of an increase in temperature could also have restricted the entry of methane molecules, assuming a simple linear pore filling model (Sakurovs et al. 2008). In order to further evaluate the reason behind this trend, the Clausius-Clapeyron plot was used to obtain the heat of adsorption for the

biochars and GAC under the pressure and temperature ranges pertaining to the study conditions. The relationship between the equilibrium pressure of the adsorbate and the temperature of the adsorption medium can be thermodynamically represented by the Clausius-Clapeyron plot in order to evaluate the nature of the adsorption process (McLaughlin et al. 1998; Vasanth Kumar et al. 2011; Ning et al. 2012). The Clausius-Clapeyron equation is represented as shown in Eqn. (5-10).

$$-\frac{Q_{st}}{R} = \left(\frac{d \ln p}{d(1/T)} \right) \tag{5-10}$$

where Q_{st} is the isosteric heat of adsorption (KJ mol^{-1}), p is the equilibrium pressure of adsorption, (kPa), T is the temperature (K), and R is the universal gas constant. The slope of the plot of lnC versus 1/T in Eqn. (10) gives the value for isosteric heat of adsorption.

The adsorption of methane onto pyrogenic substances has a positive heat of adsorption, which implies that the adsorption process is exothermic in nature (Ning et al. 2012; Bagheri et al. 2011) and results in decreased levels of adsorption as the temperature increases. The isosteric heat of adsorption calculated for biochars and GAC ranged from 1.2 – 40 KJ mol^{-1} (Table 5-4). The reported values for the isosteric heat of adsorption for methane onto coal range between 9 and 12 KJ mol^{-1} at temperatures ranging from 308 and 328 K for much higher pressure ranges (Sakurovs et al. 2008) as compared to the pressure range used in this study. The heat of adsorption values for the biochars and GAC in this study encompassed a much wider range as compared to the previously reported values (Sakurovs et al. 2008); this could be attributed to the differences in the study conditions, such as temperature and pressure.

TABLE 5-4: HEAT OF ADSORPTION FOR CH_4 ONTO BIOCHARS AND GAC

Material Tested	Heat of Adsorption ($KJ.mol^{-1}$)
BS	7.5 – 15.8
CK	12.1 – 25.5
AW	9.9 – 12.8
CE-WP1	2.6 – 6.2
CE-WP2	4.7 – 12.9
CE-AWP	2.0 – 39.8
CE-WC	2.5 – 2.5
GAC	1.2 – 10.0

5.4.4 Coupled Adsorption, Dispersion and Transport

The methane adsorption capacity of the biochars increased with an increase in the methane inflow rates under dry and wet conditions (Figure 5-8). The high microporosity and greater availability of surface sites in biochars could have potentially accommodated the adsorption of excessive amounts of methane delivered to the column at higher inflow rates within a short time period. The presence of interconnected pore spaces in biochars in combination with varying levels of pore sizes (Yargicoglu et al. 2015) could have facilitated the rapid storage and capture of methane gas, thereby enhancing the adsorption capacity at higher rates of CH_4 supply. The retention times of methane within a conventional soil cover was comparatively shorter in an advection-driven transport setting, which meant that the potential for methanotrophs to intercept the methane at such environments were lower due to higher gas flow velocities (Chanton et al. 2011). This could mean that the addition of biochars to soil might reduce the potential of advective methane emission from

soil covers as a result of adsorption and increased gas retention times even under high velocity conditions.

The extent of methane transport through the biochars and GAC was inhibited by the presence of moisture within the packed columns as seen from the reduction in the values for retardation factors (Table 5-3). However, the range of dispersion coefficients modeled for the biochars in this study was higher than the values previously reported for soils (Aachib et al. 2004). This implies that the addition of biochars to landfill cover soils can enhance the gas transport properties within the cover system. From previous studies, it was found that the amendment of biochar to cover soil can significantly increase the cover material's potential to oxidize methane (Reddy et al. 2014; Yaghoubi 2011) as a result of enhanced transport, adsorption and the greather depth of oxygen ingression in biochar-amended soil cover systems (Xie et al. 2013). The presence of moisture within the biochar-based cover system can significantly lower the rate of gas dispersion due to a reduced share of gas-filled pores that effectively contribute to the movement of gases, consequently resulting in higher water-filled pore spaces. This phenomenon was previously reported to occur in soils where the diffusion coefficient decreased by several orders of magnitude with an increase in the degree of saturation (Aachib et al. 2004). However, in this study, the extent of reduction in methane transport for the biochars with increasing moisture was not as prominent compared to that of the soil. This could be because the biochars have much greater porosities when compared to soil, thereby facilitating certain amounts of gas transport even in the presence of moisture.

5.5 Conclusion

This study evaluated the effects of moisture, temperature and varying levels of exposed CH_4 concentrations and inflow rates on the CH_4 adsorption capacities of seven types of hardwood biochars that exhibited distinct physical-chemical properties and surface characteristics. In the absence of moisture, GAC had a much better capacity to adsorb CH_4 compared to all the biochars tested. However, the inhibition in the extent of CH_4 adsorption at increased levels of moisture content on the biochars was less pronounced as compared to that of the GAC implying that the biochars had a higher potential for continued CH_4 adsorption under more dynamically varying moisture conditions as is very likely to occur in field scenarios. Moreover, the modeled dispersion coefficients for the biochars and GAC ranged between $1.3 \times 10^{-3} – 4.8 \times 10^{-3}$ $m^2 s^{-1}$ and were found to decrease with increasing levels of moisture content. However, the effects of moisture on the transport of methane through biochars were less pronounced than that reported to occur in soil. The ability of methanotrophs to effectively oxidize methane is highest in landfill cover soils when the moisture content is close to its WHC (Spokas and Bogner 2011). If biochars are amended to cover soils, the transport of gases and adsorption of CH_4 onto its porous structure can occur even in the presence of moisture and can possibly result in enhanced microbial methane oxidation by ensuring a sufficient supply of CH_4, O_2 and moisture to the methanotrophs.

The use of a simple, linear sorptive model was found to be sufficient to determine the transport characteristics of methane through the small-scale biochar columns indicated by the high R^2 values between 0.94 and 0.99. However, the non-equilibrium, non-linear behaviour may be significant in determining the sorptive behaviour of biochars in a transport-driven conditions, especially as the final covers are expected to be subjected to highly variable mass flowrates and concentrations of CH_4. Further field-scale evaluation of biochar-amended cover systems are strongly recommended

in order to better understand the effects of more dynamic environmental and gas transport conditions on the performance of these cover systems. Long-term field studies should be validated by developing a comprehensive numerical model that incorporates the effects of combined processes such as adsorption, diffusion, oxidation, and transport of CH_4 by accounting for seasonal variations in temperature, pressure and moisture to better understand the performance of biochar-based biocover systems.

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6. ADSORPTION AND TRANSPORT OF METHANE IN LANDFILL COVER SOIL AMENDED WITH WASTE-WOOD BIOCHARS

6.1 Introduction

The content of this chapter has been previously published during the author's doctoral work [**Sadasivam, B.Y.**, & Reddy, K.R. (2015). "Adsorption and transport of methane in landfill cover soil amended with waste-wood biochars." J*ournal of environmental management 158 (2015): 11-23*].

The use of organic amendments to landfill cover soils enhances the CH_4 oxidation rates and reduces the CH_4 fluxes emitted from landfills (Park et al. 2004; Stern et al. 2007; Nikiema et al. 2007; Huber-Humer et al. 2008; Huber-Humer et al. 2009; Pederson et al. 2011; Scheutz et al. 2011; Roncato et al. 2012). Albeit the addition of organic rich compost amendments to landfill cover soils enhances the microbial methane oxidation capacity, exo-polymeric substances form over time within the cover system that clog the pores and hinder the diffusion of gases (Wilheusen et al. 2004; Hilger et al. 2000; Powelson et al. 2006). To design an efficient biocover system for methane emissions from landfills, a stable biocover material needs to be selected where the material has a high porosity with the capability to enhance the methane adsorption capacity as well as favor the growth of methanotrophs and promote the microbial methane oxidation process. Limited studies have been conducted that investigate such porous, organic amendments, which have a high potential for the adsorption of CH_4 and also facilitate enhanced gas transport properties that can together increase the CH_4 oxidation rates by minimizing the adverse impacts due to the clogging of pores (Sadasivam and Reddy, 2014).

Biochar is a porous, organic material produced by the pyrolysis or gasification of waste biomass (Lehmann and Joseph, 2009). The process of biomass conversion and the treatment conditions are based on the desired end product, which can be biofuel for energy (Lehmann, 2007) or biochar for the purpose of environmental management (Lal, 2004; Lehmann and Joseph, 2009). The physicochemical properties of biochars are controlled by the initial characteristics of the feedstock, reactor treatment conditions such as temperature and residence time and also the post-treatment processes (if any) such as activation (Lua et al. 2004; Boateng, 2007). The porosity and specific surface area of biochars are dictated by the highest treatment temperature (Brown et al. 2006) and post-processing such as activation (Zhang et al. 2004). The increased presence of micropores in biochars makes it highly preferable for gas adsorption purposes (Rouquerol et al. 1999). Biochars, when used as a soil amendment, have a high potential to increase the sorption ability of soils mainly due to their pyrogenic production process. Several studies that compared the sorption properties of pyrogenic and non-pyrogenic or fresh biomass have found that the sorption ability of pyrogenic substances such as biochars is a couple of orders of magnitude higher than that of fresh biomass (Baring et al. 2002; Huang et al. 2003; Nguyen et al. 2004). The highly porous structure of biochars was previously shown to favor the growth and activity of methanotrophs when amended to a cover soil and enhance the potential for increased methane oxidation (Reddy et al. 2014).

The purpose of this study is to investigate and compare the CH_4 sorption and transport properties of four waste-wood derived biochars amended to landfill cover soil at varying percentages (2, 5 and 10% by weight) as opposed to that of soil when used solely as a cover material. The specific objectives of this study are to: (1) quantify the kinetic rate of CH_4 adsorption and the maximum methane adsorption capacity of landfill cover soil and biochar-amended landfill

cover soils under three levels of moisture (dry, 25%WHC and 75%WHC) and temperature (25^0C, 35^0C and 45^0C); (2) determine the effects of moisture, temperature and biochar-amendment percentages on CH_4 adsorption and transport; and (3) determine the effect of landfill gas (LFG) inflow rate and presence of moisture on the CH_4 transport and diffusion through soil and biochar-amended soils. The results from this study can help identify the potential use of biochars as amendments to landfill soil with the aim of achieving effective methane mitigation.

6.2 Materials and Methods

6.2.1 Biochars and Soil

Four types of biochars produced from waste-wood were chosen for this study based on preliminary screening and tests conducted on seven waste-wood biochar types (Yargicoglu et al. 2015). The waste-wood biochars were obtained from Chip Energy Inc. (Goodfield, IL) in 5-gallon buckets, and were stored in labeled, airtight containers. The biochars were produced by gasification using an updraft gasifier at a temperature of about 500^0C. The feedstock for all the biochars was hardwood either in the chipped or pelleted forms. The fine ash fraction of the pelleted hardwood was retained in the case of CW-WP1, whereas, the ash fraction was sieved in the case of CE-WP2. CE-AWP was made out pelleted hardwood and the biochar was allowed to age under room temperature in a sealed drum for 3 years prior to its use in this study. CE-AWP was made of hardwood chips. The photographs of biochars are presented in Figure 4-1. The cover soil for the biochar amendment studies was obtained from the top 12 inches of an intermediate cover area in a DeKalb County, IL landfill. The cover soil was sieved using a 2-mm mesh and the fraction of soil passing the sieve was homogenized and stored in plastic bags at 4°C prior to usage. All the test materials were autoclaved using a Napco® model 8000-DSE autoclave at 121°C for 30 min

for two consecutive days (Bennett et al. 2003) and were sealed at 22°C for 24 hours between autoclave treatments (Carter et al. 2007) prior to conducting adsorption experiments.

6.2.2 Physicochemical Characterization Testing

In this study, the physicochemical properties of soil and biochar-amended soils were characterized in accordance with specific ASTM methods. The test materials were characterized for pH (ASTM D 4972), moisture content (MC) (ASTM D2216), organic content (OC) (ASTM D2974 by Loss-on-Ignition), average particle size (ASTM D422), specific gravity (SG) (ASTM D854), water holding capacity (WHC) (ASTM D2980), and dry density (ASTM D2937). All the physical-chemical characterization tests were conducted in duplicate on the sterilized materials. SEM images of soil and biochars were used to quantify the porosities using Particles (Pores) and Cracks Analysis System (PCAS) software (Liu et al., 2011). Elemental C was determined using Perkin Elmer Elemental Analyzer. Further details on the characterization test procedures can be found in Yargicoglu et al. (2015).

6.2.3 Batch Adsorption testing

Batch adsorption tests were conducted to determine the methane adsorption capacity of soil and biochar-amended soils under different levels of MC, temperature and exposed methane concentrations. Sterilization was performed on the materials prior to the adsorption tests to eliminate microbial interference on methane adsorption during the tests. A total of 5g of the test material was placed inside 250 ml amber glass bottles and sealed tight using long sleeved rubber stoppers. Then, 10, 25, 40, 50, 75, and 100 ml of air from the headspace of the test units was replaced with respective volumes of synthetic landfill gas comprising 50% CH_4 and 50% CO_2 to

achieve headspace CH_4 concentrations of 2, 5, 8, 10, 15, and 20% (v/v), respectively. Control test units were set up like the sample test units that did not include the adsorbents, to determine the initial CH_4 headspace concentration (v/v) achieved for each experimental set. To determine the effects of biochar-amendment percentages on CH_4 adsorption, three amendment levels (2, 5 and 10% w/w) were selected by mixing the appropriate mass of biochars to the soil, keeping the total mass of the amended cover material constant at 5g for all the tests. To determine the effects of moisture content on the methane adsorption, test units were set up that followed the procedure above, but with the addition of measured volumes of de-ionized water using a calibrated pipette to achieve moisture levels of 25 and 75% with respect to the biochar's WHC based on dry weight. The temperature in the test units was maintained at 25°C and the CH_4 gas pressure ranged from 0.15 to 1 KPa for all the tests conducted to study the effects of MC on the adsorption of CH_4 onto cover materials. A hydrometer water bath (Model H - 4239A) manufactured by Humboldt Co. was used to maintain the specified temperature conditions within the test units at the required preset levels of 35°C and 45°C to test the effects of temperature on methane adsorption. All the test units (including the controls) were placed in the water bath and allowed to acclimate to the respective preset temperature levels. A thermometer was used to ensure that the appropriate temperature conditions existed within the test units prior to the start of the tests. All the adsorption tests were conducted until the material's maximum adsorption capacity was achieved. Gas samples were collected at intervals until the equilibrium conditions were achieved.

6.2.4 Column Adsorption Testing

The column tests were conducted to assess the adsorption and transport characteristics of methane through the soil and biochar-amended soils. The tests were conducted under influent

methane flow rates of 7.3, 5.4 and 3.1 ml min^{-1} and moisture levels of dry, 25% and 75% with respect to the material's WHC. The tests were conducted using a Kontes brand Chromaflex® glass chromatography column (420870) measuring 2.5 cm in diameter and 30 cm in length. The columns were fitted with a bed support mesh screen, PTFE tubing, end connections, and screw caps. To control the influent methane gas flow rates and to monitor the effluent flow rates, flow meters (GF -8330-1001, Gilmont Instruments) were installed at both ends of the column (Figure 5-1). The glass column and the fittings were sterilized prior to filling it with the sterilized soil and biochar/soil mixes. The columns were filled with test materials in two 15 cm thick layers; light tamping followed the placement of each layer. For the tests conducted at different moisture levels, 25% and 75% of the biochar's WHC, a biochar stock was prepared with a known mass by adding a known volume of de-ionized water and used to fill the column as mentioned previously. For each test, synthetic landfill gas mixture comprising 5% CH_4 (v/v), 5% CO_2 (v/v) and 90% N_2 (v/v) was introduced through the column bottom at a pre-selected constant flow rate and the effluent flow rates were monitored. Gas samples were collected from the effluent sampling port at intervals until breakthrough was achieved.

6.2.5 Gas Sampling and Analysis

All the gas samples were collected using a BD 10 ml louver lock syringe and non-coring needle fitted with a two-way plastic stop-cock. The sampling syringe, needle and stop-cock were sterilized to avoid bacterial contamination of the test units and the samples. Gas samples were then stored in evacuated 5 ml glass vials and analyzed within 4 hours from the time of collection using an HP 6890 GC with FID and GS- Carbon Plot column. Prior to analyzing the gas samples, the GC was

calibrated using ultra high purity methane standards (0.1, 1, 5, and 25% CH_4 v/v) and a calibration curve was developed to interpret CH_4 concentrations of the samples.

6.2.6 Statistical Analysis

Statistical Analysis System (SAS®) software, version 9.3, was used to perform all the statistical analyses on the data obtained from batch adsorption tests to determine if the sample means were statistically different by using the Tukey's analysis. Analysis of Variance (ANOVA) procedures were used to determine the significant differences between the data sets from the batch isotherm tests. All the statistical analyses assumed that the error is normally distributed and relatively constant at all treatment levels. The assumptions were validated using the Proc univariate procedure and the null hypothesis was tested for means at an alpha level of 0.05.

6.2.7 Batch Adsorption Modeling

Based on the batch adsorption test results, adsorption kinetic parameters were obtained based on the methane adsorbed at various time periods using the plots of linear forms of Lagergren first-order and second-order models shown in Eqns. (5-1) and (5-2), respectively. Linear forms of Langmuir and Freundlich adsorption isotherm models as shown in Eqns. (5-3) and (5-4), respectively, were used to fit the adsorption data obtained for all the materials tested.

6.2.8 Column Adsorption and Transport Modeling

For modeling the transport of CH_4 through biochar columns, the linear sorption coefficient (K_d) is calculated from the corresponding batch sorption experiments conducted on the biochars at low exposed CH_4 concentartions (< 8% CH_4 v/v). The linear and non-kinetic sorption is assumed

for the column tests; however, the nonlinear and kinetic sorption may be approriate to consider in the field scale cover systems. The one-dimensional advection-dispersion mass balance for a conservative substance coupled with sorption as a retardation factor is shown in Eqns. (5-5) through 5-8). The following initial and boundary conditions are applicable for the column experiments for this study:

$$C(x, 0) = 5\% \text{ (v/v) for } x \geq 0$$

$$C(0, t) = C_0 \text{ for } t \geq 0$$

$$C(\infty, t) = 5\% \text{ (v/v) for } t \geq 0$$

The solution derived in Eqn. (5-9) assumes that equilibrium exists between the solute concentration and the adsorbed phase surface concentration and the relationship is linear. The transport of methane through the adsorbent is modeled based on the assumption that the lateral dispersion of the gas is negligible, while accounting for the linear dispersion only. The methane breakthrough curves were modeled using MATLAB to compute the dispersion coefficients for the soil and biochar-amended soils.

6.3 Results

6.3.1 Physicochemical Characterization Testing

The physicochemical properties of soil and different biochar-amended soils are shown in Table 6-1. The pH of soil and different biochar-amended soils were neutral to slightly basic, ranging from 7.0 – 7.6. The moisture content of the sterilized soil was 2.1 % (d.w.) and was comparatively higher than that of the biochar-amended soils, which ranged from 0 – 1.3% (d.w.). The organic content of the cover soil was 0.8% (d.w.), while that of the biochar-amended soils was much higher. Notable, the amount of organic content increased steadily with an increase in the

percentage of biochar amendment to the soil (Table 6-1). Sample S+10%WP1 exhibited the highest level of organic content (14.5% d.w.), followed closely by S+10%WP2 (12.45% d.w.). The magnitude of increase in organic content for the CE-AWP and CE-WC biochar amended soils was relatively lower that of the other two biochar types tested. The average soil particle size was much smaller (0.03 mm) compared to the biochar-amended soil samples. In fact, the average particle size of the amended soil increased with an increase in the amendment percentages irrespective of the biochar type tested. CE-WC biochar amended samples had the highest average particle size, which ranged from 0.34 – 0.43 mm, followed by CE-AWP amended soils, which ranged from 0.22 – 0.26 mm. The average particle size of CE-WP2 amended soils were slightly lower than that of CE-AWP amended soils, with a range of 0.20 – 0.22 mm. The CE-WP1 samples showed the lowest particle sizes among all the biochar-amended soils at different amendment percentages (0.10 – 0.20 mm). The specific gravity value for the soil was 2.59 and the addition of biochar to soil consistently decreased the specific gravity as the percentage of the biochar amendment increased, for all of the biochar types tested. The cover soil exhibited the least capacity to retain water within its pores as compared to biochar-amended soils. The WHC of the biochar-amended soil samples increased as the amendment percentages increased for the four biochar types tested. The dry density of the soil was 1.89 g/cm^3 and the density of cover materials consistently decreased with the increase in the biochar-amendment to soil percentage irrespective of the biochar type that was tested. In general, the CE-WC amended soils had the lowest dry density, ranging from 1.24 – 1.61 g/cm^3, compared to other materials. SEM images of soil and biochars that were used for the quantification of porosity using PCAS software are presented in Figure 6-1. Soil had much lower porosity (25%) compared to the biochars (35 – 45%). The elemental carbon content of biochars (70 – 84 % d.w.) were much higher than that of soil (4.7% d.w.).

TABLE 6-1: PHYSICAL-CHEMICAL PROPERTIES OF SOIL AND BIOCHAR-AMENDED SOILS

Material	pH	ORP (mV)	MC (%)	OC (%)	Average Particle Size (mm)	SG	WHC (%)	Dry Density (g/cm^3)	Porosity (%)	Elemental Carbon (%)
Soil (S)	7.3	-35.9	2.1	0.8	0.03	2.59	20.9	1.89	25	4.7
S+2%WP1	7.4	-43.4	0.55	2.14	0.10	2.53	34.99	1.69	--	--
S+5%WP1	7.3	-40.4	1.34	5.39	0.20	2.41	36.91	1.66	--	--
S+10%WP1	7.3	-39.1	0.00	14.50	0.24	2.24	37.10	1.49	--	--
CE-WP1	6.2	35.1	0.18	96.0	1.13	0.77	142.4	0.56	44.4	70.7
S+2%WP2	7.5	-45.5	0.00	1.65	0.20	2.51	21.00	1.54	--	--
S+5%WP2	7.4	-47.8	0.34	6.28	0.21	2.38	21.73	1.60	--	--
S+10%WP2	7.4	-48.5	0.62	12.45	0.22	2.33	22.13	1.66	--	--
CE-WP2	6.8	2.3	0.14	97.0	3.15	0.59	50.6	0.52	41.4	74.0
S+2%AWP	7.5	-43.7	0.56	2.81	0.22	2.55	27.23	1.65	--	--
S+5%AWP	7.6	-48.3	0.66	4.21	0.23	2.49	29.27	1.61	--	--
S+10%AWP	7.5	-45.2	0.52	8.53	0.26	2.46	32.43	1.33	--	--
CE-AWP	6.1	-48.7	0.47	82.3	5.75	0.91	80.8	0.53	39.9	78.1
S+2%WC	7.0	-47.8	0.89	2.04	0.34	2.50	34.10	1.61	--	--
S+5%WC	7.1	-49.2	1.09	2.27	0.38	2.44	35.46	1.54	--	--
S+10%WC	7.2	-52.4	0.69	2.41	0.43	2.33	36.52	1.24	--	--
CE-WC	7.0	-58.1	0.65	91.0	6.1	0.87	96.4	0.38	35.6	84.0

ORP=oxidation-reduction potential; MC=moisture content; OC=organic content; SG=specific gravity; WHC=water holding capacity

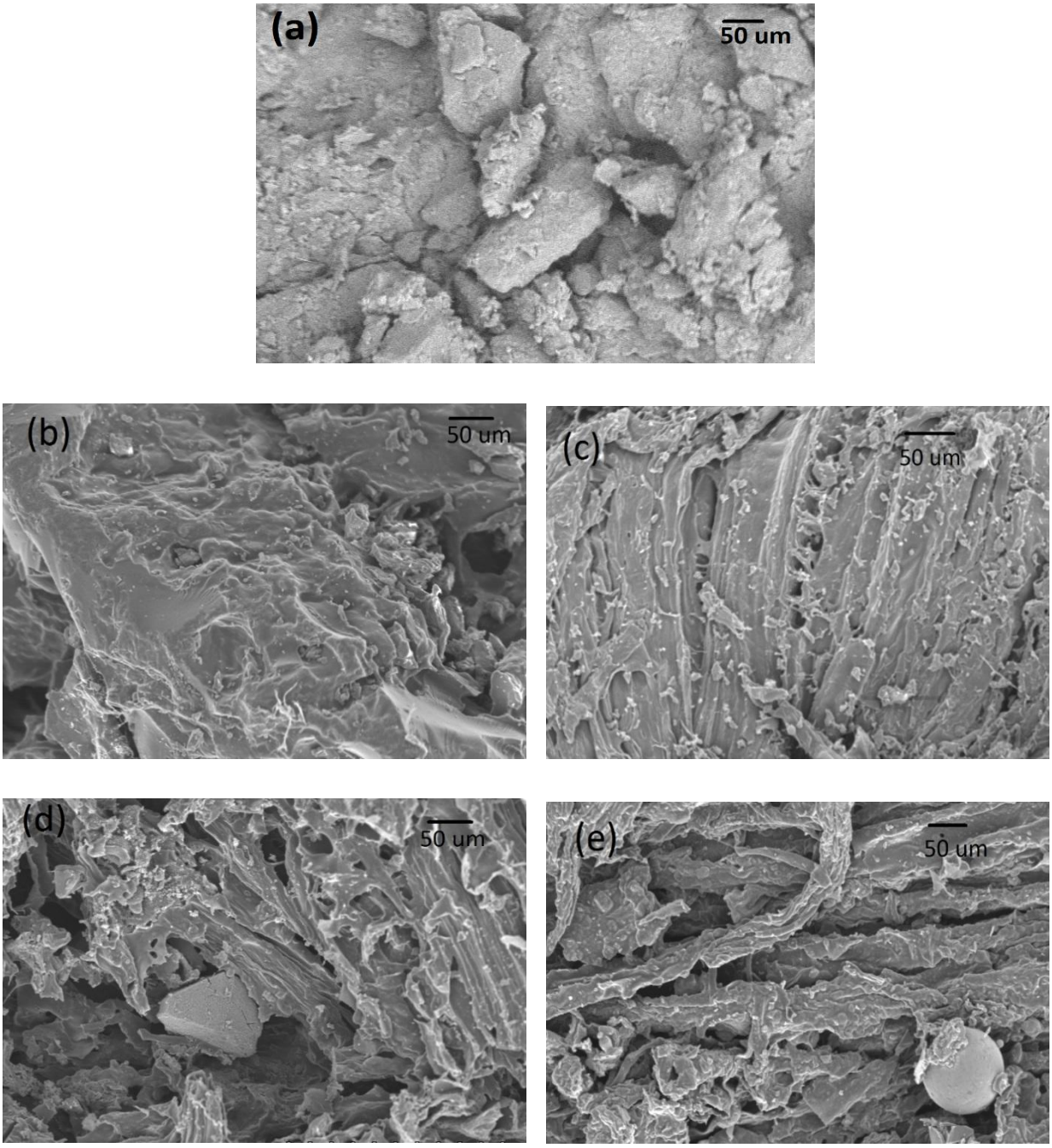

FIGURE 6-1: SEM IMAGES OF: (A) SOIL; (B) CE-WP1; (C) CE-WP2; (D) CE-AWP AND (E) CE-WC AT MAGNIFICATION OF 1000

6.3.2 Batch Adsorption Tests

The linear form of the pseudo second-order kinetic model appeared to fit all the adsorption data better with much higher R^2 values that ranged from 0.95 - 0.99, than the linear form of first-order kinetic model. Similar results were observed by Luo et al. (2011) that considered the adsorption kinetics of methane onto activated carbon. Equilibrium conditions within all the batch adsorption test units in the current study were achieved at the end of two hours from the initiation of the tests. The equilibrium CH_4 adsorption capacity at higher headspace CH_4 concentrations was reached in all the tests, which indicated that the CH_4 adsorption sites in the soil and biochar-amended soils were exhausted and the materials could no longer adsorb further CH_4 despite any increase in the levels of the initial headspace CH_4 concentration. The linear form of the Langmuir isotherm model best represented the mechanisms of methane sorption in the cover materials tested (Tables 6-2 and 6-3). The pseudo second-order kinetic model parameter (q_e) that refers to the equilibrium CH_4 adsorption capacity was compared for the soil and biochar-amended soils under dry, 25% and 75% WHC (Figures 6-2, 6-3 and 6-4). The extent of CH_4 adsorption onto biochar-amended soils was at least an order of magnitude higher than that of the cover soil alone. The presence of moisture in the cover materials resulted in a significant ($\alpha = 0.05$) decrease in the equilibrium adsorption capacity for all four types of biochar-amended soils, no matter what the amendment percentages. The equilibrium CH_4 adsorption capacity for soil and biochar-amended soils increased with an increase in the levels of the initial CH_4 concentrations, within the concentration range of this study (2 to 15% CH_4 v/v) regardless of the presence of moisture within the system. The equilibrium adsorption capacity under various moisture levels for the CE-WP1 amended soils was the highest, followed closely by the CE-WP2 and CE-AWP amended soils, while the least capacity was exhibited by the CE-WC amended soils.

TABLE 6-2: EFFECT OF MC ON ADSORPTION ISOTHERM PARAMETERS FOR BIOCHAR-AMENDED SOILS

Material	Langmuir Model Parameters			Freundlich Model Parameters		
	Q^0 (mol/kg)	b	R^2	K_F (mol/kg)	n	R^2
Dry Conditions						
Soil (S)	0.0019	2.45	0.98	0.0016	1.67	0.93
S+2%WP2	0.0136	2.03	0.99	0.0107	1.55	0.95
S+5%WP2	0.0314	2.61	0.99	0.025	1.79	0.93
S+10%WP2	0.0797	1.68	0.97	0.0513	1.67	0.86
S+2%WP1	0.0146	3.83	0.99	0.0140	1.91	0.95
S+5%WP1	0.0656	2.76	0.99	0.0620	1.56	0.96
S+10%WP1	0.0845	1.62	0.99	0.0560	1.56	0.92
S+2%AWP	0.0136	2.03	0.99	0.0107	1.55	0.95
S+5%AWP	0.0292	2.19	0.99	0.0242	1.54	0.97
S+10%AWP	0.0690	1.38	0.99	0.0460	1.39	0.95
S+2%WC	0.0103	2.51	0.99	0.0087	1.65	0.96
S+5%WC	0.0204	2.89	0.99	0.0186	1.68	0.98
S+10%WC	0.0361	2.96	0.99	0.0331	1.69	0.96
25% WHC						
Soil (S)	0.0018	2.53	0.98	0.0015	1.68	0.93
S+2%WP2	0.0119	1.96	0.99	0.0101	1.51	0.97
S+5%WP2	0.0260	2.79	0.99	0.0229	1.70	0.94
S+10%WP2	0.0725	1.38	0.98	0.0425	1.60	0.87
S+2%WP1	0.0126	3.92	0.99	0.0122	1.90	0.98
S+5%WP1	0.0350	3.51	0.99	0.0336	1.80	0.95
S+10%WP1	0.0759	1.69	0.99	0.0559	1.45	0.94
S+2%AWP	0.0104	2.54	0.99	0.0090	1.63	0.97
S+5%AWP	0.0246	2.50	0.99	0.0213	1.61	0.97
S+10%AWP	0.0620	1.13	0.98	0.0360	1.37	0.93
S+2%WC	0.0083	2.83	0.99	0.0073	1.72	0.96
S+5%WC	0.0169	3.11	0.99	0.0153	1.79	0.94
S+10%WC	0.0345	2.54	0.99	0.0302	1.61	0.96
75% WHC						
Soil (S)	0.0017	2.37	0.99	0.0014	1.62	0.95
S+2%WP2	0.0072	3.65	0.99	0.0069	1.85	0.98
S+5%WP2	0.0186	3.35	0.99	0.0176	1.77	0.97
S+10%WP2	0.0603	1.23	0.99	0.0349	1.48	0.94
S+2%WP1	0.0105	4.34	0.99	0.0104	2.0	0.97
S+5%WP1	0.0280	3.42	0.99	0.0272	1.74	0.98
S+10%WP1	0.0647	1.44	0.99	0.0441	1.40	0.94
S+2%AWP	0.0070	3.76	0.99	0.0066	1.95	0.93
S+5%AWP	0.0164	3.41	0.99	0.0154	1.81	0.97
S+10%AWP	0.0356	1.75	0.99	0.0274	1.44	0.98
S+2%WC	0.0063	4.04	0.99	0.0061	1.98	0.95
S+5%WC	0.0128	3.94	0.99	0.0123	1.94	0.96
S+10%WC	0.0171	4.54	0.99	0.0170	2.04	0.96

TABLE 6-3: EFFECT OF TEMPERATURE ON ADSORPTION ISOTHERM PARAMETERS FOR BIOCHAR-AMENDED SOILS

Material	Langmuir Model Parameters			Freundlich Model Parameters		
	Q^0 (mol/kg)	b	R^2	K_F (mol/kg)	n	R^2
25^0C						
Soil (S)	0.0019	2.45	0.98	0.0016	1.67	0.93
S+2%WP2	0.0135	2.03	0.99	0.0107	1.5518	0.95
S+5%WP2	0.0314	2.61	0.99	0.025	1.79	0.93
S+10%WP2	0.0797	1.68	0.97	0.0513	1.67	0.86
S+2%WP1	0.0146	3.83	0.99	0.0140	1.91	0.95
S+5%WP1	0.0656	2.76	0.99	0.0620	1.56	0.96
S+10%WP1	0.0845	1.62	0.99	0.0560	1.56	0.92
S+2%AWP	0.0136	2.03	0.99	0.0107	1.55	0.95
S+5%AWP	0.0292	2.19	0.99	0.0242	1.54	0.97
S+10%AWP	0.0690	1.38	0.99	0.0460	1.39	0.95
S+2%WC	0.0103	2.51	0.99	0.0087	1.65	0.96
S+5%WC	0.0204	2.89	0.99	0.0186	1.68	0.98
S+10%WC	0.0361	2.96	0.99	0.0331	1.69	0.96
35^0C						
Soil (S)	0.004	2.32	0.99	0.003	1.61	0.95
S+2%WP2	0.010	2.64	0.99	0.009	1.64	0.98
S+5%WP2	0.0216	4.04	0.99	0.0216	1.87	0.98
S+10%WP2	0.0585	2.14	0.98	0.0426	1.74	0.88
S+2%WP1	0.0107	3.48	0.99	0.0100	1.84	0.96
S+5%WP1	0.0440	3.07	0.99	0.0411	1.70	0.95
S+10%WP1	0.0755	1.56	0.99	0.0547	1.39	0.96
S+2%AWP	0.0074	3.51	0.99	0.0070	1.82	0.98
S+5%AWP	0.0140	4.84	0.99	0.0139	2.15	0.94
S+10%AWP	0.0357	1.75	0.99	0.0279	1.43	0.96
S+2%WC	0.0073	3.10	0.99	0.0066	1.77	0.96
S+5%WC	0.0130	4.55	0.99	0.0127	2.10	0.94
S+10%WC	0.0187	3.64	0.99	0.0178	1.87	0.95
45^0C						
Soil (S)	0.008	1.24	0.98	0.005	1.39	0.94
S+2%WP2	0.009	3.0	0.99	0.008	1.76	0.95
S+5%WP2	0.0214	3.39	0.99	0.0205	1.77	0.98
S+10%WP2	0.0341	3.41	0.99	0.0310	1.85	0.97
S+2%WP1	0.0104	3.16	0.99	0.0093	1.82	0.93
S+5%WP1	0.0409	2.46	0.99	0.0352	1.60	0.95
S+10%WP1	0.0531	2.20	0.99	0.0440	1.54	0.95
S+2%AWP	0.0069	2.98	0.99	0.0062	1.74	0.97
S+5%AWP	0.0135	3.39	0.99	0.0123	1.79	0.98
S+10%AWP	0.0191	2.71	0.99	0.0166	1.70	0.95
S+2%WC	0.0053	3.48	0.99	0.0049	1.89	0.94
S+5%WC	0.0128	3.55	0.99	0.0121	1.84	0.97
S+10%WC	0.0140	3.79	0.99	0.0133	1.93	0.95

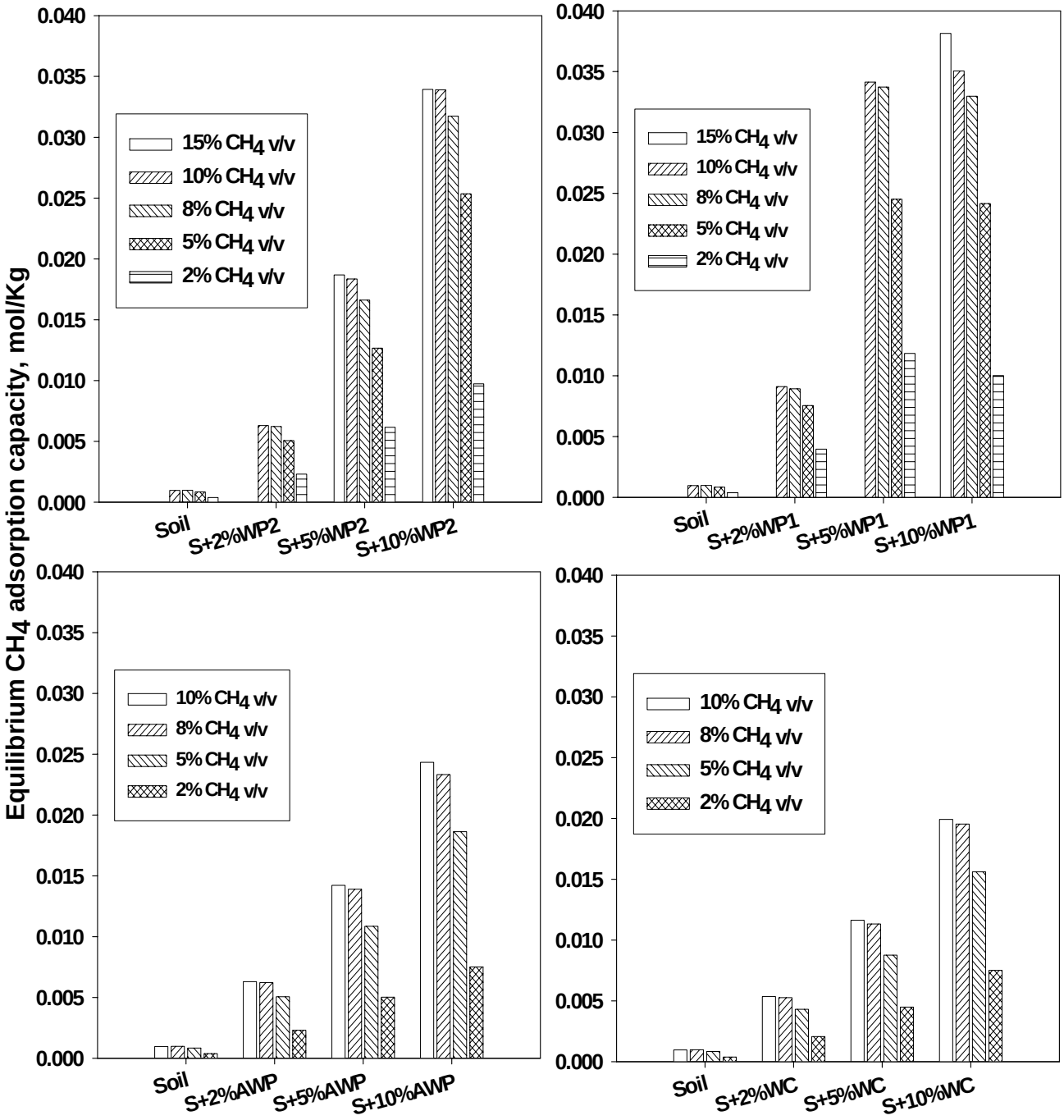

FIGURE 6-2: EQUILIBRIUM CH4 ADSORPTION CAPACITY OF SOIL AND BIOCHAR-AMENDED SOILS (AS-IS, 25°C)

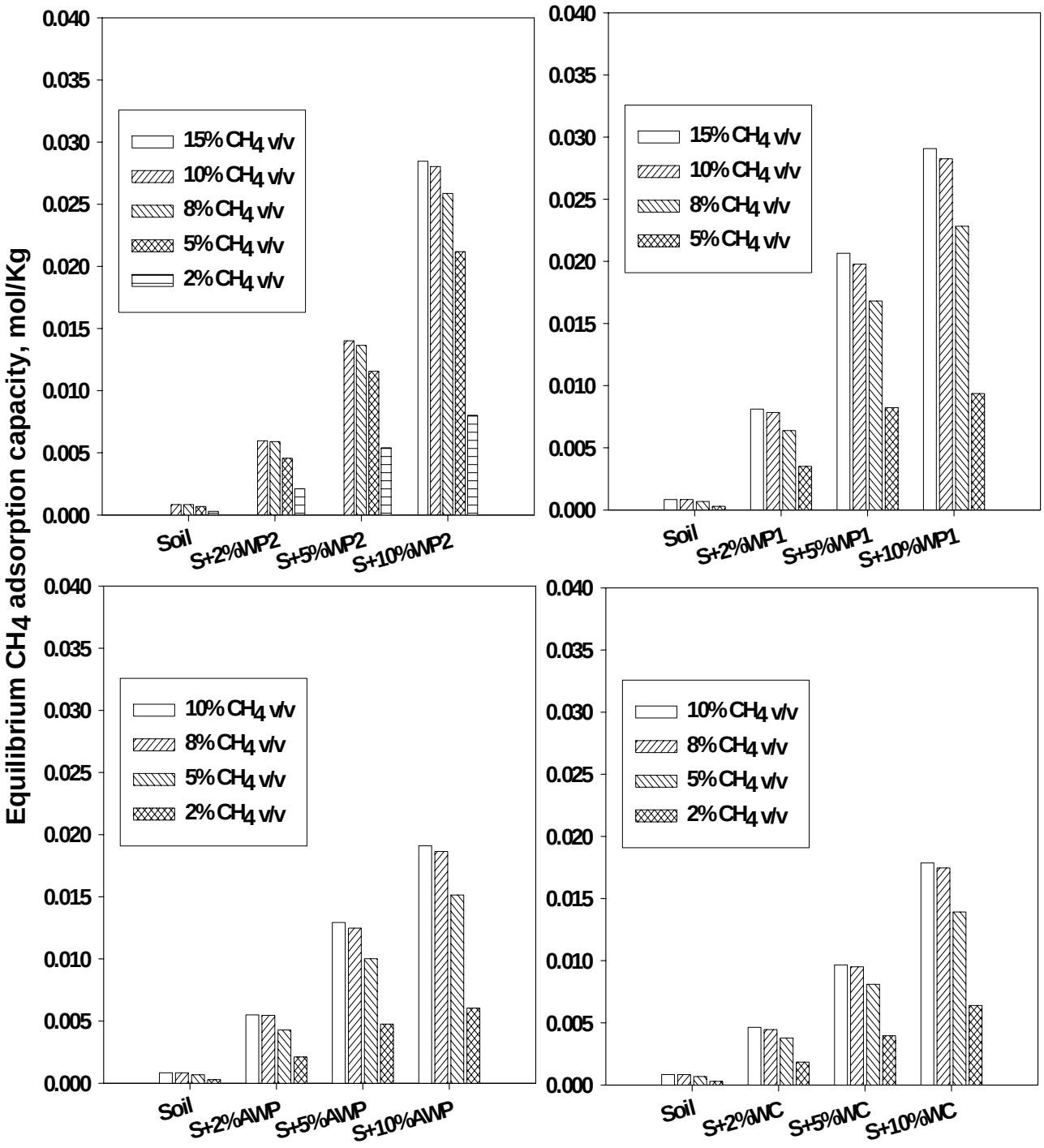

FIGURE 6-3: EQUILIBRIUM CH_4 ADSORPTION OF SOIL AND BIOCHAR-AMENDED SOILS (25% WHC, 25°C)

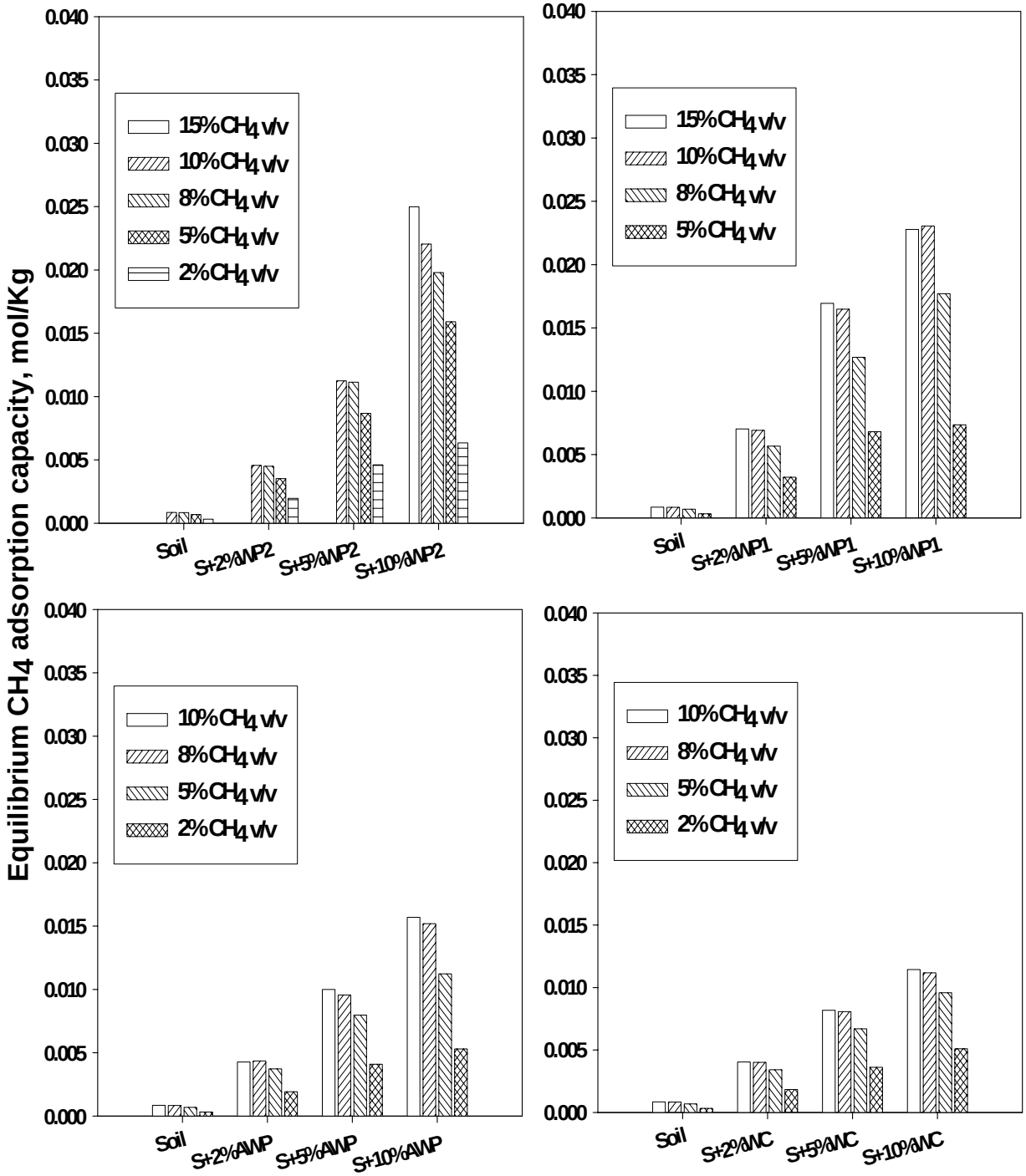

FIGURE 6-4: EQUILIBRIUM CH_4 ADSORPTION CAPACITY OF SOIL AND BIOCHAR-AMENDED SOILS (75% WHC, 25°C)

The second-order kinetic rate (k_2) of CH_4 adsorption in soil and biochar-amended soils is quantified under different moisture conditions (dry, 25%WHC and 75% WHC). Figures 6-5, 6-6 and 6-7 show the k_2 results for soil and biochar-amended soils under varying moisture. The kinetic rate of CH_4 adsorption in soil and biochar-amended soil decreased as the amount of moisture in the cover materials increased under all levels of initial headspace CH_4 concentrations (% v/v). Adsorption isotherm modeling was performed to determine the mechanisms that control the exchange of CH_4 molecules between the adsorbent and the gas phase adsorbate, i.e. synthetic LFG mixture containing 50% CH_4 (v/v). Both Langmuir and Freundlich isotherm models were investigated and the isotherm modeling parameters are presented in Tables 6-2 and 6-3. The R^2 values fit for all the tests ranged from 0.97- 0.99. The maximum CH_4 adsorption capacity onto soil and biochar-amended soils was found to decrease significantly ($\alpha = 0.05$) with the increase in the moisture content, irrespective of the type of biochar amended. Under dry conditions, the maximum CH_4 adsorption capacity was the highest for all CE-WP1 amended soils, in the range of 0.015 - 0.085 mol/kg, followed closely by all CE-WP2 amended biochars, in the range from 0.014- 0.080 mol/kg at various amendment ratios tested. Soils amended with CE-WC biochar exhibited the capacity for CH_4 adsorption, which ranged between 0.010 - 0.047 mol/kg under as-is conditions. Overall, the CH_4 adsorption capacity of all biochar-amended soils was an order of magnitude higher, ranging between 0.010 – 0.085 mol/kg, as compared to that of the cover soil, which had a sorption capacity of 0.0019 mol/kg.

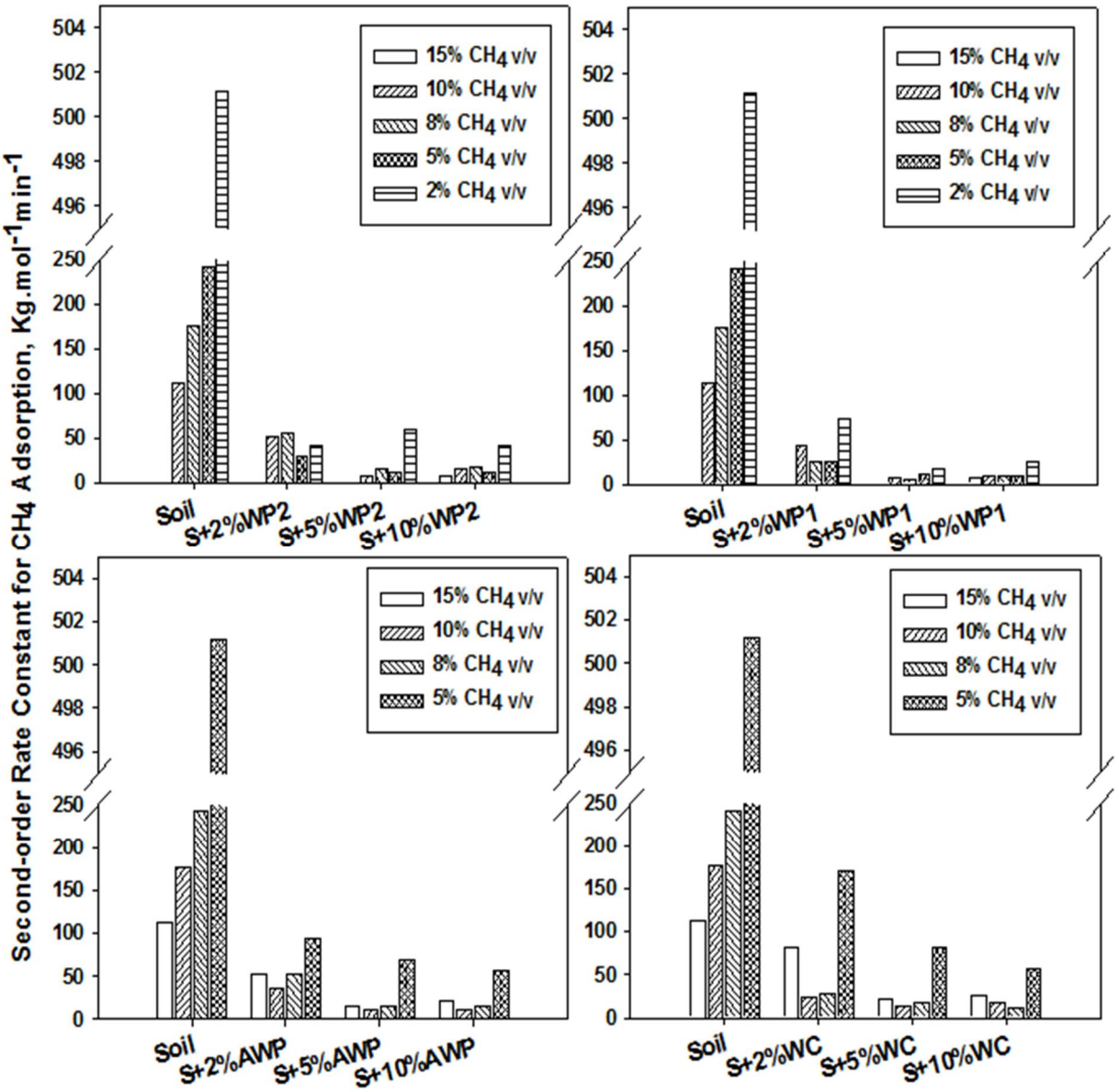

FIGURE 6-5: KINETIC RATE OF CH_4 ADSORPTION ONTO SOIL AND BIOCHAR-AMENDED SOILS (AS-IS, 25°C)

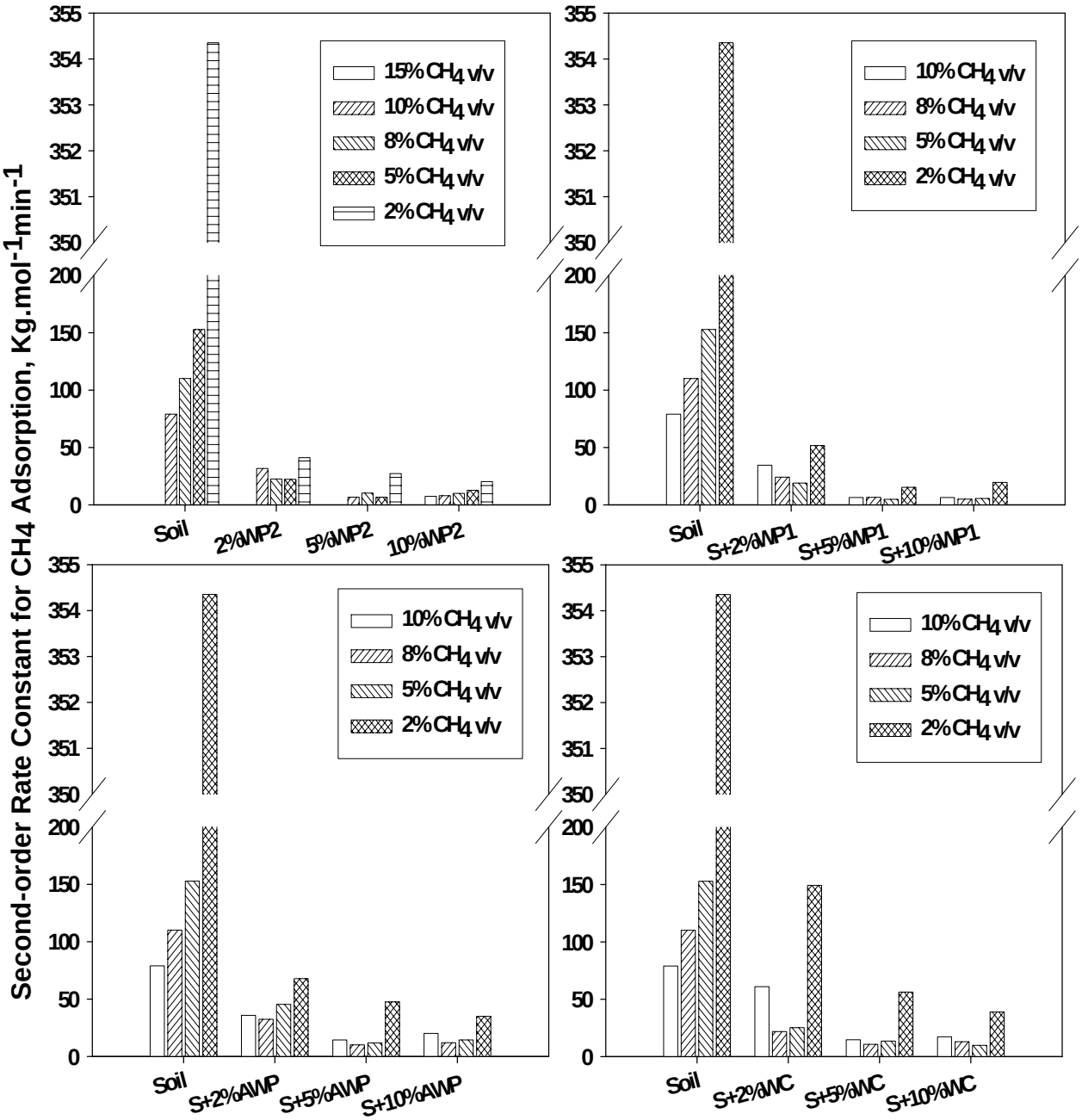

FIGURE 6-6: KINETIC RATE OF CH_4 ADSORPTION ONTO SOIL AND BIOCHAR- AMENDED SOILS (25% WHC, 25°C)

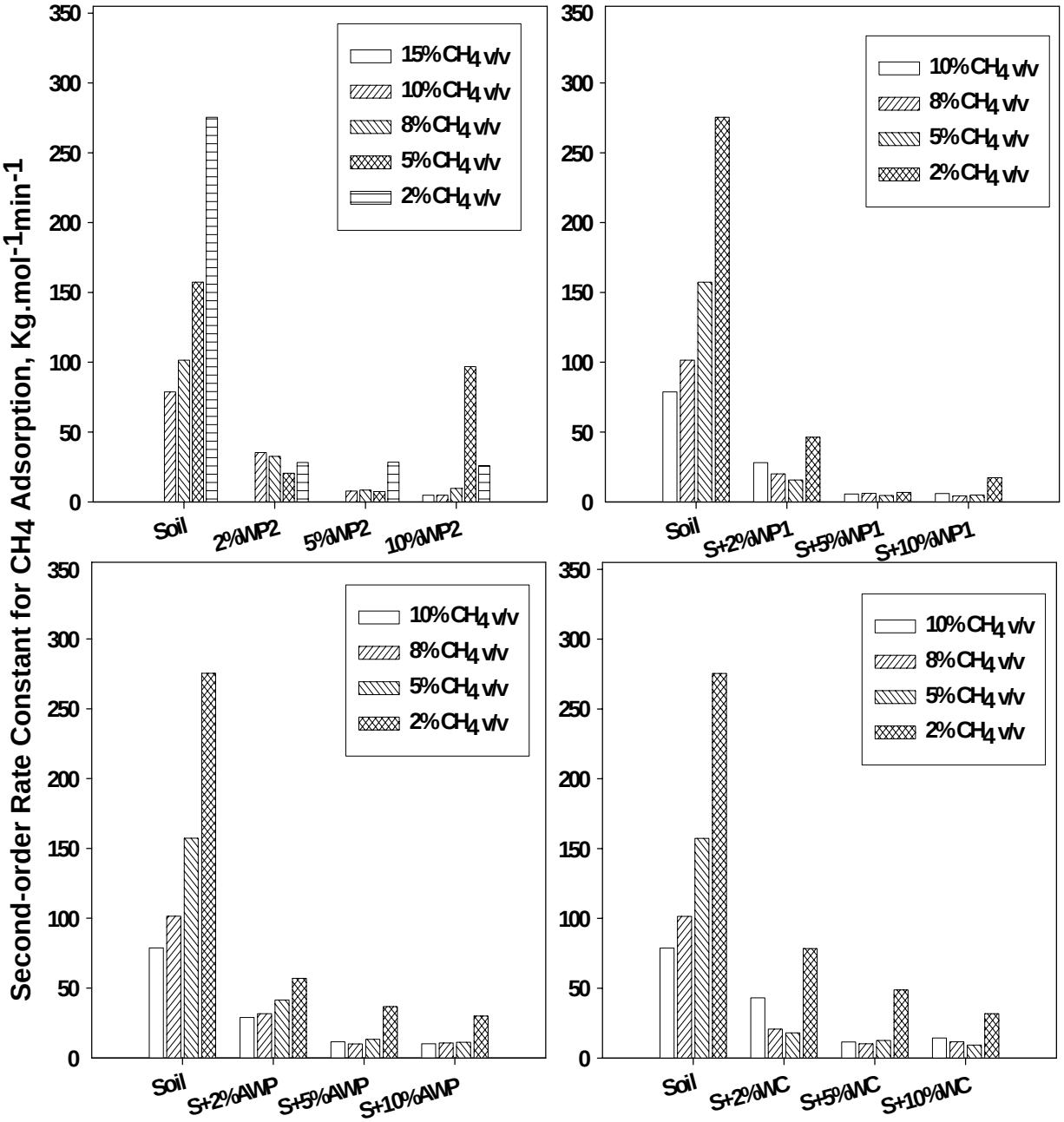

FIGURE 6-7: KINETIC RATE OF CH_4 ADSORPTION ONTO SOIL AND BIOCHAR- AMENDED SOILS (75% WHC, 25°C)

The second-order kinetic model parameter (q_e) that corresponds to the equilibrium CH_4 adsorption capacity of soil and biochar-amended soils at room temperature (25^0C), 35^0C and 45^0C, are presented in Figures 6-2, 6-8 and 6-9. The equilibrium adsorption capacity values for all biochar-amended soils dropped as the temperature rose, while that of soil rose with the increase in temperature, under the test conditions specific to this study. The kinetic rate of CH_4 adsorption, k_2 ($kg.mol^{-1}min^{-}1$) onto soil and biochar-amended soils at 25^0C, 35^0C and 45^0C, is presented in Figures 6-5, 6-10 and 6-11. Rate of methane sorption was found to decrease with the increase in temperature for all of the materials tested. The Langmuir and Freundlich isotherm model parameters for soil and biochar-amended soils under room temperature (25^0C), 35^0C and 45^0C are presented in Sadasivam (2015). The Langmuir model produced the best fit for the adsorption data for all the materials with higher R^2 values (0.97 - 0.99) as compared the Freundlich model. The maximum CH_4 adsorption capacity for soil and biochar-amended soils at different temperature is shown in Figure 6-12. The maximum adsorption capacity for soil increased as the temperature increased, while that of all biochar-amended soils decreased with the increase in temperature. The CE-WP1 amended soils exhibited the highest levels of CH_4 adsorption capacity and the order of adsorption capacity for other materials showed trends similar to the results presented for CE-WC amended soils having the least CH_4 adsorption capacity.

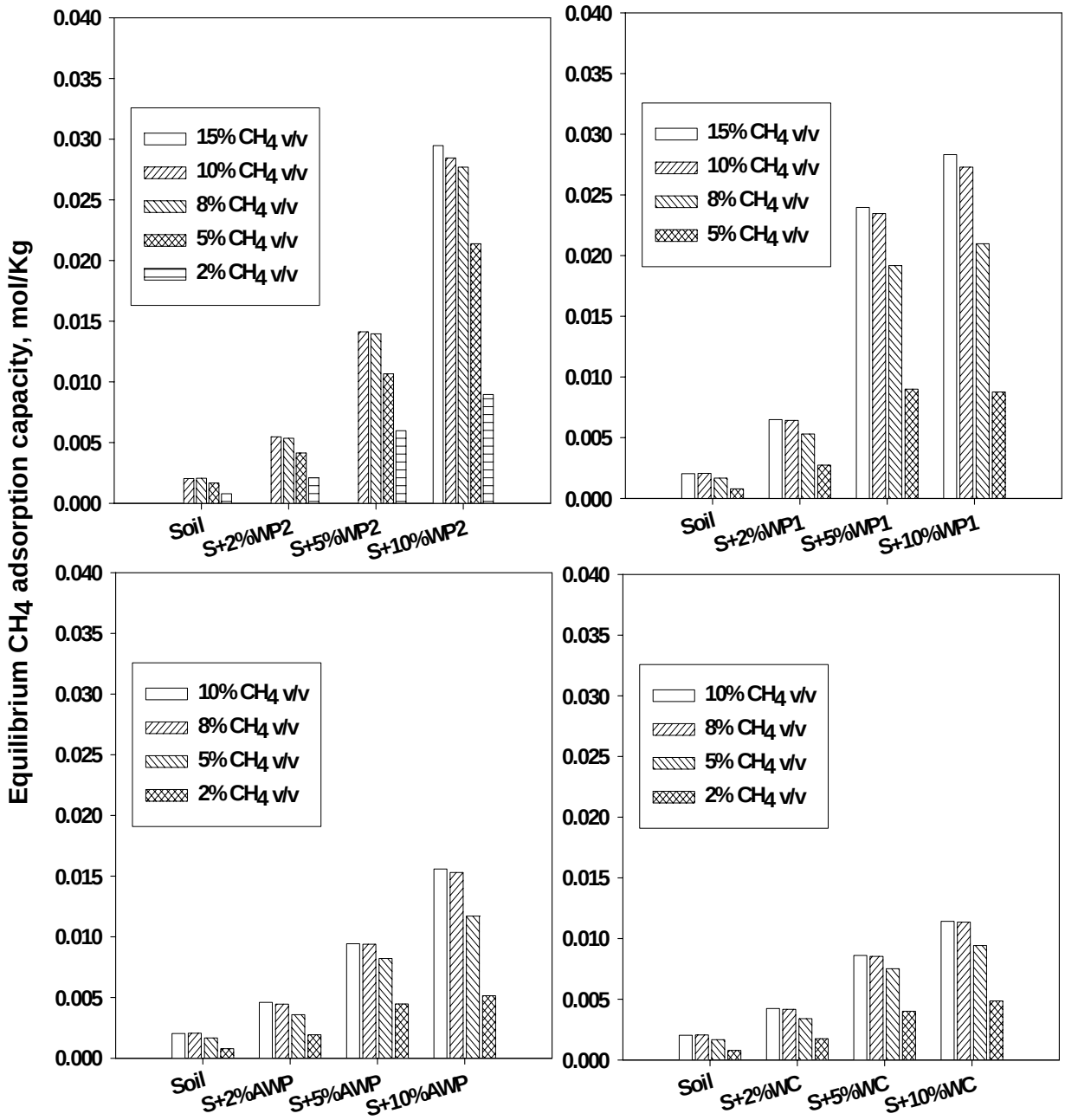

FIGURE 6-8: EQUILIBRIUM CH_4 ADSORPTION CAPACITY OF SOIL AND BIOCHAR-AMENDED SOILS (AS-IS, 35°C)

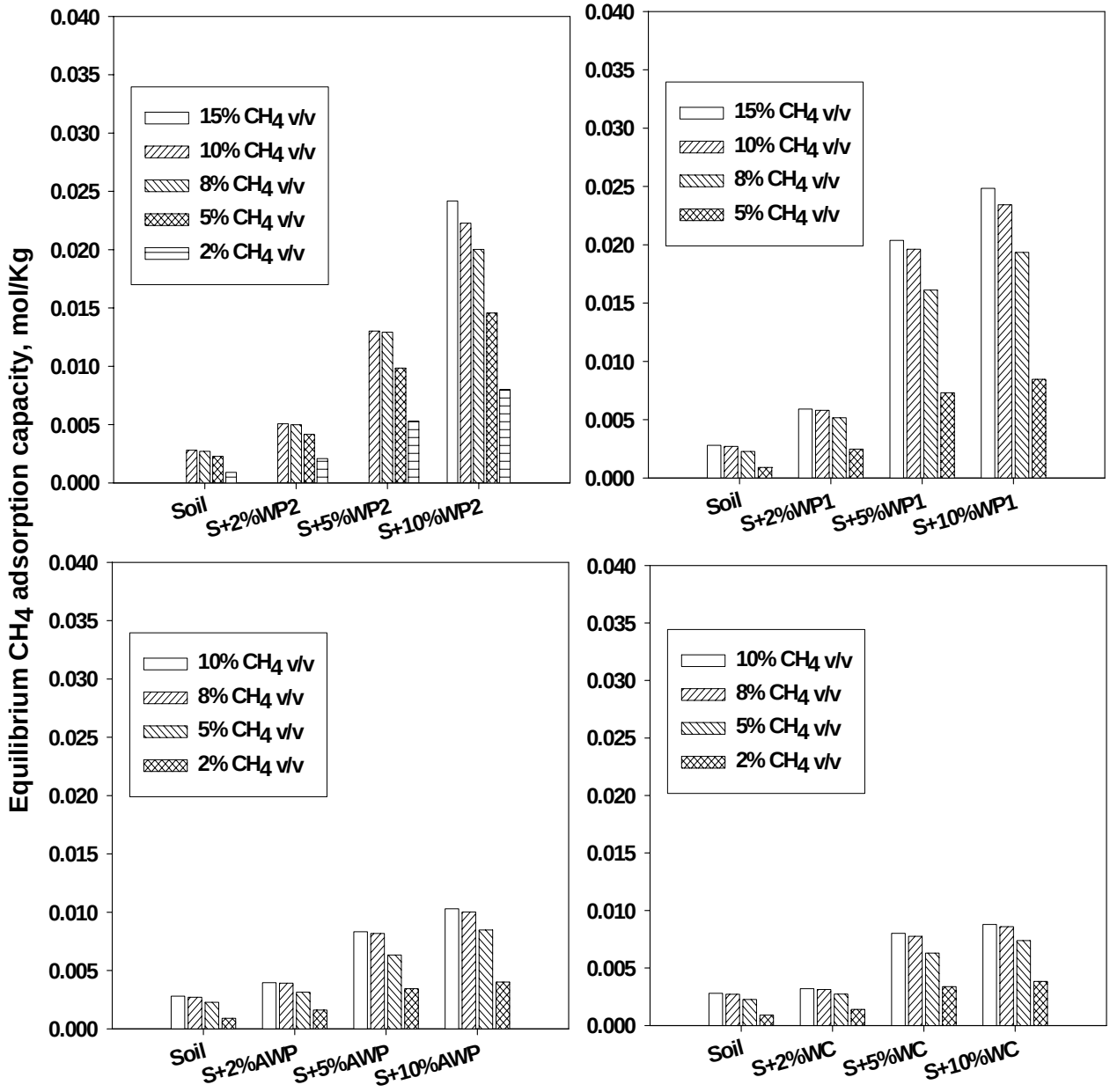

FIGURE 6-9: EQUILIBRIUM CH_4 ADSORPTION CAPACITY OF SOIL AND BIOCHAR-AMENDED SOILS (AS-IS, 45°C)

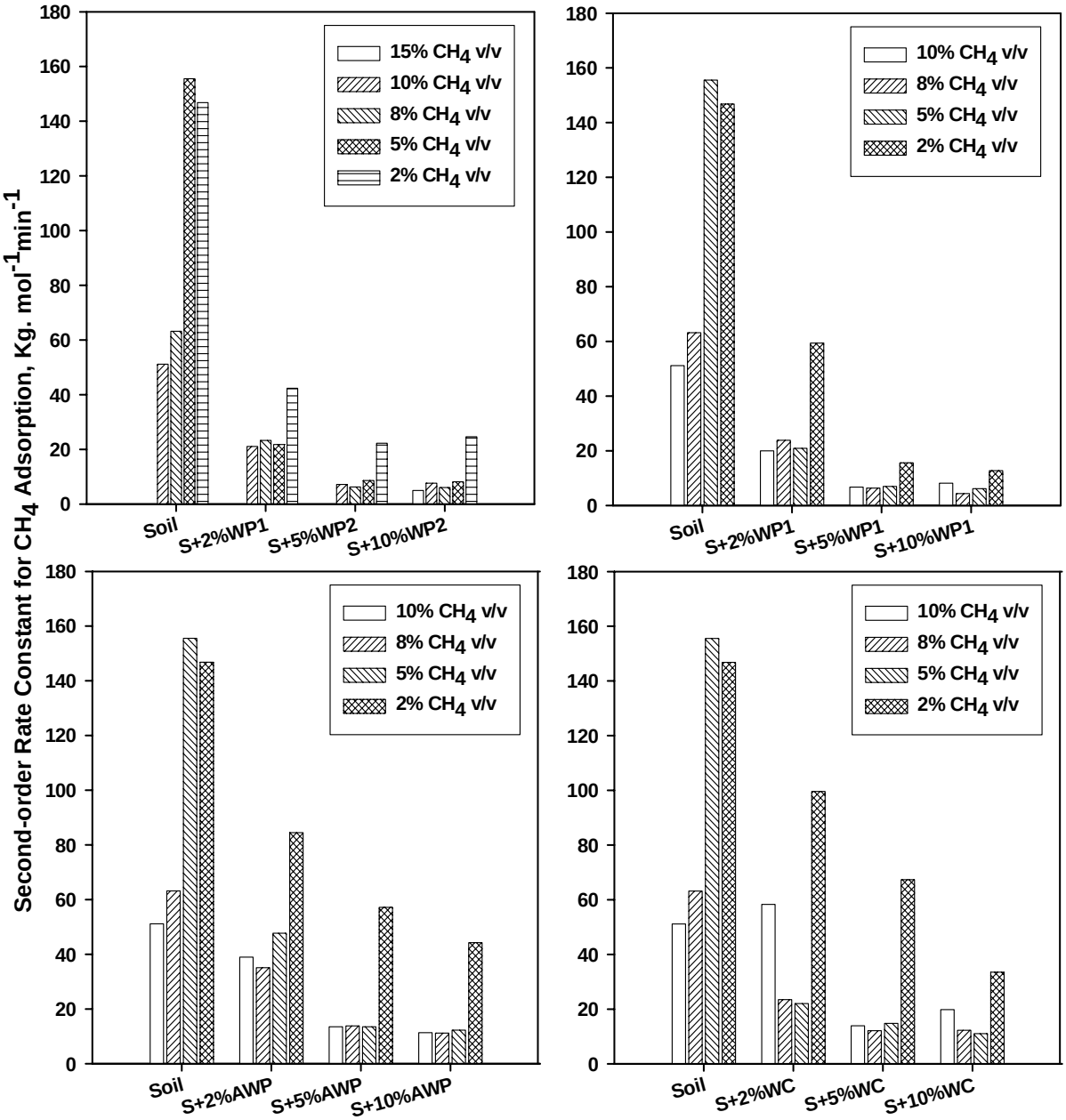

FIGURE 6-10: KINETIC RATE OF CH_4 ADSORPTION ONTO SOIL AND BIOCHAR- AMENDED SOILS (AS-IS, 35°C)

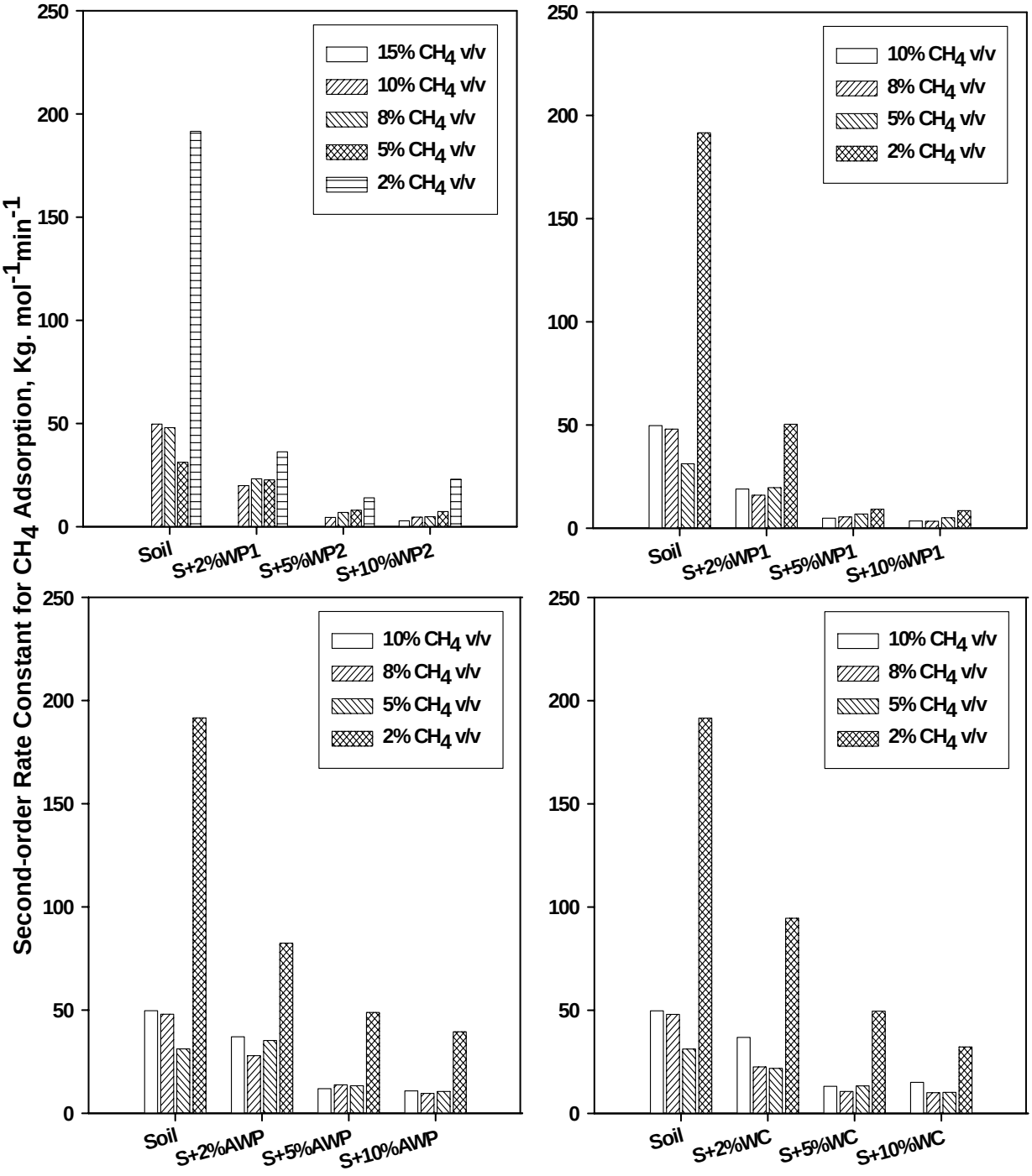

FIGURE 6-11: KINETIC RATE OF CH_4 ADSORPTION ONTO SOIL AND BIOCHAR- AMENDED SOILS (AS-IS, 45°C)

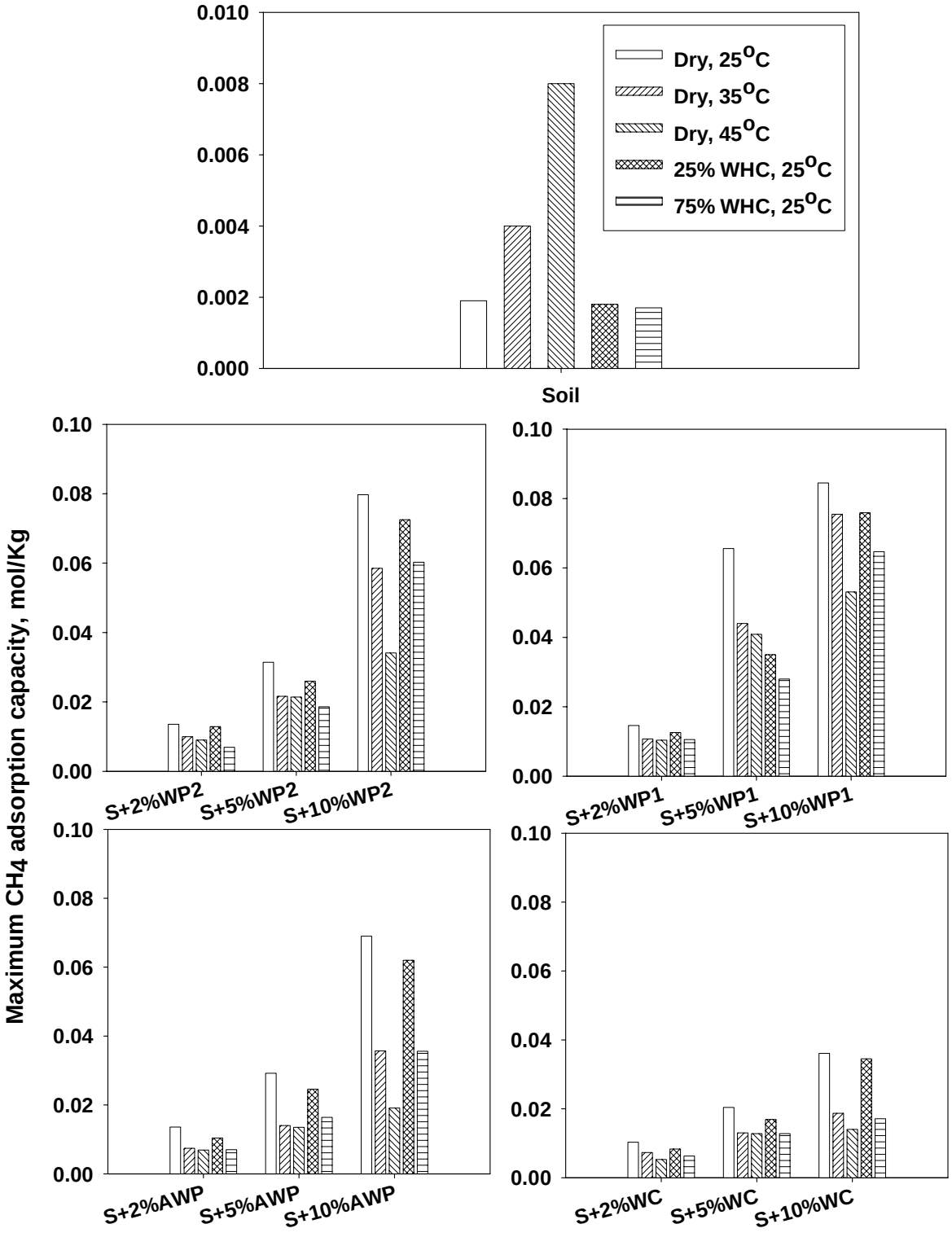

FIGURE 6-12: EFFECT OF MOISTURE CONTENT AND TEMPERATURE ON MAXIMUM CH4 ADSORPTION CAPACITY OF SOIL AND BIOCHAR-AMENDED SOILS

6.3.3 Column Adsorption Tests

The effects of CH_4 inflow rates and moisture on the CH_4 adsorption capacity for soil and biochar-amended soils are presented in Sadasivam (2015). The CH_4 adsorption capacity for soil was lower than all of the biochar-amended soils irrespective of the moisture levels within the packed columns. Increase in adsorption capacity was consistent with an increase in the percentage of biochar-amendment. The presence of moisture within the materials appeared to reduce the CH_4 adsorption capacity for all cover materials. However, the changes in CH_4 adsorption capacity were not statistically significant ($\alpha = 0.05$) between dry and 25% WHC conditions, while the reduction was significant ($\alpha = 0.05$) between dry and 75% WHC conditions for soil and biochar-amended soils. The CH_4 adsorption capacity was higher for all materials under low flow-rates (3 - 5 ml/min) as compared to higher flow rate corresponding to 7.3 ml/min. Overall, with respect to the order of adsorption capacity for the biochar-amended materials, the column test results agree with the batch adsorption test results. This means that the CE-WP1 amended soils had the highest capacity followed by CE-WP2 amended soils, and the CE-WC amended soils had the least CH_4 adsorption capacity.

6.3.4 Column Adsorption and Transport Modeling

Predictive transport modeling was performed to determine the CH_4 dispersion coefficients by using the 1-D advection dispersion equation given by Eq (5-9). The experimental breakthrough curves obtained for soil and the biochar-amended soils under different moisture conditions were fitted by changing the dispersion coefficient values from knowing all the other parameters in the transport equation. Typical experimental and model breakthrough curves for soil under different moisture levels are shown in Figure 6-13.

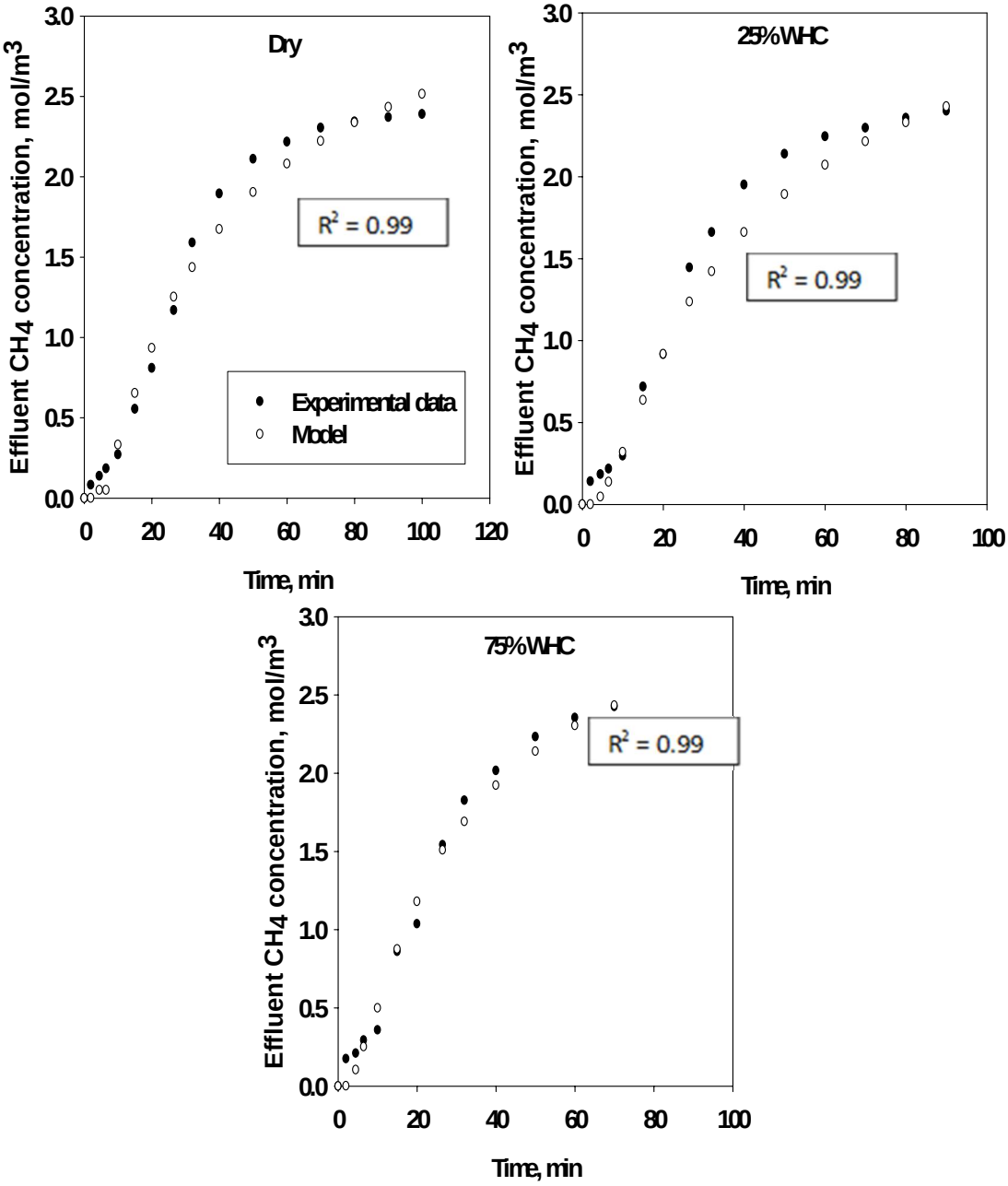

FIGURE 6-13: COMPARISON OF EXPERIMENTAL AND MODELING BREAKTHROUGH CURVES FOR SOIL

The various parameters used for transport modeling for the soil and biochar-amended soils under different moisture conditions are listed in Table 6-4. The dispersion coefficients for soil ranged between 4.3 $x10^{-3}$ - $4.5x10^{-3}$ m^2 min^{-1}. The dispersion coefficients for biochar-amended soils were one to two orders of magnitude higher than that of soil and ranged between 2.7 x 10^{-2} - 1.4 x 10^{-1} m^2 min^{-1}. The goodness of fit (R^2) values for the transport modeling ranged between 0.96 - 0.99. The CH_4 dispersion coefficients were found to increase with an increase in the biochar-amendment percentages and to decrease with increase in moisture levels (Figure 6-14). The retardation factors for cover materials under dry conditions were much higher compared to those values under moist conditions (Table 6-4). Retardation factors quantified in this study are indicative of the ability of soil and biochar-amended soils to adsorb and retain CH_4 within the cover system prior to breakthrough and is indicative of the retention time. Higher retardation factors imply that a longer time is required to achieve breakthrough the cover system.

TABLE 6-4: SUMMARY OF COLUMN ADSORPTION MODELING PARAMETERS

Cover Material	D (m^2/min)	K_D (m^3/kg)	ε (%)	ρ (kg/m^3)	R^2	Retardation Factor
Dry Conditions						
Soil (S)	0.0045	0.0003	25	1890	0.99	3.3
S+2%WP2	0.030	0.002	26	1540	0.99	12.8
S+5%WP2	0.108	0.005	28	1600	0.99	29.6
S+10%WP2	0.122	0.012	30	1660	0.99	67.4
S+2%WP1	0.029	0.003	34	1690	0.99	15.9
S+5%WP1	0.142	0.0107	35	1660	0.99	51.7
S+10%WP1	0.148	0.012	36	1490	0.98	50.7
S+2%AWP	0.039	0.002	26	1650	0.99	13.7
S+5%AWP	0.076	0.0046	27	1610	0.99	28.4
S+10%AWP	0.085	0.0083	29	1330	0.99	39.1
S+2%WC	0.060	0.0017	27	1610	0.98	11.1
S+5%WC	0.095	0.0037	28	1540	0.99	21.4
S+10%WC	0.098	0.0068	29	1240	0.98	30.1
25%WHC						
Soil (S)	0.0044	0.0003	25	1890	0.99	3.2
S+2%WP2	0.029	0.002	26	1540	0.99	12.8
S+5%WP2	0.107	0.0047	28	1600	0.99	27.9
S+10%WP2	0.119	0.0082	30	1660	0.96	46.4
S+2%WP1	0.028	0.0026	34	1690	0.99	13.9
S+5%WP1	0.110	0.0071	35	1660	0.98	34.7
S+10%WP1	0.140	0.0105	36	1490	0.97	44.5
S+2%AWP	0.036	0.0017	26	1650	0.99	11.8
S+5%AWP	0.071	0.0041	27	1610	0.98	25.4
S+10%AWP	0.079	0.0064	29	1330	0.99	30.35
S+2%WC	0.058	0.0014	27	1610	0.98	9.3
S+5%WC	0.091	0.0032	28	1540	0.98	18.6
S+10%WC	0.095	0.006	29	1240	0.99	26.7
75%WHC						
Soil (S)	0.0043	0.0002	25	1890	0.99	2.5
S+2%WP2	0.027	0.0014	26	1540	0.99	9.3
S+5%WP2	0.106	0.0036	28	1600	0.99	21.6
S+10%WP2	0.118	0.0061	30	1660	0.98	34.8
S+2%WP1	0.027	0.0023	34	1690	0.99	12.4
S+5%WP1	0.095	0.0030	35	1660	0.99	15.2
S+10%WP1	0.110	0.008	37	1490	0.99	34.1
S+2%AWP	0.034	0.0014	26	1650	0.99	9.9
S+5%AWP	0.070	0.0032	27	1610	0.99	20.1
S+10%AWP	0.070	0.005	29	1330	0.98	23.9
S+2%WC	0.054	0.0013	27	1610	0.99	8.8
S+5%WC	0.088	0.0027	28	1540	0.99	15.9
S+10%WC	0.092	0.0038	29	1240	0.99	17.2

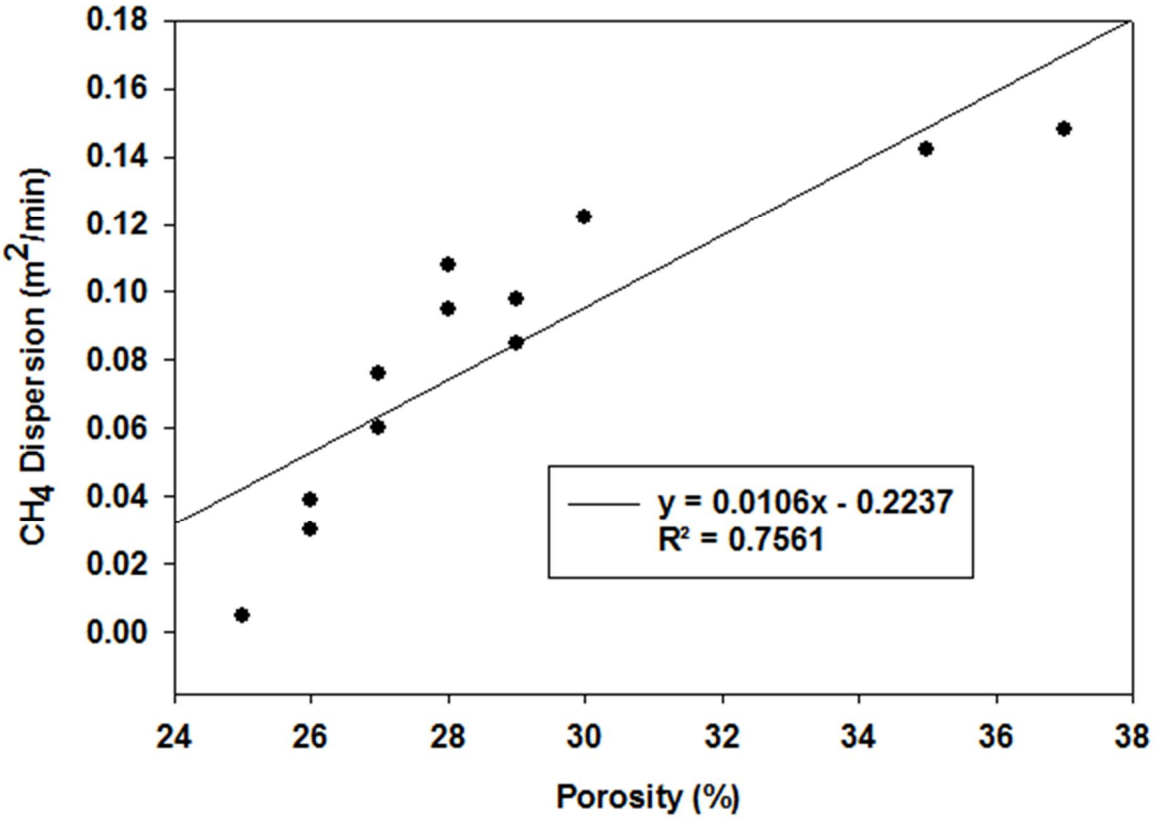

FIGURE 6-14: CORRELATION BETWEEN DISPERSION COEFFICIENT AND POROSITY OF SOIL AND BIOCHAR-AMENDED SOILS

6.4 Discussion

6.4.1 Physicochemical Characteristics

The adsorption, dispersion and transport of methane through biochar-based landfill covers, availability of oxygen and water for the microbial methane oxidation and prevailing environment for methanotrophic activity can be significantly impacted by the physical and chemical characteristics of the cover materials. Optimal methanotrophic activity occurs under neutral to

slightly basic soil conditions (Scheutz and Kjeldsen, 2004), and the cover materials tested in this study had neutral to slightly basic pH. In general, methanotrophic activity in soils is fairly resistant to significant pH gradients. Thus, the pH of cover materials tested in this study appear to favor the methanotrophic activity and promote methane oxidation when used as a biocover in landfills. It is critical to account for the effects of moisture since water in biochar pores can increase the habitability of biochar to microbial activities (Lehmann and Joseph, 2009). However, the high moisture content may also slow down the gaseous transport processes in the soil since molecular diffusion in water is many times slower than in air (Cabral and Jugnia, 2010).

The organic content of biochar-amended soils is much higher than that of soil, which indicates a significant increase in the organic fraction of cover materials with an increase in the biochar amendments. The organic matter fraction of all the sterilized CE-biochars ranged from 82 - 97% (Sadasivam and Reddy, 2015a). Though the biochar-soil mixtures exhibited much lower organic content compared to that of the biochars alone, there was a significant increase in the organic matter fraction compared to that of soil alone. The organic contents reported here, for the sterilized samples, are representative of all the available carbon content (fixed or volatile) that can burn off in the muffle furnace temperature ranging from 450 - 550^0C. In general, the adsorption capacity of soils can be increased with an increase in the amounts of organic soil fraction. As the amount of organic matter in any particular soil increases, the available surface area for adsorption increases (Lehmann and Joseph, 2009); this, in turn, results in better adsorption capacity for that soil. The characterization of all materials for their respective organic contents is critical to this study since previous studies showed that the extent of microbial methane oxidation can be increased by adding organic rich amendments to landfill cover soils (Stern et al. 2007; Huber-Humer et al. 2008; Huber-Humer et al. 2009; Pederson et al. 2011).

The particle size of the cover materials can significantly affect the extent of adsorption by altering the available surface area of the adsorbent and can serve as a controlling factor in the transport of gases through the cover layers (Sadasivam and Reddy, 2015b). Organic cover soil amendments with greater particle sizes can adversely affect the landfill performance in the long-term by allowing higher infiltration of rainwater, resulting in excessive leachate generation. This means that it is critical to limit the percolation of water through cover systems and imperative to meet the site-specific design standards with respect to hydraulic conductivity. The CE-WC biochar had the largest average particle size since the feedstock was comprised of wood chips with visibly large, chunky pieces of charred wood. The finer ash fraction in CE-WP1 biochar resulted in much smaller average particle sizes for all CE-WP1-amended soils compared to the other biochar-amended soils.

The water holding capacity (WHC) values correspond to the maximum amount of water that a known mass of the adsorbent can hold when excessive quantities of water are passed through it. From a practical point of view, this test can be used to determine the amount of water retained within the pores of the cover materials during a rain event. The addition of biochars to the soil increased the water retention capacity of soil and this can favor the growth and activity of MOB as it limits the potential for water-stressed conditions to occur within the cover system.

The porosity of biochar-amended soils increased significantly with the increase in the percentage of biochar amendment. The SEM images for soil and biochars are shown in Figure 6-1. Image analysis results clearly show that the biochars are highly porous materials with greater inter-particle and intra-particle porosity as compared to that of soil, thereby enhancing the porosity of soil with an increase in the level of amendment. The elemental carbon content of the biochars was much higher than that of the soil mainly due to the pyrogenic production conditions and the

feedstock of the biochars. Thus, amending the soil with carbon-rich biochars can result in a subsequent rise in the carbon content of the cover material, thereby facilitating enhanced CH_4 adsorption, diffusion and oxidation within the biochar-based cover system.

6.4.2 Effect of Moisture on Methane Adsorption

The kinetic data for CH_4 adsorption onto soil and biochar-amended soils under different levels of moisture, temperature and initial CH_4 headspace concentrations were best represented by Lagergren's second-order kinetic model. Similar observations were reported in a recent study that investigated the adsorption kinetics of methane onto activated carbon (Luo et al. 2011). The pseudo second-order kinetic model parameters are used to determine the extent of molecular exchange at the interface between the adsorbate in the gas phase and the adsorbent. From the adsorption kinetic data, it is evident that the amount of methane adsorbed onto the materials at equilibrium increases with increasing initial headspace CH_4 concentrations irrespective of the level of MC and temperature. This could be attributed to the increase in the amount of methane molecules readily available for adsorption onto soil and biochar-amended soil surfaces at higher headspace concentrations, as it promotes elevated amounts of CH_4 adsorbed at equilibrium.

Several studies examined the effects of moisture content on the adsorption of methane onto coals (Levy et al. 1997; Bustin et al. 1998) and activated carbon (Zhou et al. 2001; Farzad et al. 2007). From these studies, it is evident that the presence of moisture reduces the amount of methane adsorbed onto pyrogenic substances within the temperature and pressure ranges used in this study. The inhibition of the extent of CH_4 adsorption at equilibrium onto soil and biochar-amended soils with an increase in the MC is in accordance with the second-order kinetic model assumption that the extent of adsorption depends on only the available surface sites that are affected by the presence

of moisture in the adsorbents (Liu, 2008). Moreover, a water molecule has a diameter of 0.306 nm as compared to a methane molecule, with a diameter of 0.38 nm, which makes it harder for methane to penetrate the surface pores in the presence of moisture (Zhou et al. 2001), thus lowering the values of both q_e and k_2 in the presence of moisture as opposed to those values observed under dry conditions. Biochar-amended soils exhibited a greater inhibition in the rate at which CH_4 was adsorbed than soil. This higher reduction in the extent of CH_4 adsorption can be attributed to greater competition between the CH_4 and H_2O molecules in the case of pyrogenic substances.

The maximum CH_4 adsorption capacity of CE-WP1-amended soils was consistently higher for all amendment ratios under dry conditions (Figure 6-12). CE-WP1 exhibited greater porosity of 44.4% than soil (25%). The adsorption capacity of CE-WC amended soils was the least as they also exhibited the least porosity among the biochars. The maximum adsorption capacity for only the biochars tested showed a similar order with respect to the biochar types, and more detailed information on this is presented elsewhere (Sadasivam and Reddy 2015a). Typically, the sorption of methane onto carbon surfaces was hydrophobic which implies that the adsorbate (CH_4) - adsorbent interactions and bonding are strong and are not affected by the presence of water molecules. On the other hand, the presence of oxygenated active sites on carbon surfaces result in more of a hydrophilic behavior wherein, the presence of water molecules significantly hinders the extent of adsorbate (CH_4) – adsorbent bonding resulting in higher amounts of sorption sites being occupied by water (Müller and Gubbins, 1998).

6.4.3 Effect of Temperature on Methane Adsorption

Reduction in the kinetic rate of CH_4 adsorption at higher temperatures for soil and all biochar-amended soils can be attributed to the decrease in micropore width on the adsorbent's surface as a

result of increases in temperature, thus restricting the entry of methane molecules by assuming a simple linear pore filling model (Sakurovs et al. 2008). To evaluate the reason behind the increasing and decreasing trends in CH_4 adsorption capacity with the increase in temperatures, the Clausius-Clapeyron plot was used to obtain the heat of adsorption for the materials. The relationship between the equilibrium pressure of the adsorbate and the temperature of the adsorption medium is thermodynamically represented by the Clausius-Clapeyron plot to evaluate the nature of adsorption process (McLaughlin et al. 1998; Vasanth Kumar et al. 2011; Ning et al. 2012). The Clausius-Clapeyron equation is represented as shown in Eqn. (5-10).

The slope of the plot of lnC versus 1/T in Eq (5-10) gives the value for isosteric heat of adsorption. The isosteric heat of adsorption values for soils and biochar-amended soils are presented in Table 6-5. The adsorption of methane onto soil was found to be endothermic (-30 to -118 kJ/mol) because of which the adsorption capacity was shown to increase with an increase in temperature. The positive heat of adsorption values for biochar-amended soils were indicative of exothermic reactions that resulted in a decrease in the adsorption capacity as the temperature increased. Several studies have found that the adsorption of methane onto pyrogenic substances has a positive heat of adsorption, which, in turn, implies that the adsorption process is exothermic in nature (Ning et al. 2012; Bagheri et al. 2011; Jagiello et al. 1995). It is to be noted that the temperatures within a landfill cover under field conditions is expected to vary widely and can also drop to sub-zero levels depending upon the climatic conditions. However, the results from this study can be used to understand the overall trends in the sorption capacity of biochar-based cover soils with temperatures around the optimal values previously reported for the process of methane oxidation to occur (Spokas and Bogner, 2011).

TABLE 6-5: HEAT OF ADSORPTION FOR CH_4 IN BIOCHAR-AMENDED SOILS

Material Tested	Heat of Adsorption (kJ/mol)
Soil (S)	-30 to -118
S+2%WP2	24 - 61
S+5%WP2	42 - 256
S+10%WP2	57 - 380
S+2%WP1	38 - 248
S+5%WP1	30 - 297
S+10%WP1	50 - 440
S+2%AWP	30 - 240
S+5%AWP	34 - 402
S+10%AWP	125 - 400
S+2%WC	33 - 300
S+5%WC	39 - 290
S+10%WC	26 - 380

The range in heat of adsorption values for all biochar-amended soils increased with the increase in the biochar amendment. The addition of biochars to soil changes the nature of CH_4 adsorption process from endothermic to exothermic, a change in the enthalpy of the CH_4 adsorption that could be attributed to the changes in the oxidation-reduction potential of soil brought about by the biochar amendments. The *oxidation reduction potential* (ORP) values for biochar-amended soils indicate that they appear to be under more reduced conditions as compared

to that of soil and that the ORP values become more negative with the increase in the biochar-amendment. This could explain the possible increase in the enthalpy of adsorption with increasing biochar-amendment. Similar trends in the enthalpy of CH_4 adsorption were observed by Rychilki and Terzyk (1995). The presence of a potential energy barrier in the case of materials under slightly more oxidized conditions restricted the entry of CH_4 as the smallest of the pores were blocked by surface functionalities (Rychilki and Terzyk, 1995). The presence of such physical barrier on the soil surface could be possible since the ORP value of soil was less negative as compared to that of biochar-amended soils, which may have resulted in an endothermic effect to the overall adsorption enthalpy. The packing and the placement of methane molecules within the porous structure of biochars is largely dependent upon the pore size distribution and the presence of activated surfaces. The majority of biochar porosity was found to be contributed by the micropores (< 2nm size) and the extent of methane adsorption onto microporous materials were found to be much stronger compared to meso- and/or macropores (Sadasivam and Reddy, 2015b).

6.4.4 Coupled Adsorption, Dispersion and Transport

The CH_4 adsorption capacity appeared to be higher at low flow rates since the residence time for inlet CH_4 gas is higher at low inflow rates, resulting in a better contact between the adsorbate molecules and adsorbent surfaces over a longer duration of time. The CH_4 adsorption capacity was the highest in the case of the CE-WP1 amended soils, followed closely by the CE-WP2 amended soils, while the lowest adsorption capacity was exhibited by CE-WC amended soils. This trend in the adsorption capacity of materials to concur with that of the batch test results. The presence of moisture within the columns appears to impede the CH_4 adsorption onto material surfaces

regardless of the biochar-types and biochar amendment percentages to soil. These observations also agree with the batch adsorption test results.

The CH_4 dispersion coefficient values for soil, based on previous studies for different gas mixes ranged between 1.794×10^{-5}– 2.047×10^{-5} m^2 gas/s (Scheutz et al. 2009). In this study, the CH_4 dispersion coefficients appeared to be slightly higher (between 7.167×10^{-5}– 7.5×10^{-5} m^2 gas/s). This could be due to the possible differences in the physical properties of the soils such as porosity. In general, the dispersion coefficients decreased slightly with increases in the level of moisture within the columns (Table 6-4) and could be due to the impedance in the movement of CH_4 through moist cover materials caused by the presence of water molecules. The presence of water in carbonaceous materials was found to reduce the gas diffusivity through the pores since water acts as a swelling agent. However, the permeability of CH_4 in water is very low, in the order of 10^{-5} cm^2/s (Busch et al. 2004), which implies that the presence of moisture is not a major contributor to the hindrance of gas diffusion process because there is only a very slight, statistically insignificant decrease in the diffusion coefficients of the soil and biochar-amended soils with the increase in moisture levels.

Amendment of biochars to soil significantly ($\alpha = 0.05$) increased the CH_4 dispersion, which could be due to the rapid transport of CH_4 within the highly porous structures of biochar-amended soils. The transport CH_4 through highly microporous carbon structures increased by 3-4 orders of magnitude as compared to its transport through zeolites and crystalline structures (Skoulidas et al. 2002). There was an increasing trend ($R^2 = 0.77$) in the dispersion of CH_4 through cover materials as porosity increased. Similarly, the diffusivity of oxygen within soil covers increased with the increasing porosity of the material (Aachib et al. 2004). The porosity of biochar-amended soils was positively correlated with the CH_4 dispersion coefficients (Figure 6-14). Overall, the transport

of CH_4 through cover soil was enhanced by the addition of biochars, thereby increasing the diffusivity and allowing for higher rates of gas transport through the biochar-amended soils.

6.5 Conclusion

In this study, the CH_4 adsorption and transport properties of landfill cover soil and four different types of biochar-amended landfill cover soils were investigated and compared at different levels of moisture, temperature and biochar amendment. The physicochemical properties of the cover materials were characterized and were found to strongly influence the CH_4 adsorption and transport properties. Based on the results obtained from this study, the following conclusions can be derived:

- The kinetic and equilibrium sorption data for soil and biochar-amended soils were represented by the pseudo second-order kinetic model and linear form of Langmuir isotherm model, respectively.
- A significant decrease in the CH_4 adsorption capacity of soil and biochar-amended soils was found with an increase in the level of moisture.
- The maximum adsorption capacity for soil increased with an increase in temperature, while the opposite trend was observed in biochar-amended soils, which is attributed to the enthalpy of adsorption that was endothermic in the case of soil and exothermic in the case of biochar-amended soil.
- The extent of CH_4 transport through soil (by accounting for adsorption) was two orders of magnitude lower (7.5×10^{-5} m^2/s) compared to all biochar-amended soils (1×10^{-3} - 2.5×10^{-3} m^2/s).

- The amendment of even a small quantity of biochar (2% by weight) to soil dramatically increased the CH_4 transport and adsorption within the cover material by at least one order of magnitude implying the significant impact of the addition of biochars to the soil.
- The physicochemical properties of biochar considerably impacted the CH_4 adsorption and transport properties of biochar-amended soil cover, implying the importance of prescreening biochars prior to their use for field applications.

The overall implications of this study indicate that amending cover soil with certain types of biochars can be a promising approach to promote the enhanced CH_4 adsorption and gas transport within the cover system, thereby resulting in better environment for potentially higher rates of methane oxidation.

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7. COMBINED ADSORPTION AND OXIDATION OF METHANE IN BIOCHAR-AMENDED SOILS DURING PREINCUBATION PERIOD

7.1 Introduction

Landfills have been ranked third among the top contributors of anthropogenic methane emissions in the US (USEPA 2012). The typical composition of landfill gas (LFG) comprise 50% CH_4 and 50% CO_2 by volume along with trace amounts of non-methane organic compounds (NMOCs). The Global Warming Potential of CH_4 is 28 over a period of 100 years (IPCC 2013) and thus, methane is a more powerful greenhouse gas compared to CO_2 with a higher radiative forcing (IPCC 2007). Engineered landfills are designed with gas extraction systems to collect the LFGs that are generated which is then diverted to a flaring station for energy generation. Though the gas extraction systems currently serve as a control in mitigating methane emissions from engineered landfills, the use of such systems in old/ abandoned landfills are not cost-effective to operate since the rates of CH_4 generation is comparatively lower than an active landfill. The landfill gases that are not captured by gas extractions systems tend to be emitted to the atmosphere as fugitive emissions. Engineered landfill cover systems can be employed either to complement the gas extraction systems or as a stand-alone passive technique in old/ abandoned landfills to address these fugitive CH_4 emissions (Sadasivam and Reddy, 2014).

Bio-chemical methane oxidation process occurs naturally in landfill covers due to the presence of methane oxidizing bacteria (MOB) which uses CH_4 as their sole carbon source to synthesize cellular carbon in the presence of oxygen (Reddy et al. 2014). To date, several studies have reflected on the importance of amending organic materials to enhance the microbial methane oxidation capacity in landfill cover systems (Scheutz et al. 2009, Sadasivam and Reddy, 2014).

Compost has been the most commonly used biocover material and due to its insufficient porosity, it was found to hinder the gas transport through cover systems with the formation of exopolymeric substances over time (Sadasivam and Reddy, 2014). In some studies, it was found that self-degradation of compost occurred if the material was not fully mature (i.e., having a high biological oxygen demand) and the cover becomes saturated generating anaerobic conditions which favors the methanogenesis process wherein, methane is generated (Barlaz et al. 2004). In order to design an efficient biocover system for the purpose of methane mitigation in landfills, a stable biocover material with sufficiently good porosity which can enhance methane adsorption capacity as well as favor the growth of methanotrophs and promote microbial methane oxidation process needs to be selected. One such material that could potentially enhance the methane mitigation in landfill cover system is biochar (Yaghoubi, 2011).

Biochar is a highly porous, organic material that is produced by subjecting plant-based biomass to pyrolysis/ gasification under limited oxygen environments (Lehmann & Joseph, 2009). The presence of micropores in biochars makes it highly preferable for gas adsorption purposes (Rouquerol et al. 1999). The methane dynamics in a landfill cover system is controlled by the soil micro-environmental conditions which can either favor the growth of methanogens under anoxic/anaerobic conditions or methanotrophs under oxic conditions (Dalal et al. 2008). Methanogens are responsible for the release of methane due to anaerobic degradation of organic matter while methanotrophs exist in their close proximity and use the methane generated as substrate and oxidize it to CO_2 and H_2O. Thus, the major limiting factor for the microbial methane oxidation process is the availability of oxygen (Dalal et al. 2008). Thus, amending biochar to soils containing a high fraction of clay content, as in the case of commonly used landfill cover soils can increase the aeration and thus limit the fraction of anoxic/anaerobic pore volume and subsequently

promote microbial methane oxidation by methanotrophs (Chan et al. 2007, Yanai et al. 2007). Biochars have found to be highly recalcitrant to decomposition in soils (Liang et al. 2008). Studies show that the stability of biochars in soil is at least one order of magnitude higher with a mean residence time of 1000 years as compared to the stability of other organic substances (Lehmann and Joseph, 2009).

The addition of woody biochars to cover soil was found to increase the shear strength of soil, thereby, increasing the safety factor for cover slope stability by almost two times (Sadasivam and Reddy, 2015a). This implies that the addition of biochars derived from gasification of hardwood is not expected to negatively impact the structural stability of the landfill covers. Recent studies show that biochar has high potential to enhance the combined adsorption, transport and oxidation of methane when used as a landfill cover soil amendment (Xie et al. 2013, Reddy et al. 2014). However, only one type of biochar produced by gasification of wood pellets was tested at 20% amendment ratio to landfill cover soil (by weight) in long-term column studies (Yaghoubi, 2011). To design an effective biochar-based landfill cover system, it is critical to understand the changes to the microbial methane oxidation capacity under varying levels of biochar amendment to soil, temperature and moisture conditions. Additionally, the physical-chemical properties of biochars are highly dependent upon the type of feedstock, production conditions and post-treatment processes such as screening or activation (Yargicoglu et al. 2015). Hence, it also becomes critical to analyze the effects of amending different types of biochars to cover soil.

Overall, the objectives of this study are to examine the effect of varying factors such as: (1) types of wood-derived biochar, (2) moisture within cover materials, (3) exposed temperature and, (4) biochar to soil amendment ratio on the mechanistic parameters that determine the rate of combined methane adsorption and bio-chemical oxidation in biochar-based cover systems.

Moreover, recent studies indicate that the addition of biochars to landfill cover soil was found to significantly increase the methane adsorption capacity of soil, implying that the process of adsorption plays a critical role in modeling the migration of methane through biochar-based landfill cover systems (Yaghoubi, 2011, Xie et al. 2013, Sadasivam and Reddy, 2015b). Hence, results from this study can help evaluate the extent of only adsorption which contributes to the overall methane mitigation processes (i.e., combined adsorption and microbial oxidation) in a biochar-based landfill cover system.

7.2 Materials and Methods

Four different types of commercially available biochars produced from waste wood were obtained from Chip Energy Inc. (Goodfield, Illinois) in 5-gallon buckets and stored in air-tight containers at room temperature (≈ 25°C). All the biochars were manufactured under limited presence of oxygen using an updraft gasifier at a temperature of about 500°C. The biochars that were obtained from the vendor were not subjected to any physical-chemical or biological modification and were used as such (As-is) in all the tests. The photographs and scanning electron microscopy (SEM) images of biochars (As-is) used in this study are published elsewhere (Sadasivam and Reddy, 2015b). CE-WP1 and CE-WP2 biochars were produced from pelleted hard wood approximately 6 months prior to testing. The only difference between both these biochars is that CE-WP1 contained a large fraction of ash materials (≈ 50% v/v) whereas, the fine ash fraction (< 2 mm diameter) was sieved as a post-treatment process in the case of CE-WP2. CE-AWP was also produced from pelleted hardwood (screened to eliminate ash fraction) but, it was obtained approximately four years prior to testing. CE-WC was produced from hardwood chips without ash particles approximately 6 months prior to testing that had a much higher particle size compared to

all the other biochars. Further details regarding the characterization of physical, chemical and surface properties of biochars used in this study are published elsewhere (Yargicoglu et al. 2015, Sadasivam and Reddy, 2015c).

The cover soil for the biochar amendment studies was obtained from the top 12 inches of an intermediate cover area in a DeKalb County, IL landfill. The cover soil was sieved using a 2-mm mesh and the fraction of soil passing the sieve was homogenized and stored in plastic bags at 4°C prior to usage. Cover soil was classified to be 'silty clay' type (USCS classification – CL) with 30.8% clay, 27.8% silt and 41.4% sand. Further details on the physical-chemical characterization of cover soil is published elsewhere (Sadasivam and Reddy, 2015a).

7.2.1 Pre-Incubation of Cover Soil

Sieved and homogenized landfill cover soil was loosely packed in an acrylic column with dimensions of 0.5 m in length and an inner diameter of 0.13 m. The landfill soil in the column was acclimated by passing air along with 5% CH_4, 5% CO_2 and 90% N_2 gas mix for a period of 45 days. During the acclimatization period, the soil column was moisturized periodically in order to avoid the formation of water-stressed environment which can in turn inhibit the growth of methanotrophs.

7.2.2 Batch Incubation Testing

The experimental design involved testing four types of biochars (CE-WP1, CE-WP2, CE-AWP and CE-WC) at four levels of biochar to soil amendment ratios (0, 2, 5 and 10% by weight) under two levels of moisture expressed as a percentage of the material's water holding capacity (WHC) (i.e., 25% and 75% WHC) and under four levels of temperature (5, 25, 35 and 45°C). All

tests were conducted in triplicate to account for the variability in experimental errors. A total of 384 tests were conducted in this study.

All the incubation tests were conducted using 125 ml clear, glass serum vials (Wheaton Glass, Milville, NJ). Measured amounts (by weight) of the acclimatized landfill cover soil and the biochars (As-Is) were placed inside the vials, mixed and homogenized to achieve the aforementioned amendment ratios such that total mass of the cover material adds up to 20g for each of the trials. Then, measured volumes of water were added to the cover materials inside the vials and then stirred using a spatula prior to sealing them tight with red butyl rubber stoppers (IV Packs, Houston, TX) and aluminum crimps. The headspace of the incubation chambers was then replaced with 12.5 ml of synthetic landfill gas comprising 50% CH_4 and 50% CO_2 gas mix in order to achieve a headspace concentration of 5% CH_4 v/v. The incubation chambers were then placed inside an oven that was pre-set to 35 and 45°C in order to test the effects of increasing temperatures on the rates of methane reduction in cover materials. For experiments conducted at room temperature (≈ 25°C), the incubation chambers were placed in enclosed cabinets to avoid the effects of light on microbial methane oxidation. For the tests conducted under low temperature (≈ 5°C), the incubation chambers were placed inside the cabinets of a refrigerator where entry of internal light was minimal.

Approximately, 1ml of headspace gas was sampled at various times using a BD 1 ml louver lock syringe and non-coring needle fitted with a two-way plastic stop-cock. The samples were directly injected into a SRI 9300B GC equipped with TCD detector and packed silica-gel column to analyze for the concentrations of CH_4 and CO_2. The GC was calibrated using ultra high purity methane standards (1, 5 and 25% CH_4 v/v obtained from Airgas) and a calibration curve was prepared to interpret the CH_4 concentrations of the samples. The calibration procedure was

repeated for every 50 - 60 samples analyzed in order to ensure sufficient quality control on the results. The sampling and monitoring of headspace CH_4 concentrations in the chambers were continued until the CH_4 concentration in the headspace was below 0.5% (v/v).

7.2.3 Methane Oxidation Modeling

Most methanotrophic bacteria are obligate methanotrophs and strict aerobes (Scheutz et al. 2009; He et al. 2011). The reaction kinetics associated with methane oxidation is shown in Eqn. (7-1) (Pawlowska and Stepniewski, 2006; Scheutz et al. 2009; Chiemchaisri et al. 2010):

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{heat} \quad \Delta G° = -780\ \text{kJ/mol}\ CH_4 \qquad (7\text{-}1)$$

In a landfill cover system, methane generated in the waste migrates upwards through the soil cover and is oxidized to CO_2 and H_2O via methanotroph-mediated biochemical oxidation. The methane oxidation kinetics is commonly described by the Michaelis-Menten equation, shown in Eqn. (7-2), which is widely used to model the single substrate enzyme kinetics:

$$r = \frac{V_{\max}[CH_4]}{K_m + [CH_4]} \qquad (7\text{-}2)$$

where r = CH_4 oxidation rate, V_{max} = Maximum CH_4 oxidation rate, and K_m = Michaelis-Menten (half-saturation) constant which relates to the affinity of microbial community to methane when '*r*' is half of V_{max}. To model the kinetics of methane oxidation, CH_4 is generally noted to be the substrate and methane monooxygenase (MMO) as the enzyme that acts as a catalyst for the biochemical oxidation reaction given in Eqn. (1). The Michaelis-Menten equation was derived based on the following assumptions: (1) the biochemical reaction is in equilibrium, which implies that the products formed are not converted back to the substrate; (2) the reaction is in steady-state, which implies that the rate of formation and breakdown of the intermediate, substrate-bound enzyme is constant; and, (3) the maximum rate of the reaction is obtained when all the catalytic

sites in the enzyme are saturated within the substrate (Segel, 1993). The Michaelis-Menten kinetic model implies that the rate of the reaction is dependent upon the initial concentration of the substrate as previously reported in studies conducted to determine the methane oxidation rates of various landfill cover materials (Abichou et al. 2011; Chanton et al. 2011).

7.2.4 Statistical Analyses

A multi-level factorial experimental design is used to determine the level of significance of main factors and interactions between different factors on the response variable (V_{max}). Statistical Analysis System (SAS) software will be used to determine the level of significance (p value) based on 95% confidence interval ($\alpha = 0.05$). The extent of influence of each factor (amendment ratio, temperature or MC) can be determined on methane oxidation rates of cover materials based on the resulting order of p value from the ANOVA table for each treatment either individually or in combination with other treatments. For example, a low p value of ≤ 0.0001 would indicate that the respective factor strongly influences the response variable.

7.3 Results

7.3.1 Batch Incubation Tests

The typical results showing the concentrations (% v/v) of headspace CH_4 and CO_2 at various sampling times within the duration of batch testing are shown in Figure 7-1. The results shown in Figure 7-1 correspond to the tests conducted on CE-WP2 amended soils at room temperature (≈25°C) under varying levels of moisture content. Similar trends were observed for the reduction in the levels of headspace CH_4 concentrations and increase in the headspace CO_2 concentrations for other biochar types and test conditions as well. However, the duration of tests (i.e., time taken

for headspace CH_4 concentration to drop below 0.5% v/v) and the rate at which the headspace CH_4 concentration levels reduced within the incubation chambers varied considerably among different test conditions.

In order to model the mechanism of methane mitigation occurring within the test chambers and to determine the kinetic parameters corresponding to the methane oxidation process (V_{max} and K_M), the Michaelis-Menten, single-substrate enzyme kinetic equation as shown in Eqn. (2) was used. The typical plots of methane oxidation rates, V ($\mu g\ CH_4\ g_{soil}^{-1}\ d^{-1}$) corresponding to the initial headspace CH_4 concentrations prior to each sampling event, CCH_4 (% v/v) are shown in Figure 7-2 for CE-WP2 amended soils under various test conditions. Based on the typical plots shown in Figure 7-2, it is evident that the methane oxidation rates are initially high and decreases as the initial headspace CH_4 concentrations decrease under all test conditions. In general, the plots of VCH_4 versus CCH_4 obtained for different biochar types under various test conditions indicate that the methane oxidation rate is strongly dependent upon the initial substrate (i.e., CH_4) concentration and conforms to the critical assumption of Michaelis-Menten kinetics. Linearized form of the typical plots (i.e., plots of 1/V versus 1/C) were used to determine the maximum methane oxidation rates (V_{max}) and the constants relating to the affinity of methane to MOB (K_M) for different test conditions.

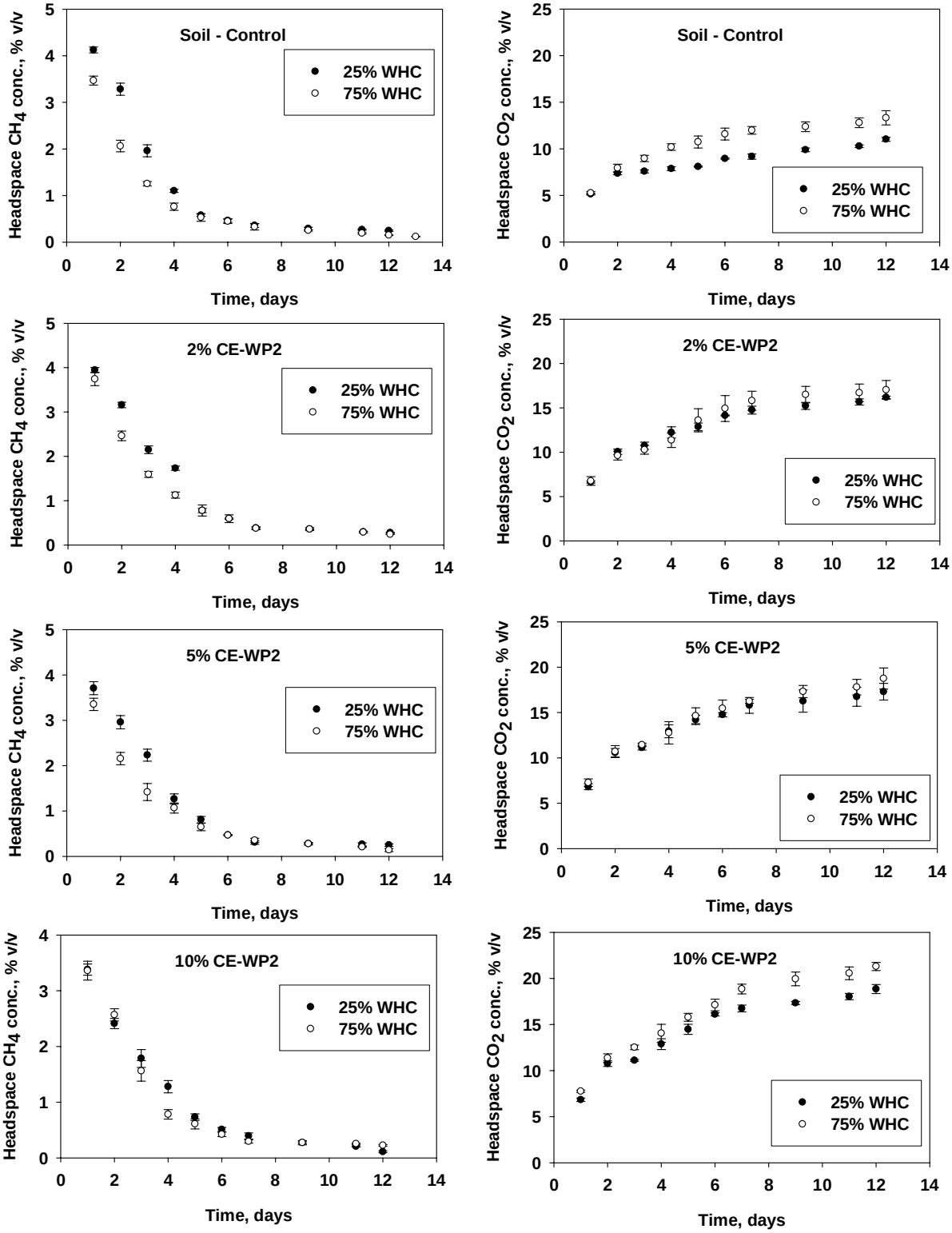

FIGURE 7-1: TYPICAL RESULTS FOR BATCH INCUBATION TESTS AT 25°C

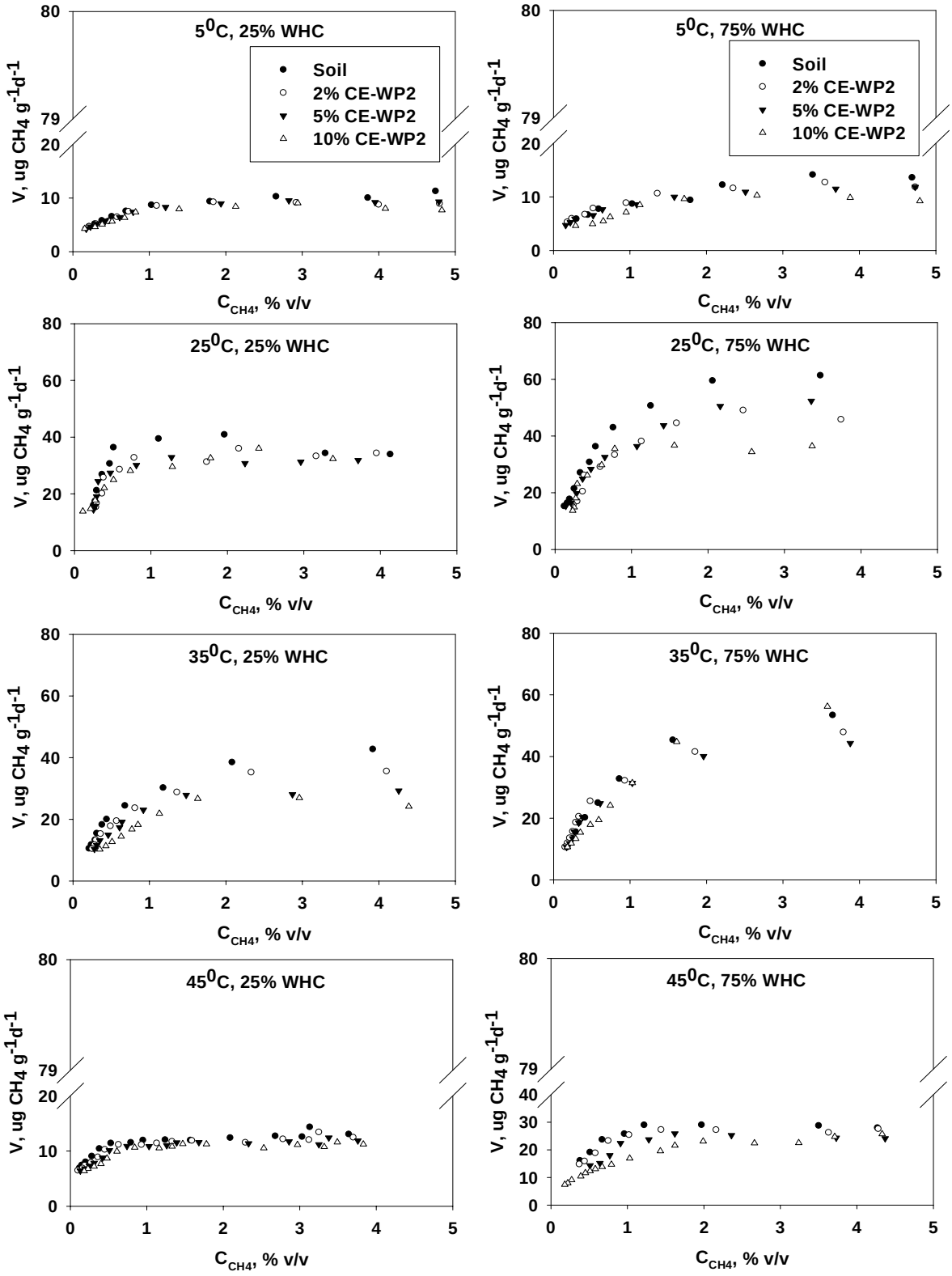

FIGURE 7-2: TYPICAL PLOTS FOR V_{CH4} VERSUS C_{CH4} FOR CE-WP2 AMENDED SOIL

7.3.2 Effect of Moisture and Temperature on V_{max} and K_M

Both, moisture and temperature were found to significantly ($p < 0.0001$) affect the V_{max} and K_M values of all the types of biochars tested. The V_{max} and K_M values of all the cover materials increased significantly ($p < 0.0001$) when the moisture was increased from 25% WHC to 75% WHC (Figures 7-3 to 7-10). The values of V_{max} and K_M were also found to significantly ($p < 0.0001$) increase with increasing temperature conditions up to 35°C. At 45°C, the values of both, V_{max} and K_M significantly ($p < 0.0001$) decreased. Among all the types of biochars tested, the lowest values of methane oxidation rates occurred at temperature and moisture conditions of 5°C and 25% WHC and the highest values of methane oxidation rates corresponded to a temperature of 35°C and 75% WHC.

7.3.3 Effect of Biochar Type and Amendment Ratio on V_{max} and K_M

The type and the amount of biochar added to landfill cover soil resulted in significant ($p < 0.0001$) differences in the V_{max} and K_M values obtained. The maximum methane oxidation rates for CE-WC (wood chips biochar) amended soils were the lowest and that of all CE-AWP (aged wood pellet biochar) amended soils were the highest. The V_{max} and K_M values of CE-WP1 (wood pellet biochar with ash) amended soils were significantly ($p < 0.0001$) lower than that of CE-WP2 (wood pellet biochar without ash) amended soils. The lowest values of K_M were obtained for all CE-WC amended soils. Amending biochar to cover soil significantly ($p < 0.0001$) decreased the V_{max} and the K_M values for irrespective of the type of biochar tested. It is further evident that the decrease in Vmax values compared to the soil control was more pronounced in the case of CE-WC (Figure 7-9) and CE-WP1 (Figure 7-5) amended soils.

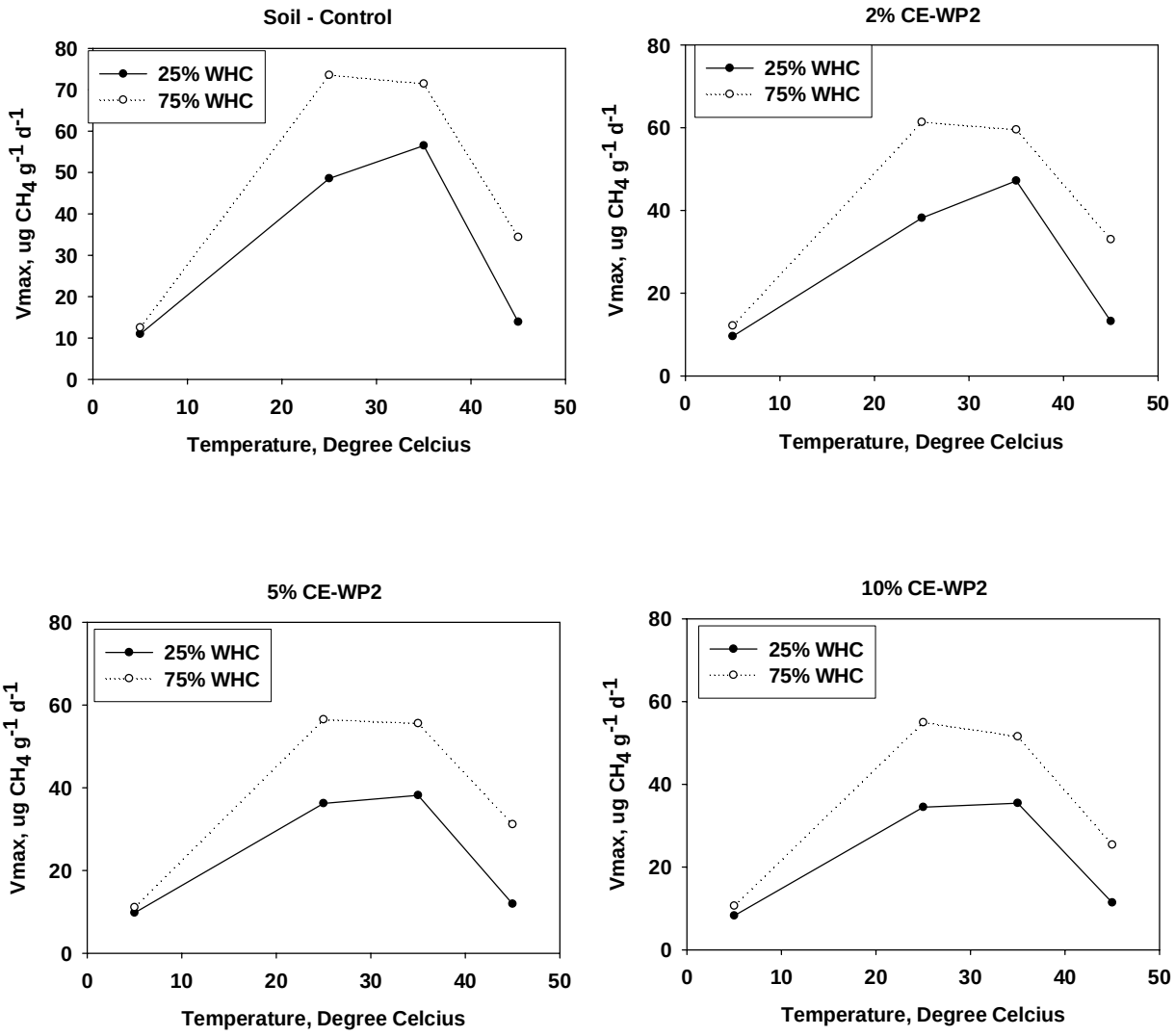

FIGURE 7-3: EFFECT OF TEMPERATURE AND MOISTURE ON V_{MAX} OF CW-WP2 AMENDED SOIL

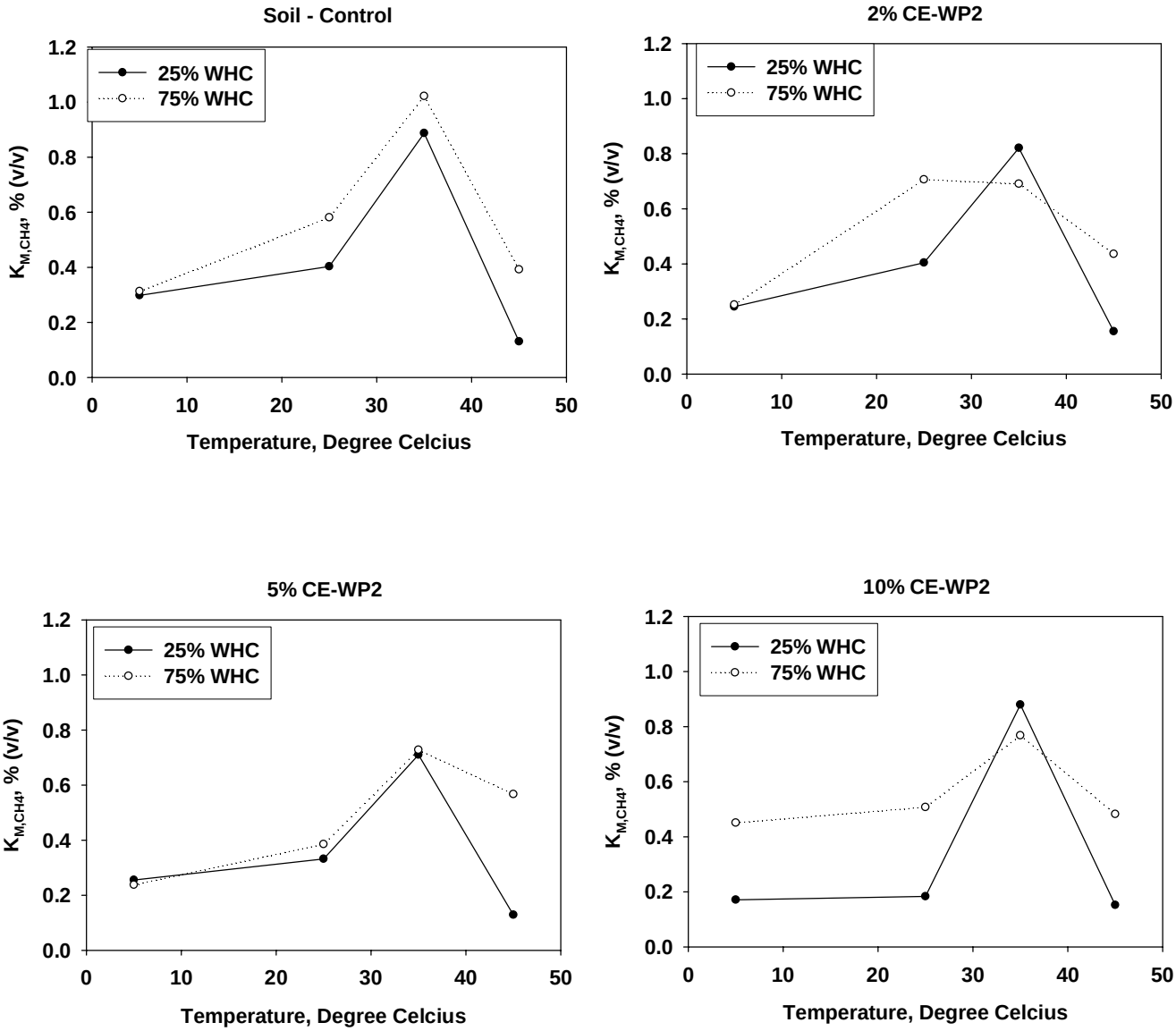

FIGURE 7-4: EFFECT OF TEMPERATURE AND MOISTURE ON K_M OF CE-WP2 AMENDED SOIL

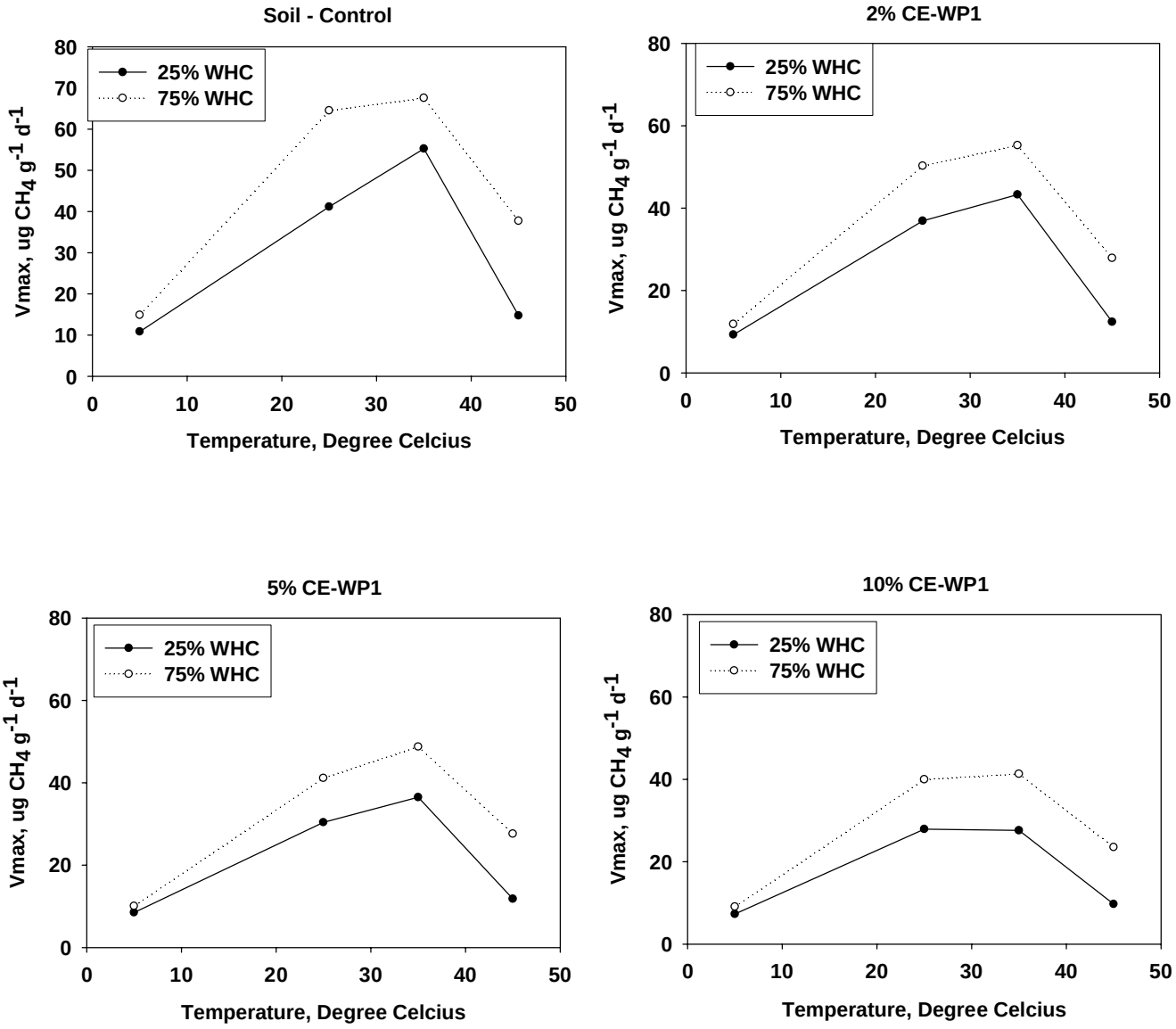

FIGURE 7-5: EFFECT OF TEMPERATURE AND MOISTURE ON V_{MAX} OF CE-WP1 AMENDED SOIL

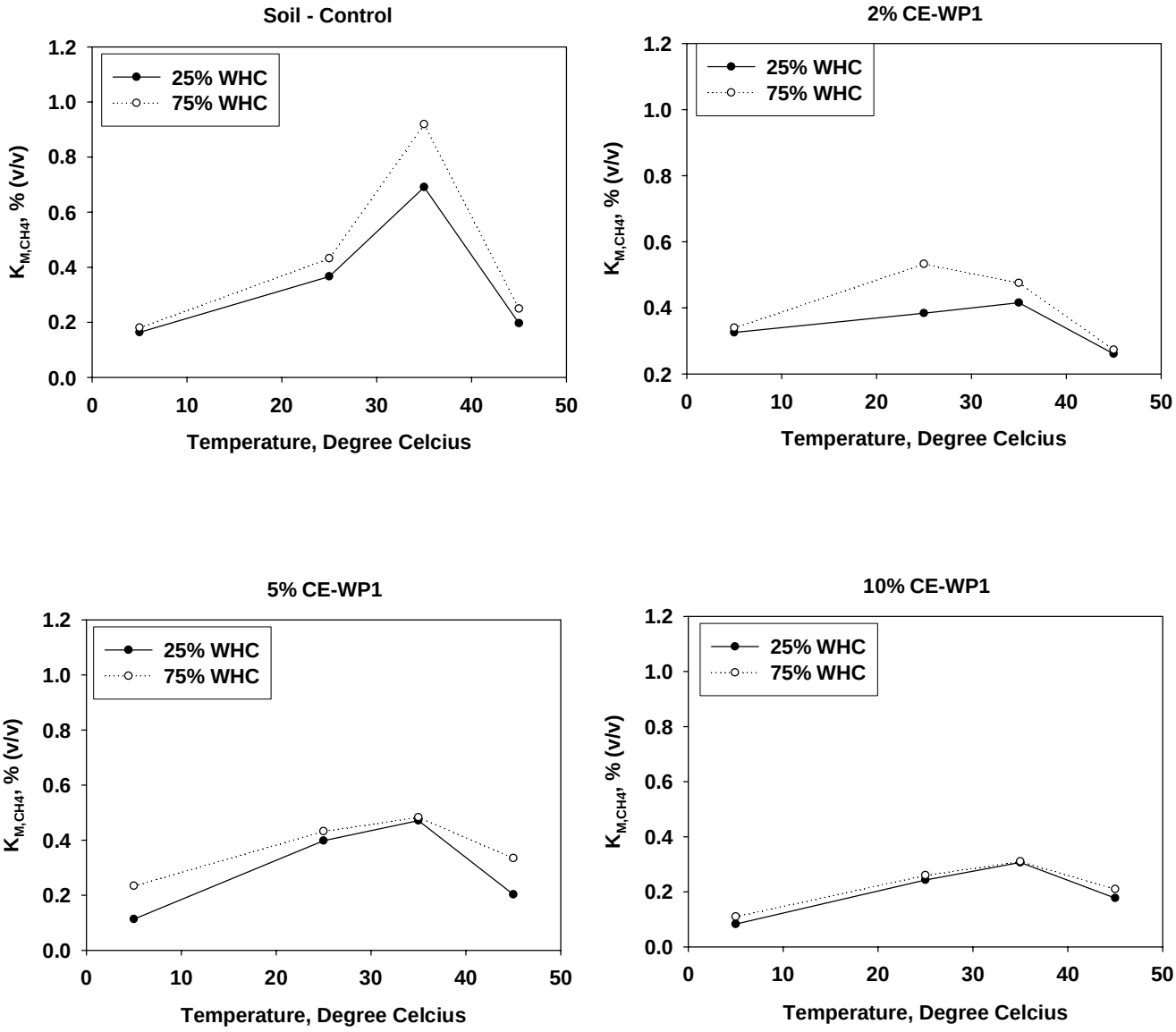

FIGURE 7-6: EFFECT OF TEMPERATURE AND MOISTURE ON K_M OF CE-WP1 AMENDED SOIL

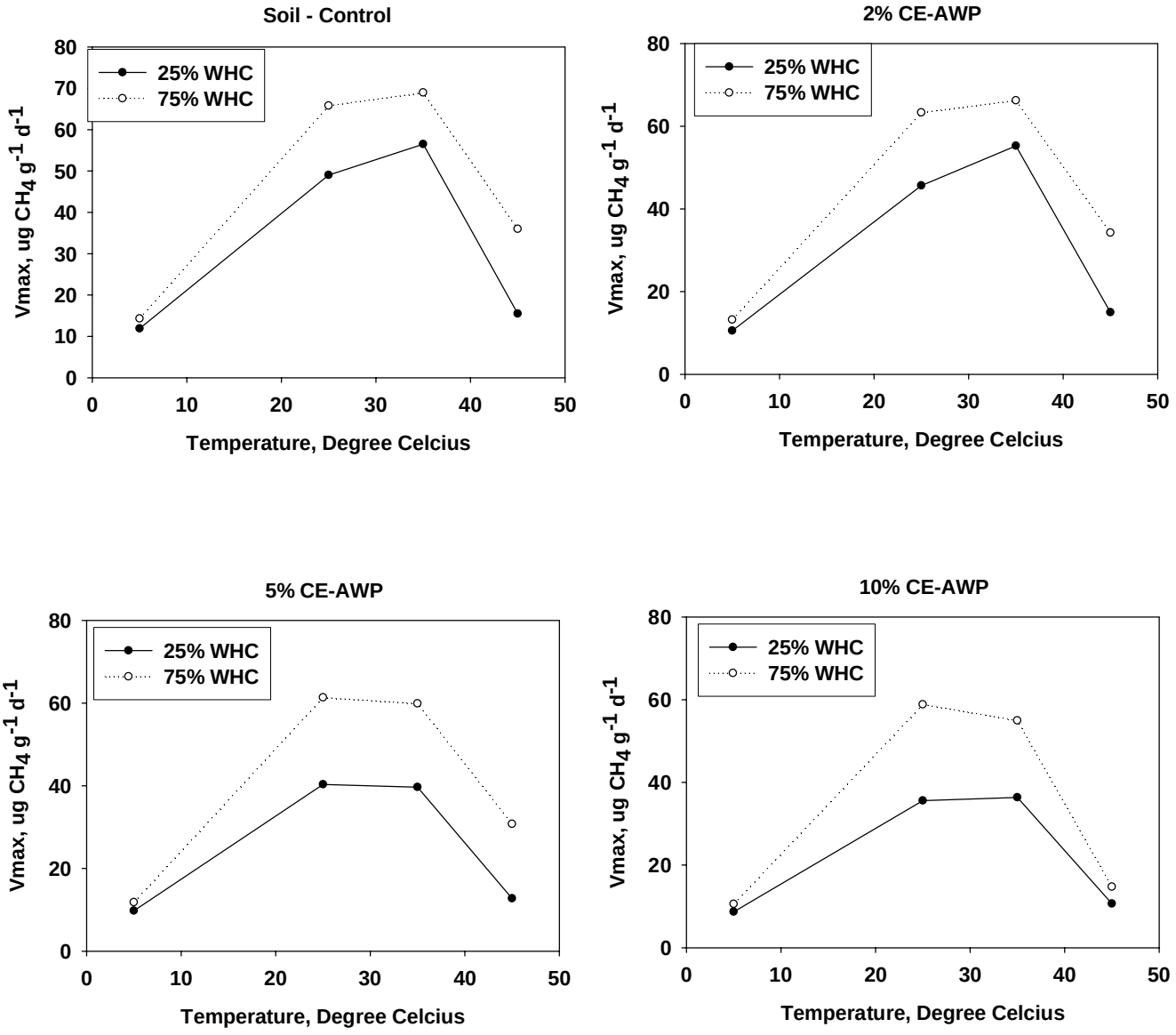

FIGURE 7-7: EFFECT OF TEMPERATURE AND MOISTURE ON V_{MAX} OF CE-AWP AMENDED SOIL

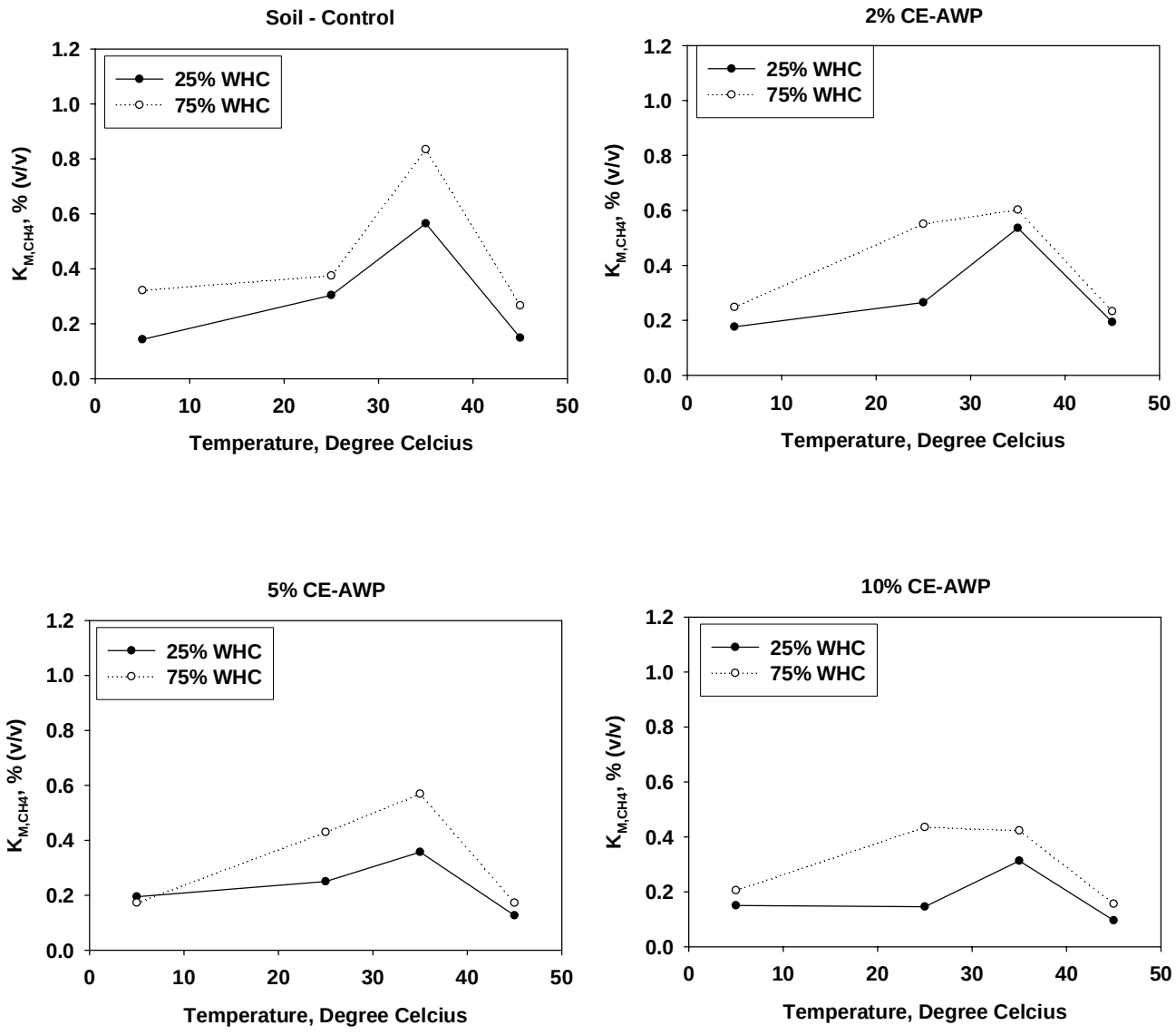

FIGURE 7-8: EFFECT OF TEMPERATURE AND MOISTURE ON K_M OF CE-AWP AMENDED SOIL

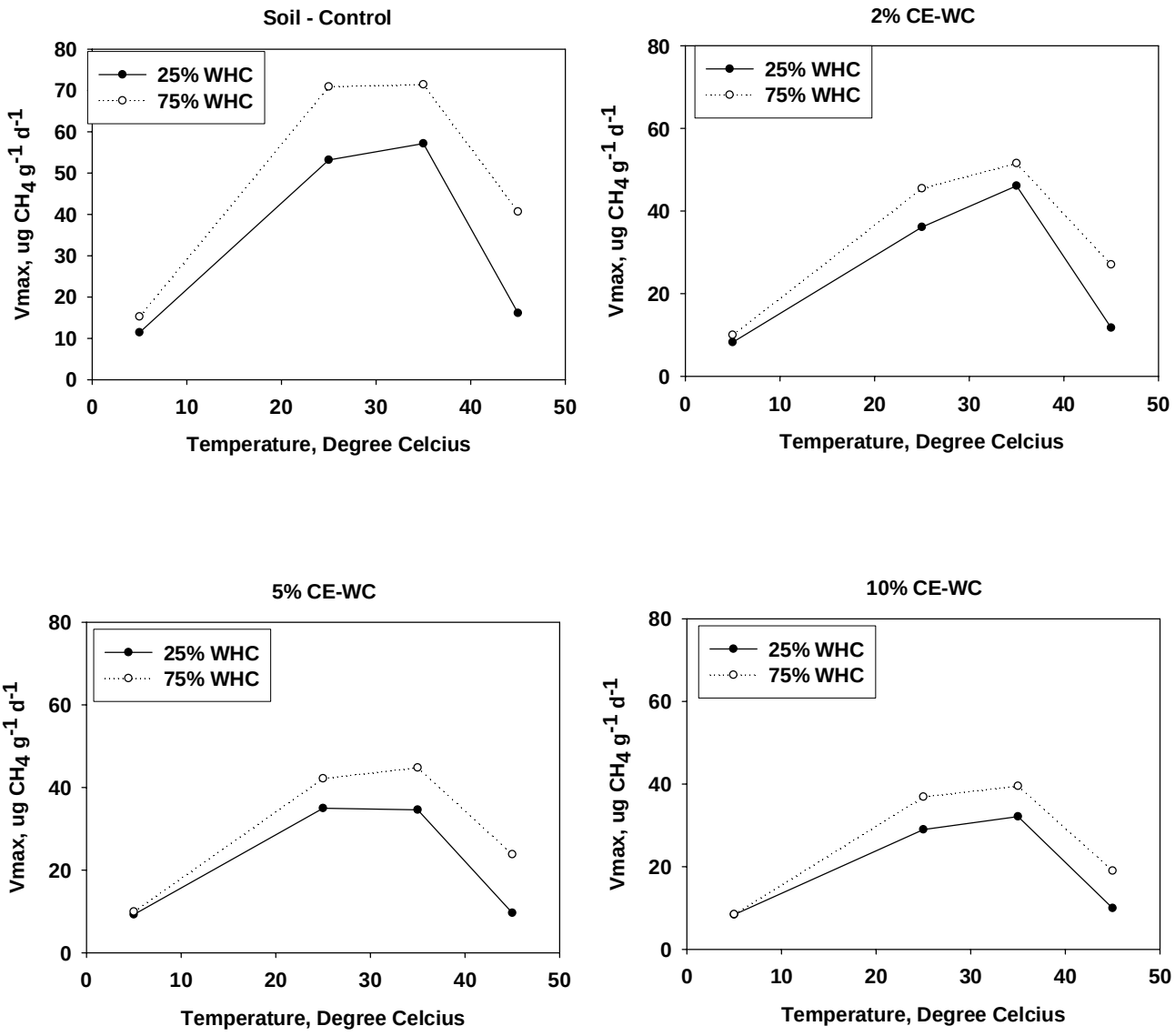

FIGURE 7-9: EFFECT OF TEMPERATURE AND MOISTURE ON V_{MAX} OF CE-WC AMENDED SOIL

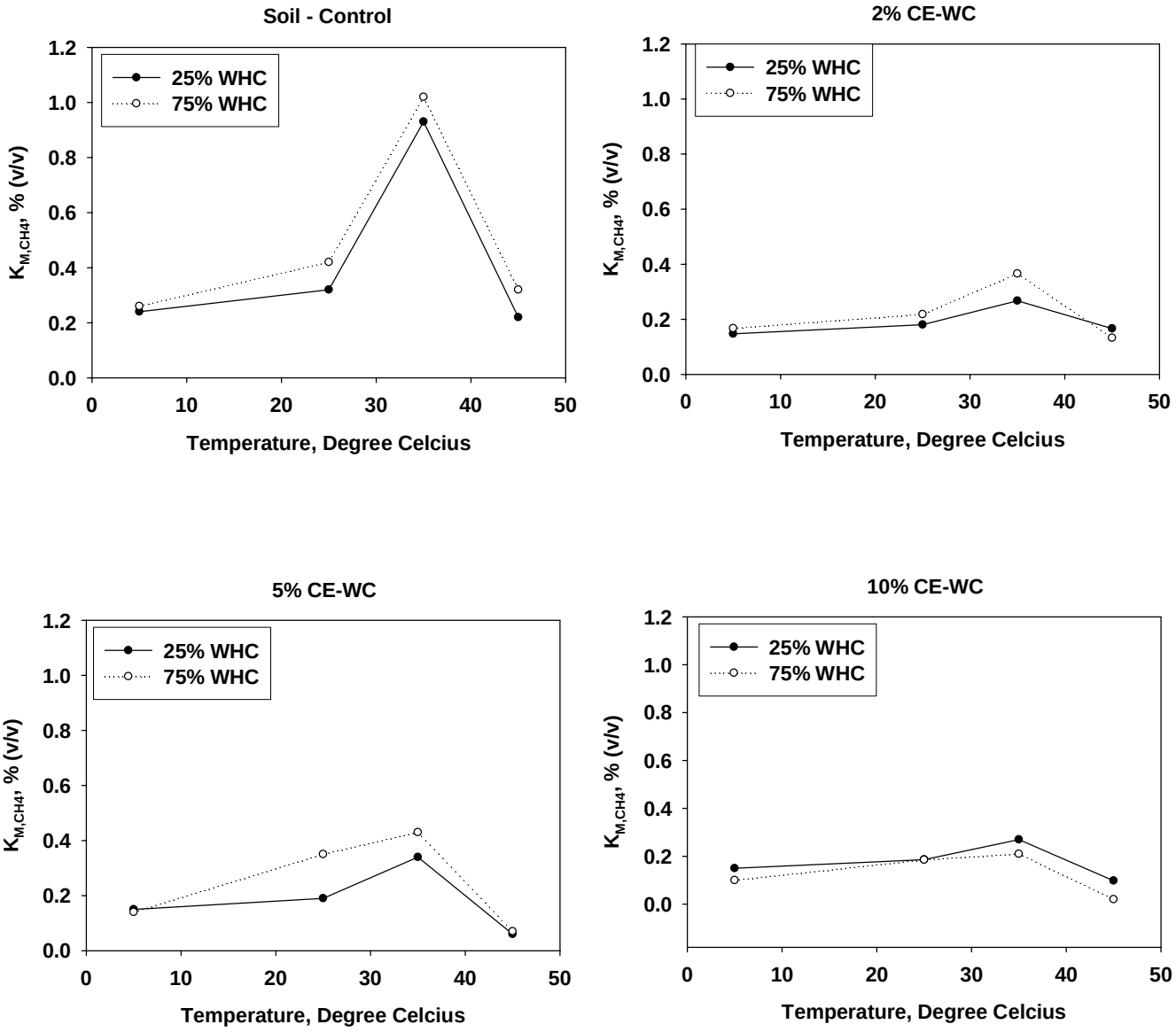

FIGURE 7-10: EFFECT OF TEMPERATURE AND MOISTURE ON K_M OF CE-WC AMENDED SOIL

7.4 Discussion

7.4.1 Effect of Moisture and Temperature on V_{max} and K_M

The optimum moisture content for all the cover materials tested in this study was found to be at 75% WHC (i.e., close to the field capacity) and the optimum range of temperature was between 25 - 35°C. The trends in the response of V_{max} to varying temperature and moisture conditions have been extensively studied for different types of landfill cover materials (Scheutz et al. 2009, Sadasivam and Reddy, 2014) and it was found that the maximum oxidation rates occurred when the moisture content was close to the field capacity and temperature was approximately 30°C (Spokas and Bogner, 2011). Overall, the results from this study conform to the reported ranges of optimum conditions required to achieve maximum methane oxidation rates in soils and biocover materials. The reduced rate of methane oxidation at low moisture content (25% WHC) in this study could be due to the microbial water stress generated under these conditions which can negatively affect the activity of methanotrophic communities. A steep drop in the values of V_{max} for all cover materials was consistently noted at a temperature of 45°C (i.e., beyond the optimum temperature of ≈35°C). It was reported that the methanotrophic activity in landfill cover soils were completely inhibited when the temperature increased to 50°C. On the other hand, low temperatures of around 2°C was found to sustain a certain level of methanotrophic activity implying that methane oxidation could still occur during the winter months and reduce the methane emissions from landfills (Scheutz and Kjeldsen, 2004).

The maximum V_{max} obtained for the landfill cover soil in this study (73.5 μg CH_4 g^{-1} d^{-1}) appears to be at the low end of the reported range (48 – 2500 μg CH_4 g^{-1} d^{-1}) for V_{max} values of landfill cover soils (Scheutz et al. 2009). In another study, it was found that the pre-incubating landfill cover soil with 50 ml L^{-1} CH_4 at field capacity water content for a period of 60 days allowed

for the quantification of maximum methane oxidation rates in batch incubation testing (Spokas and Bogner, 2011). The landfill cover soil in this study was pre-incubated only for a period of 45 days at field-collected moisture contents which could be one of the possible reasons for the low V_{max} value obtained as compared to those values reported in the literature.

The K_M values for methane oxidation in landfill cover soil (control) was found to range between 1000 – 10,300 ppmv (i.e., 0.1 – 1% v/v) which also conformed to the low end of the range of values reported (1000 – 25, 000) ppmv in literature (Scheutz et al. 2009). The trends in both, V_{max} and K_M can be used to assess the dominant mechanism controlling the methane oxidation within the landfill cover system. Previously, studies have shown that V_{max} and K_M values can be considerably affected by the type of methanotrophic community that is dominant within the cover system which, in turn, is controlled by the extent of methane and oxygen available within the system (Scheutz et al. 2009). Overall, kinetics of methane oxidation that resulted in high V_{max} (i.e., methanotrophic activity) and low methane affinity (i.e., high K_M values) indicated that the aerobic bacterial community was dominant under these conditions as expected to occur within the upper layers (oxic zone) of the landfill cover system (Xie et al. 2013, Reddy et al. 2014). The highest value of K_M (i.e., lowest affinity of microbes to CH_4) in the soil control corresponding to 10, 300 ppmv (i.e., 0.46 mol m^{-3}) occurred under the optimum conditions which resulted in the highest rate for methane oxidation (Figure 7-4). Thus, the methane oxidation rates in soil control was not found to be limited by the availability of oxygen within the incubation chambers.

7.4.2 Effect of Biochar Type and Amendment Ratio on V_{max} and K_M

The addition of biochar to landfill cover soil was found to significantly ($p < 0.0001$) inhibit the methane oxidation rates under all test conditions, irrespective of the type of biochar added.

From Figure 7-1, it is evident that amending biochar to soil considerably increased CO_2 production within the headspace of the incubation chambers. Also, the amount of CO_2 generated within the test chambers increased with increasing amounts of biochar amended to soil (Figure 7-1). The extent of CO_2 production was observed to increase with the addition of moisture to the cover materials (Figure 7-1). This trend in the production of CO_2 within the incubation chambers was consistent for all the types of biochars tested and under different levels of temperature. Several studies have reported increased levels of soil respiration resulting in production of CO_2 with the addition of biochars, especially during the initial stages of amendment (Hamer et al. 2004, Hilscher et al. 2009, Spokas and Reicosky, 2009, Novak et al. 2010, Major et al. 2010, Yu et al. 2013). In a study conducted by Spokas and Reicosky (2013), it was found that among sixteen different types of biochars tested, the wood pellet biochar obtained from the same vendor that supplied the biochar tested in this study (Chip Energy Inc.) stimulated significantly higher rates of CO_2 production when amended to landfill cover soil. Biochars were reported to increase the mineralization rates of native soil organic carbon by providing mineralizable (i.e., labile) organic carbon and micronutrients within a short period of time thereby enhancing the soil respiration rates (Yu et al. 2013). During the initial period of incubation, this priming effect on the soil can result in the depletion of oxygen within the system due to excessive heterotrophic bacterial activity, thereby, promoting competition between bacterial communities for the use of oxygen. In the pre-incubated landfill cover soils used in this study, where methanotrophs are expected to be abundant prior to the addition of biochars, the aforementioned priming effect could have possibly resulted in inhibiting the methane oxidation rates, with higher rates of inhibition noted at increased levels of biochar amendment ratios.

The extent of inhibition of methane oxidation rates was found to be the least when aged wood pellet (CE-AWP) biochar was added to soil (Figure 7-7). Studies have found that the extent of thermal alteration that the biomass undergoes during charring was reported to have significant effects on the rates of biochar decomposition. Wood-derived biochars that were subjected to lower treatment temperatures (< 200°C) were found to undergo higher levels of mineralization due to low amounts of aryl C (Hamer et al. 2004). For biochars, the molar H:C ratios can serve as indicators to represent the degree of carbonization with lower ratios indicating higher levels of complete carbonization resulting in lesser labile C. Detailed physical-chemical characterization of the biochars tested in this study indicated that the molar H:C ratio of CE-AWP biochar (0.28) was approximately half as much as that of CE-WP1 (0.63) and CE-WP2 (0.61) biochars (Yargicoglu et al. 2015) implying that the CE-AWP biochar had a much lower potential to undergo decomposition compared to other biochars. This implies that the competition between bacterial communities for oxygen would be lower due to lower respiration by other heterotrophic bacteria, thereby, favoring increased methanotrophic methane oxidation to occur within the CE-AWP amended soil. In one study, it was noted that the enhanced respiration of soil resulting from addition of fresh biochar (Macademia nut shell subjected to fast pyrolysis) consequently suppressed the methane oxidation rates by about 60% (Spokas, 2013). In the same study it was observed that hardwood biochar subjected to weathering under room temperature within an enclosed container for about 3 years resulted in the lowest amount of inhibition on methane oxidation activity. The reason for this was attributed to the significantly lesser amounts of microbial inhibitors such as organic compounds on the weathered (i.e., aged) biochar as compared to the fresh biochars. Inhibition in soil microbial activity was reported to occur due to the presence of sorbed organic compounds such as phenols (Major et al. 2009), and other organic compounds

such as furan, ethylene, acetylene, pyridine and furfurals (Spokas, 2013). However, further microbial evaluations (pPCR analysis) of the biochar-amended soil samples need to be conducted to validate the aforementioned possibilities for lower inhibition of methanotrophic activity in CE-AWP biochar soil.

The inhibition of methane oxidation rates in CE-WP1 (biochar with ash) amended soils were more pronounced as compared to CE-WP2 (biochar without ash) amended soils. Physical characterization of the tested biochars (Yargicoglu et al. 2015) indicated that the average particle size for CE-WP1 biochar was much smaller (1.13 mm) compared to that of CE-WP2 biochar (3.15 mm) due to the presence of higher ash fractions. This in turn resulted in higher surface area (≈0.4 m^2 g^{-1}) and porosity (≈ 50%) for CE-WP1 biochar compared to that of CE-WP2 biochar (surface area ≈ 0.1 m^2 g^{-1} and porosity ≈ 40%). Previous studies have reported that the sorption of potential inhibitors of microbial activity (for ex: catechol) from the soil onto biochars were higher is ash-rich chars, thereby, rendering the growth inhibiting compounds unavailable for microbes which resulted in increased microbial growth and higher rates of soil respiration (Lehmann et al. 2011). The potential for this phenomenon to have occurred in CE-WP1 amended soils is higher than CE-WP2 amended soils due to the increased surface area, porosity and sorption capacity of CE-WP1 amended soils (Sadasivam and Reddy, 2015b). Greater microbial abundance and higher respiration rates within the system meant that the competition between microbial communities for oxygen was also higher. Hence, the possibility of oxygen limiting conditions occurring within the headspace of incubation chambers containing CE-WP1 amended soils could have been higher compared to that of CE-WP2 amended soils thereby, negatively impacting the methane oxidation rates of CE-WP1 amended soils. However, further analysis of microbial assays via advanced

quantitation techniques that target the *pmoA* gene abundance is highly recommended to validate the explanation behind higher inhibition of methane oxidation rates in CE-WP1 amended soils.

CE-WC amended soils exhibited the highest level of inhibition on the methane oxidation rates among all the biochars tested (Figure 7-9). The reason for this could have been the amount of biochar that was added to the soil. The amendment percentages were on the basis of weight and CE-WC biochars had the lowest density (0.38 g cm^{-3}) compared to all the other CE- biochars (0.5 – 0.6 g cm^{-3}) (Sadasivam and Reddy, 2015c), thereby, necessitating higher amounts of CE-WC biochar (by weight) to be mixed with the soil in the incubation chambers. This could have possibly resulted in the highest level of soil respiration and competition between methanotrophs and other heterotrophic bacteria for oxygen within the headspace of the CE-WC amended soils, thereby, resulting in greater levels of inhibition in the methane oxidation rates.

7.4.3 Contribution of CH_4 Adsorption to Overall CH_4 Mitigation

Based on the results from another study conducted to quantify the extent of methane mitigation from solely the process of adsorption (Sadasivam and Reddy, 2015b), it is possible to estimate the expected proportion of the headspace methane that is adsorbed onto the biochar-amended soils immediately upon exposure which is critical information to model the combined processes that contribute to the overall methane mitigation in biochar-amended systems. The process of methane adsorption onto biochars was also found to be a dominant mechanism that affects the migration of methane through the landfill cover systems in addition to diffusion and biochemical oxidation (Xie et al. 2013). In order to effectively model the transport of methane through biochar-based landfill cover systems, it is critical to ascertain the amount of exposed methane concentrations that is adsorbed onto the porous structure of biochars within the system

and which could possibly be accessed by the methanotrophs more conveniently as opposed to the methane that is dynamically moving within the system, especially the advective transport controlled by the physical nature of the cover system.

Table 7-1 shows the estimated proportions of methane that is adsorbed onto different types and amendments of biochars shortly upon exposure within the incubation chambers as opposed to the proportion of methane that is expected to undergo combined process of adsorption and oxidation. The estimated amount of exposed methane that is adsorbed onto the biochar-amended soils consistently increased with increasing amendment percentages indicating the importance of including the mechanism of sorption into modeling the transport methane through biochar-based landfill cover systems. The amount of methane estimated to be adsorbed within the incubation chambers was much higher in CE-WP1 amended soils due to its increased porosity and surface area as discussed in the previous section. Among all the biochar-amended soils, the lowest level of contribution to the overall reduction in the headspace methane concentration due to adsorption was noted for the CE-WC amended soils and the reason for this has been discussed elsewhere (Sadasivam and Reddy, 2015b). Some reduction in the amount of methane adsorbed onto biochar-amended soils occurred at higher moisture content. However, it is to be noted that the estimated values presented in Table 7-1 are based on batch testing of biochar-amended soils and could result in an overestimation of the extent of methane adsorption.

TABLE 7-1: PERCENTAGE REDUCTION IN CH_4 VIA ADSORPTION VERSUS COMBINED ADSORPTION AND OXIDATION AT THE END OF FIRST DAY OF INCUBATION

Biochar Amendment Percentage	Only Adsorption (25% WHC)	Adsorption & Oxidation (25% WHC)	Only Adsorption (75% WHC)	Adsorption & Oxidation (75% WHC)
	CE-WP2 Amended soil (25^0C & 5% CH_4 v/v)			
0	0.8	99.2	0.6	99.4
2	4.2	95.8	2.8	97.2
5	10.2	89.8	7.4	92.6
10	16.6	83.4	15	85
CE-WP1 Amended soil (25^0C & 5% CH_4 v/v)				
0	0.8	99.2	0.6	99.4
2	5.8	94.2	5	95
5	14.8	85.2	10.6	89.4
10	21	79	15.8	84.2
CE-AWP Amended soil (25^0C & 5% CH_4 v/v)				
0	0.8	99.2	0.6	99.4
2	4	96	3.4	96.6
5	9	91	7.2	92.8
10	14.6	85.4	10.2	89.8
CE-WC Amended soil (25^0C & 5% CH_4 v/v)				
0	0.8	99.2	0.6	99.4
2	3.4	96.6	3	97
5	7.4	92.6	6.2	93.8
10	12.8	87.2	8.4	91.6

7.5 Conclusion

This study evaluated the potential use of wood-derived biochars as a biocover material to address the rising levels of methane emissions from landfills. In summary, batch incubation tests were conducted to evaluate the effects of moisture, temperature, biochar amendment percentages and biochar types on the methane oxidation rates of landfill cover soil. Based on the findings reported in this study, the following conclusions can be derived:

- The amendment of biochars to soil significantly inhibited the methane oxidation rates irrespective of biochar type, amendment ratio and the test conditions (i.e., moisture and temperature).
- The extent of inhibition in the methane oxidation rates were significantly different for different biochar types and consistently increased with increasing levels of biochar-amendment percentages.
- The optimum conditions for methane oxidation in soil control and different biochar-amended soils occurred at a temperature range of 25 - 35°C and at a moisture content close to the water holding capacity of the cover materials (75% WHC).
- The addition of biochar to soil resulted in increased levels of CO_2 production within the test chambers because of enhanced soil respiration which was also previously reported by several studies.
- The extent of overall methane mitigation within the test chambers that was achieved by rapid adsorption process as opposed to the combined adsorption and oxidation process was determined and this could aid the modeling of methane migration through biochar-based cover systems.

Overall, mixed trends have been reported in literature for the effects of biochar amendment to soil and the resulting response to methane oxidation rates. Based on long-term column oxidation tests conducted in a previous study by Yaghoubi (2011), it was found that amending biochar derived from hardwood pellets to landfill cover soil (20% by weight) significantly enhanced the methane oxidation rates of the soil. However, it has to be noted that in the study by Yaghoubi (2011), the batch kinetic tests were conducted on biochar-amended soil that was incubated within the column oxidation test set-up for about three months until steady state conditions were achieved

and the acclimation of methanotrophs under these conditions could have been more dominant resulting in much higher methane oxidation rates compared to the rates reported in this study. In this study, only the landfill cover soil was pre-incubated to induce methanotrophic activity prior to testing and the biochars (As-Is) were added to the soil just before the start of testing. The results from this study points to the importance of pre-incubating the soil with biochar for sufficient amount of time under conditions that are expected to occur in landfill covers (i.e., low supply rates of methane while maintaining atmospheric concentrations of oxygen within the headspace) prior to estimating the maximum methane oxidation capacity for biochar-based cover systems.

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8. DESIGN AND SUSTAINABILITY ASSESSMENT OF SOIL AND BIOCHAR-BASED FINAL COVER SYSTEMS

8.1 Introduction

Landfilling is the most widely accepted technology for MSW management in the US with approximately 54% of the generated wastes disposed of in landfills (USEPA 2012). LFG is produced due to anaerobic bio-degradation of the organic waste fraction and, the emissions of which pose a major threat to the environment since it can adversely affect the global climatic patterns. LFG is primarily composed of CH_4 and CO_2 (50 % v/v) in addition to trace levels of NMOCs (Non-Methane Organic Compounds). CH_4 and CO_2 are major greenhouse gases with high potential to absorb and re-radiate the harmful IR rays that are reflected from the earth's surface causing global warming. The global warming potential (GWP) of methane is 28 for over a period of 100 years, which means that the capacity of CH_4 to absorb heat (IR radiation) is 28 times more than that of CO_2 (IPCC 2013). Among all the powerful, long-lived greenhouse gases, CH_4 alone contributes to 17% of the total radiative forcing (Shine et al. 1990). Since CH_4 plays a vital role in global climate change and, landfills are deemed as the thirst largest contributors to anthropogenic methane emissions, it is of utmost importance to develop cost-effective and sustainable technologies to minimize the rising levels of CH_4 emissions from landfills.

Landfill methane emissions to the atmosphere are controlled by engineered LFG extraction and recovery systems, the thickness and composition of cover soils, and seasonal methane oxidation in cover soils. Cover systems can be designed as soil covers only (with differing designs for daily, intermediate and final covers); the use of geomembrane as part of a composite final cover design (currently-approved final cover under Subtitle D of RCRA in most states); or the use of

alternative materials as part of approved designs (e.g., alternative daily covers). On the other hand, bio-based cover systems to optimize methane oxidation and reduce emissions have been researched in Europe, U.S. and Canada and indicate promise for future full-scale designs (Powelson et al. 2006; Stern et al. 2007; Bogner et al. 2010; Scheutz et al. 2011; Roncato et al. 2012; Hrad et al. 2012). The choice of cover materials, design specifications and seasonal variations play a critical role in achieving optimum methane oxidation in landfill covers. As generally designed, bio-based cover systems include a coarse-grained lower gas distribution layer (e.g. coarse aggregate) and an upper layer designed to optimize seasonal oxidation (e.g., mature compost). Recent studies show that biochar could be used as a cover soil amendment to induce higher rates of methane oxidation by promoting the growth and activity of methanotrophs while simultaneously increasing the methane adsorption and the gas transport within the simulated cover system (Yaghoubi 2011; Xie et al. 2013; Reddy et al. 2014).

If biochar-based cover systems are to be routinely implemented in the future, there is a need to compare the sustainability (i.e., the environmental, economic and social impacts) of the biochar-based cover system to conventional soil covers. The objectives of this study were to: (1) design a biochar-based cover and a soil cover system for a hypothetical landfill in Northeastern IL and compare the environmental, economic and social sustainability of both systems using a widely accepted life cycle analysis (LCA) tool such as SimaPro, (2) conduct uncertainty analysis using SimaPro to evaluate the effect of varying methane oxidation rates of the cover systems on the environmental sustainability and, (3) design a cost-effective and sustainable biochar-based final cover system capable of achieving complete oxidation of methane for field application in Northeastern IL.

8.2 Background

Repercussions of climate change associated with continually rising levels of atmospheric greenhouse gas (GHG) concentrations are evident from the reported global warming of 0.85°C and sea level rise by 0.19m over the past century in addition to the melting of Arctic sea-ice at the rate of 3.5 – 4.1% per decade (IPCC 2014). The projected rise in the mean global surface temperature of 0.3 – 0.7°C over the next couple of decades appear to be inevitable at the current rate of GHG emissions and is likely to cause extreme weather conditions such as frequent and prolonged heat waves and historical precipitation in the coming years (IPCC 2014). According to IPCC experts, if the warming exceeds a level of 2°C, the consequences of climate change on a global-scale is expected to be irreversible and this calls for effective mitigation strategies and strict regulatory policies to ensure that the future cumulative GHG emissions are held below 3650 $GtCO_2$ and over half of this value has already been released into the atmosphere by 2011. The American Clean Energy and Security Act was passed in June 2009 with the goal of achieving an overall reduction in GHG emissions by 83% relative to the 2005 levels prior to 2050 (U.S. EPA 2010). Among the most popular GHG mitigation technologies researched, the use of biochar with carbon sequestration was proposed to effectively address this challenge at both, a local as well as global-scale (Wright et al. 2014; Corner and Pidgeon 2010).

The Biochar is a carbonaceous, highly porous material generated as a byproduct in the process of producing bio-energy (bio-oil or syngas) from raw biomass (discarded wood, manure or agricultural crop residues) through pyrolysis or gasification (Lehmann and Joseph 2009). The thermochemical conversion of raw biomass to biochar through incomplete combustion (i.e., low oxygen environment) retains 50% of carbon in biochar (i.e., residual byproduct) while the rest is converted into bio-energy products (Matovic 2011). About 80% of the carbon that is retained in

the biochar is expected to be sequestered in its highly stabilized form (i.e., without undergoing decomposition) for over 1000 years while the remaining fraction is released into the atmosphere via biological respiration within the first few years of application as a soil amendment (Roberts et al. 2010). Biochar has recently garnered special interest due to its inherent ability to store atmospheric carbon, while enhancing crop growth and yield in addition to reducing the need for soil fertilization, which, on a local as well as global scale, has been found to offset the adverse impacts of increasing greenhouse gas emissions (Xie et al. 2015). The normal carbon sequestration by photosynthesis is a 'carbon neutral' process wherein, the net carbon withdrawal from the atmosphere is zero. On the other hand, the addition of biochar to soil lowers the carbon emissions from the soil biomass resulting in a net carbon withdrawal of 20% from the atmosphere which makes it a 'carbon negative' process (Lehmann 2007). At a global scale, the continued use of biochar as a soil amendment is projected to have a potential for reducing the annual net emissions of greenhouse gases by about 1.8 Pg CO_2-C equivalent, which attributes to approximately 12% of the anthropogenic CO_2-C equivalent. Over the century, this is predicted to offset the global CO_2-C emissions equivalent of 130 Pg without jeopardizing the food security and the environment (Woolf et al. 2009).

Owing to the high surface area and porosity of biochars, they have been widely used in environmental remediation as an adsorbent for both organic and inorganic contaminants (Xie et el. 2014; Mohan et al. 2014). In the U.S., it is estimated that nearly 124.7 million tons of unused forest residues are generated annually and the expansion of current market potential for biochars for large-scale applications can promote reuse of waste, production of bio-energy and sequestration of atmospheric carbon (Roberts et al. 2010). Recent studies show that the use of hardwood-derived biochars as a landfill cover soil amendment can promote the adsorption of methane while

simultaneously increasing the growth and activity of methane oxidizing bacteria (MOB), which in turn lowers the methane emissions from the simulated landfill cover system (Reddy et al. 2014). Moreover, the addition of hardwood biochars to landfill cover soil increased the shear strength and the stability of landfill cover slopes which reinforces their technical feasibility as alternative cover materials from a design perspective (Sadasivam and Reddy 2015). In order to fully understand the potential impacts of using biochar-based cover systems as opposed to the conventional soil cover systems in landfills, it is critical to perform a sustainability analysis to evaluate the environmental, economic and social impacts by accounting for the entire life cycle of various materials and processes involved.

The essence of sustainability can be captured by the "triple bottom line" approach which encompasses the environmental, economic as well as social impacts of various materials and processes throughout its life cycle (i.e., material acquisition, material production, system construction/use and demolition/disposal). There are several commercially available LCA tools to quantify the sustainability metrics, among which, SimaPro and GaBi are most globally recognized and extensively adopted for modeling by LCA practitioners (Hermann and Moltesen 2015). Based on the critical review of 42 commercially available LCA software tools, SimaPro was deemed the most advanced in terms of in-built databases and impact assessment methods which offered relatively quick results with utmost ease and flexibility for viewing the outputs (Zamagni et al. 2008). A comparative LCA study indicated that the impact assessment results obtained from SimaPro and GaBi showed considerable differences mainly due to the variations and errors noted at the inventory level for the different databases of these software tools (Hermann and Moltesen 2015). In order to provide the policy-makers with the most reliable data for decision-support and regulatory reforms, it is critical to minimize the errors in impact assessment and data interpretation

using LCA tools. Albeit, certain differences in impact assessment results can be contributed by the in-built assumptions and factors used in the LCA tools, the key to achieving minimal errors is by being transparent and highly specific while building the model and by exercising utmost caution in the interpretation of results (Lehtinen et al. 2011).

8.3 Methodology

The overall study approach is subdivided into four parts: (1) designing two different landfill cover systems (i.e. conventional soil cover and biochar-based cover) which yield complete methane oxidation for a hypothetical landfill in Northeastern Illinois, (2) comparing the sustainability metrics for both the cover systems; (3) conducting uncertainty analysis to evaluate the effects of varying bio-chemical methane oxidation rates of the cover systems on the resulting environmental impacts and, (4) designing the field implementation of biochar-based final cover systems to achieve complete methane oxidation for a hypothetical landfill in Northeastern Illinois.

8.3.1 Design of Soil Cover and Biochar Cover Systems

To compare the sustainability metrics of cover systems, it is critical to determine the input parameters for SimaPro such as the type and quantity of materials needed for both the cover system options. The criteria for designing the final cover systems is based on the resulting methane emissions for the selected cover configurations. For an unbiased comparison, both the final cover configurations are equalized to achieve maximum methane oxidation (i.e. zero methane emissions). The California Landfill Methane Inventory Model (CALMIM) was used to perform the modeling of methane emissions from a site in Northeastern Illinois in order to design the cover layer thicknesses which yields maximum methane oxidation. CALMIM is a field validated model

that integrates the effects of soil microclimate and weather patterns for user-defined input locations, and site-specific as well as cover-specific parameters. The default inputs incorporated in CALMIM and the assumptions for both the cover system designs are presented in Table 8-1. CALMIM considers the 1-D gas diffusion of CH_4 and CO_2 and it is linked to seasonal climatic and soil microclimate variability through modified versions of existing, globally validated models like STM^2, SolarcalQ, Global TempSIM and Global RainSIM which are widely used by the United States Department of Agriculture (USDA). Since CALMIM integrates the climate and precipitation data into modeling methane emissions, it requires site-specific latitude and longitude data. To design the soil cover, a two-layer system comprising silty clay soil overlain by silty clay loam top soil (i.e. low-permeability layer overlain by an erosion layer) with each layer being minimum 30 cm thick (Sharma and Reddy 2004) was considered to begin the iterations using CALMIM. The biocover generally consists of a methane oxidation layer overtopping a gas diffusion layer of 30 cm thick (Huber-Humer et al. 2008). In this study, the CALMIM option of pebbles was used in place of gravel as the gas diffusion layer. Since biochar was not a cover material in the CALMIM database, to approximately simulate the textural properties of 'biochar-amended soil', the option of 'foundry sand' was used in the emissions modeling. The particle size distribution of 20% biochar amended soil indicates a considerable amount of sand-sized to granular particles (Reddy et al. 2014). Foundry sands are used as alternate daily cover materials in landfills and typically comprise sand-size to granular material with remnants of organic binders subjected to high temperature foundry/metal casting conditions and can be assumed to fairly represent the biochar amended soil (U.S. EPA 2002). The input values for optimum bio-chemical methane oxidation rates for both the cover systems were extracted from a study by Yaghoubi (2011) wherein, the methane oxidation rates were determined by conducting long-term column oxidation

tests followed by batch kinetic experiments on the extruded column materials. To determine the ideal layer thickness for each cover option, the individual layer thicknesses were entered into the CALMIM model and iterated until a value of 100% methane oxidation and close to zero total annual methane emissions was achieved. The results were then rounded up to the nearest 6" if necessary, to achieve an even layer thickness.

TABLE 8-1: CALMIM INPUTS FOR MODELING METHANE EMISSIONS

Parameter	Value	Reference
Temperature	Bottom boundary: 40°C Top boundary: real-time air temperature	Default values (Spokas and Bogner 2011)
Methane concentration	Bottom boundary: 55% (v/v) Top boundary: 2 ppm (v/v)	
Oxygen concentration	Bottom boundary: 1% (v/v) Top boundary: 20% (v/v)	
Methane oxidation rate	Soil cover: 260 µg CH_4 g^{-1} d^{-1} Biochar cover[a]: 1800 µg CH_4 g^{-1} d^{-1}	(Yaghoubi, 2011)
Functional unit	1 acre	Assumptions for this study
Cover area	100%	
Extent of vegetation	0%	
Extent of cover area influenced by gas extraction system	100%	
Amount of organic matter in cover materials	"low"	

[a] biochar cover comprised 20% pelleted wood biochar added to cover soil by weight

8.3.2 Sustainability Assessment of Soil Cover and Biochar Cover Systems

Sustainability assessment is performed using relevant indicators and metrics for quantification of the environmental, economic and social impacts throughout the lifecycle. LCA

is a tool used to quantify the environmental impacts and, in this study, SimaPro (Version 8.01) is employed for the environmental sustainability assessment. The economic sustainability is analyzed using modern costs that could be found for each of the cover materials and by accounting for the unit cost incurred from the transport and construction of the landfill cover. In order to evaluate the social sustainability, a qualitative and quantitative method was followed in accordance with the UNEP and SETAC framework for Methodological Sheets for Social LCA (Benoit-Norris et al. 2011). This framework categorized the soil impacts of a project under five different stakeholder groups namely, worker, consumer, local community, society and value chain actors. Under each category of the stakeholder groups, subcategories corresponding to the relevant social impact is provided to facilitate the comparative assessment. A scoring system has been devised (Reddy et al. 2014) with zero value for no impacts, +1 (improved) or +2 (ideal) for positive impacts, and -1 (diminished) or -2 (unacceptable) for negative impacts in order to evaluate the metrics for sustainability indicators under all the stakeholder groups.

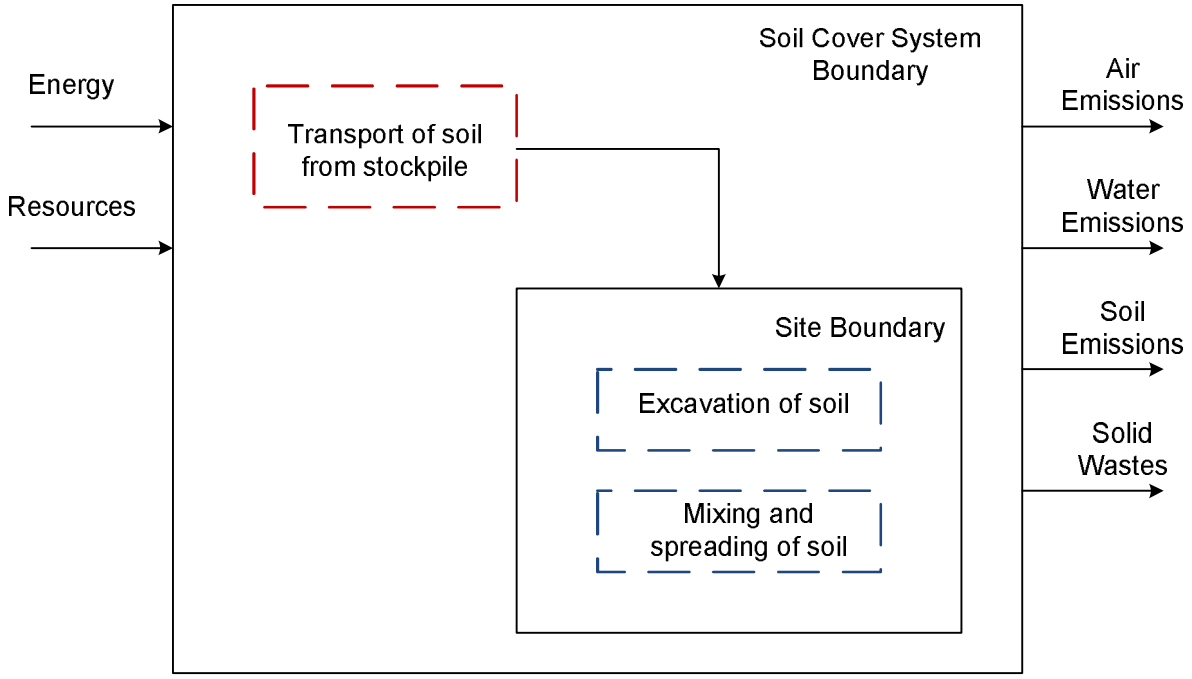
8.3.3 LCA of Soil Cover and Biochar Cover Systems

According to ISO 140001, the approach for conducting LCA comprises four different phases: (1) defining the study purpose, goal and system boundaries of the sustainability assessment, (2) performing the inventory analysis, (3) classifying and evaluating the environmental impacts and, (4) interpreting the results to identify key challenges. The goal of this LCA is to compare the environmental impacts of constructing two different types of final cover systems including soil cover and biochar cover for a landfill site in Northeastern IL. The functional unit for this study is assumed to be 1 acre of the landfill site and the design life for the landfill cover systems is assumed to be 50 years. The scope of this sustainability analysis includes the transport of materials from

the source to the construction site and the construction of the cover systems (i.e. excavation, mixing and spreading of the cover materials). The impacts incurred for the process of manufacturing biochar from waste wood can vary widely depending on the type of biomass conversion process, the conversion conditions within the reactor, pre- and post-processing techniques (if any) and proximity of the landfill site to the biomass source locations, thereby, causing a potential increase in the uncertainty levels for the comparison of cover systems. Thus, to minimize the variability, the process of biochar production has been excluded from the scope of this study.

The system boundaries for comparing the environmental sustainability of soil cover and biochar cover designs are shown in Figure 8-1. The production of cover soil for both the designs (i.e. the process of mining/ quarrying) was not included in the scope due to the natural presence of clayey soils in Northeastern IL which are commonly excavated and placed in a stockpile on-site during the construction of landfills and are re-used for the construction of covers. In the case of biochar cover, the gravel and biochar were assumed to be available on-site (i.e., at a transport distance of 1 km) and a sensitivity analysis was conducted by varying the transport distances up to a 100-km radius if it were to be obtained from off-site sources. In the baseline scenario for biochar cover with materials transported for a distance of 1 km, the biochar is assumed to be produced on-site with a mobile reactor set-up and the gravel is assumed to be available on-site from the remnants of leachate collection and removal system construction. An additional scenario pertaining to the recycling impacts of waste wood was considered for evaluating the sustainability of biochar cover system (Figure 8-2). The inputs for energy and resources were associated with the transport of materials by truck and the process of excavating, mixing and spreading the cover materials during construction. The outputs were associated with various indicators and metrics that related to the overall impacts in terms of emissions to air, water, soil and solid wastes generated.

(a)



(b)

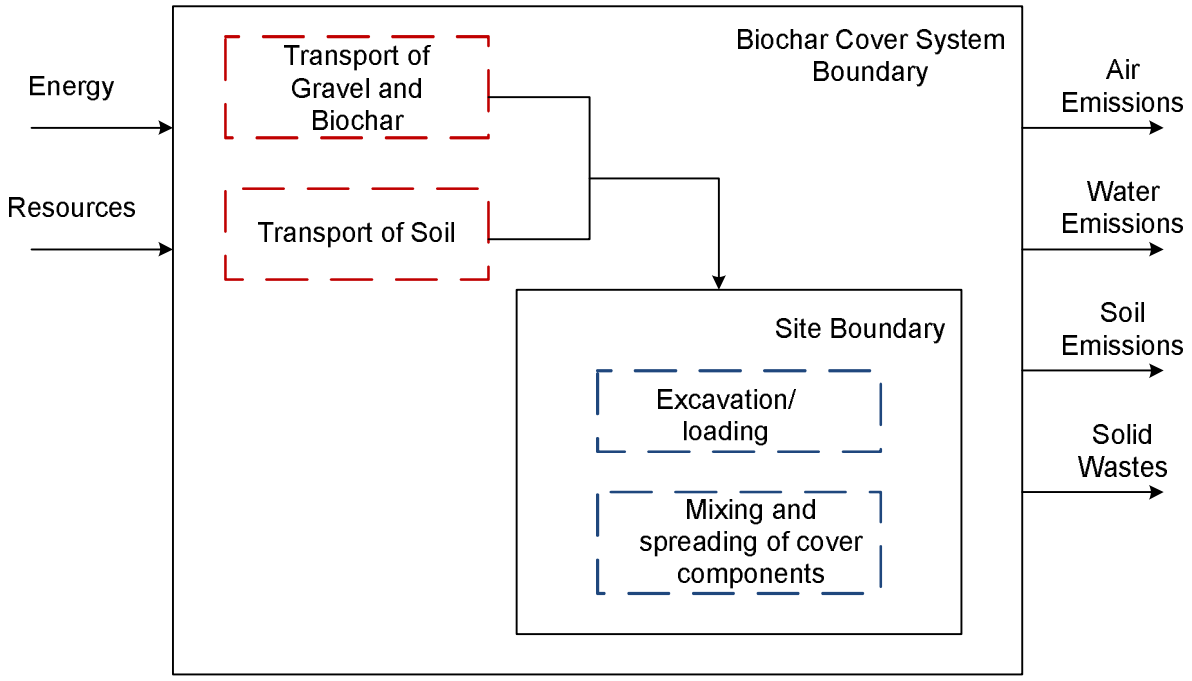


FIGURE 8-1: LCA SYSTEM BOUNDARIES FOR: (A) SOIL COVER; (B) BIOCHAR COVER

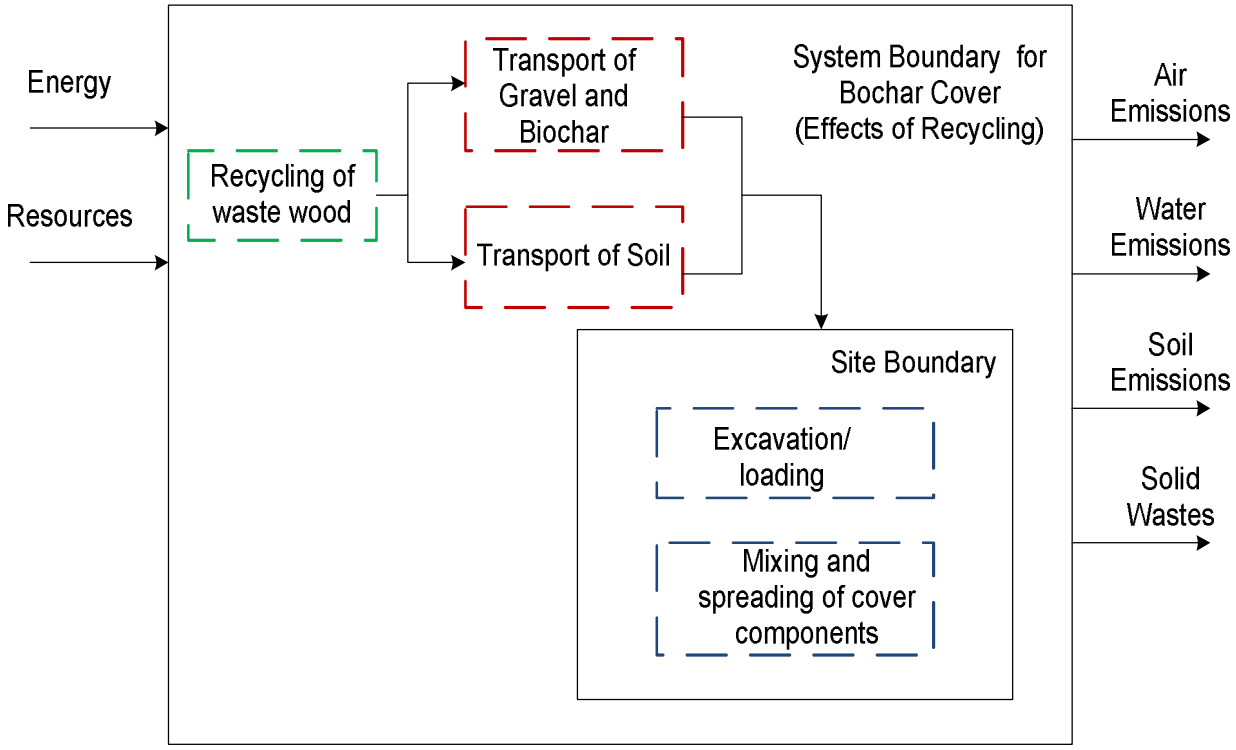


FIGURE 8-2: LCA SYSTEM BOUNDARIES TO EVALUATE THE EFFECTS OF RECYCLING WASTE WOOD IN BIOCHAR COVER SYSTEM

Any gas extraction, maintenance, or decommissioning of the landfill covers at the end of their 50 year life cycle was assumed to be the same for both the cover systems. Therefore, these stages of the life cycle were not evaluated in this study. Inventory analysis is performed in SimaPro by entering the type and quantity of materials required for cover construction along with the associated processes such as transportation, excavation, mixing and spreading. To model the effects of waste wood recycling, the material process/ assembly in SimaPro database, "_8 Recycling of waste wood, EU27" was used as input. The input for the quantity of waste wood recycled is twice as much as the amount of biochar required for the cover construction to achieve 100% methane oxidation based on an assumed biomass conversion efficiency of 50%. This input

does not directly model the process of waste wood recycling; however, it considers the service to treat the waste as a main product (i.e. the amount of waste eliminated from landfill disposal) and the major by-product supplied by this activity is categorized as “forest products” (i.e. avoided emissions from the logging of trees and the associated consumption of energy/ fuel) (Goedkoop et al. 2013).

The goal of impact assessment is to translate the inputs and the outputs of the system into perceivable results which directly relate to impact categories such as ozone depletion (kg CFC-11 eq), global warming (kg CO_2 eq), carcinogens and non-carcinogens (CTUh), respiratory effects (kg PM2.5 eq), fossil fuel depletion (MJ surplus) among others. Several in-built methods are available for assessing the environmental impacts using SimaPro. Eco-Indicator 99 method categorizes the resulting impacts under three different scenarios namely, damage to: human health, ecosystem quality and resources (Luis et al. 2013) and is widely recognized as an acceptable method to quantify the environmental impacts due to development/execution of any product/process (Raluy et al. 2005). However, this method assumes reference normalization values for impact quantification based on European standards (Dreyer et al. 2003). Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI) and Building for Environmental and Economic Sustainability (BEES) are specialized methods developed by US agencies and are equally popular worldwide (Lippiatt, 2013). The characterization factors and assumptions for computing the impacts in TRACI 2.1. are predominantly obtained from the EPA Risk Assessment Guidance for Superfund and EPA's Exposure Factors Handbook or derived from U.S. empirical models developed the U.S. National Acid Precipitation Assessment Program and the California Air Resources Board. In this study, Eco-Indicator 99(E) V2.08 method was adopted,

and a sensitivity analysis was conducted to compare the resulting environmental impacts using the TRACI method.

8.3.4 Uncertainty Analysis

The cover system designs for the landfill site were pertinent upon the inputs for methane oxidation rate in CALMIM such that the finalized configuration resulted in 100% methane oxidation. In order to assess the variability in the life cycle impact assessment results, the methane oxidation rate for soil cover was varied between a range of values reported in the literature (Yaghoubi, 2011; Scheutz et al. 2009; Sadasivam and Reddy 2014) for clayey to loamy soils (i.e. between 250 – 500 μg CH_4 $g^{-1}d^{-1}$) in order to determine the corresponding material quantities for input into SimaPro. For the biochar cover, the methane oxidation rate was varied between 350 - 1150 μg CH_4 $g^{-1}d^{-1}$ based on a study by Yaghoubi (2011). Monte Carlo analysis was performed in SimaPro by translating the inputs for the material processes and assemblies into a normal distribution by entering the mean and standard deviation (SD) for the range of values. In the Input/ Output database, the value of 2*SD is calculated and entered for the processes such as quantity of materials transported and excavated/ spread for each of the cover system designs. The uncertainty analysis is performed by specifying the impact assessment method (Eco-Indicator 99/ TRACI), a stop criterion and a fixed number of runs. A value of 0.001 was used as a stop criterion with the specified number of runs set to 1000. The Monte Carlo simulations are stopped if the standard error of mean for the data reaches the value specified for the stop criterion. The standard error of mean refers to the extent of deviation in the mean value within the number of runs for each analysis. In order to obtain a good graphical representation of the distribution and compute the uncertainty levels in the data, it is recommended that the standard error of mean is less than 0.01

and the minimum number of runs is set to 1000 (Goedkoop et al. 2013). The material transport distance for uncertainty analysis was assumed to be 1 km for both the cover systems without including the impacts associated with material production or waste wood recycling.

8.3.5 Design of Biochar Cover System for Field Application

The field-application of bio-based final cover systems can be designed as biocover, biowindows or biofilters (Sadasivam and Reddy 2015). While biocovers require placement of the cover materials over the entire expanse of the landfill, biofilters and biowindows require the placement of cover materials in discrete, excavated sections overlying a gas distribution layer which helps route the LFG into the oxidation layer. The installation of bio-based systems in the form of biowindows are thought to be more economically feasible compared to the biocover due to the minimum quantity of cover materials required for the design. The design approach for the biochar-based final cover system involved the following steps: (1) calculating the expected methane loading into the cover system (kg CH_4 d^{-1}); (2) determining the expected methane oxidation rate of the biochar cover from laboratory experiments (kg CH_4 m^{-2} d^{-1}); (3) determining the quantity of biochar cover area required to oxidize the expected CH_4 load (Scheutz et al. 2011).

CALMIM was used to model the methane emissions (i.e. the expected CH_4 load for cover system design) for 1 acre of the landfill site in Northeastern IL. To compute the emissions, an intermediate cover of 2 ft. thickness comprising silty clay soil with low organic matter was used as input and the entire 1 acre of the site was assumed to be influenced by the presence of gas extraction wells. The effect of vegetation was excluded and a methane oxidation rate of 400 μg CH_4 g^{-1} d^{-1} was assumed to compute the total load of methane from the landfill site. The methane oxidation rate for the biochar cover was determined in a previous study by Yaghoubi (2011) by

conducting long term column experiments followed by a series of batch incubation tests on the cover material extruded from the column upon reaching steady-state conditions. The total theoretical cross-sectional area of biowindows required for 1 acre of the landfill site is computed using Eqn. (8-1).

$$\frac{\mathrm{CH_4\ load\ (kgCH_4\ d^{-1})}}{\mathrm{CH_4\ oxidation\ rate\ (kgCH_4\ m^{-2}d^{-1})}} \quad (1)$$

However if all the emitted methane from the intermediate cover is routed through the biowindow due to pressure differential between the biowindows and the adjacent clayey soil, the influent flux of methane for the biowindow (q_{window}) would be much higher than the modeled flux from the entire 1 acre of the site (q_{cover}). Thus, the methane flux over the entire area of the landfill site is translated to the flux value across the area of the biowindow using Eq. (8-2).

$$q_{window} = q_{cover}\ \frac{A_{cover}}{A_{window}} \quad (2)$$

where A_{cover} is the landfill site footprint (i.e. 1 acre) for which the CH_4 emission is modeled using CALMIM; A_{window} is the cross-sectional area of each biowindow. The required depth of the biochar cover is determined such that the methane flux entering each biowindow (q_{window}) is fully oxidized.

8.4 Results

8.4.1 Design of Soil Cover and Biochar Cover Systems

The design configurations of final cover systems which resulted in 100% methane oxidation based on the modeled emissions from CALMIM are shown in Figure 8-3b and 8-3c. The soil cover configuration shown in Figure 8-3a corresponds to that of the minimum IEPA requirement (without the geomembrane) which resulted in a methane emission rate of 912.7 kg yr^{-1}. Based on the emissions modeling performed using CALMIM for the soil cover configurations, it quite evident that the cover thickness needs to be more than twice that of the minimum regulatory requirement in order to achieve 100% methane oxidation (i.e. zero methane emissions). On the other hand, the biochar cover configuration indicates that a cover thickness of 2 ft. over a foot of GDL was sufficient to achieve 100% methane oxidation. The reason for such large differences in the cover thickness is attributed to the rate of methane oxidation and the mechanism of diffusional gas transport within the cover systems.

The oxidation rate for methane in the soil cover is much lower (260 µg CH_4 g^{-1} d^{-1}) compared to that of the biochar cover (1800 µg CH_4 g^{-1} d^{-1}) which significantly impacted the resulting cover configurations to achieve 100% methane oxidation. Moreover, the use of in-built cover material, 'ADC foundry sands' in the CALMIM database for the biochar cover system resulted in enhanced gas diffusion and oxygen ingression from the atmosphere within the top 2 ft of the biochar cover as compared to that of the soil cover (Figure 8-4) implying higher methane to oxygen mixing ratios thereby, facilitating greater microbial methane oxidation in biochar cover system (Sadasivam and Reddy, 2014). This mimics the findings from previous studies that indicate a greater depth of oxygen ingression in simulated biochar-amended soil covers compared to conventional soil covers thereby, promoting the growth and activity of methanotrophs which in turn accelerate the methane

oxidation (Reddy et al. 2014; Xie et al. 2013). The quantity of materials required to install the cover systems are computed from the finalized design configurations and these values are used to conduct the LCA to determine the resulting environmental impacts.

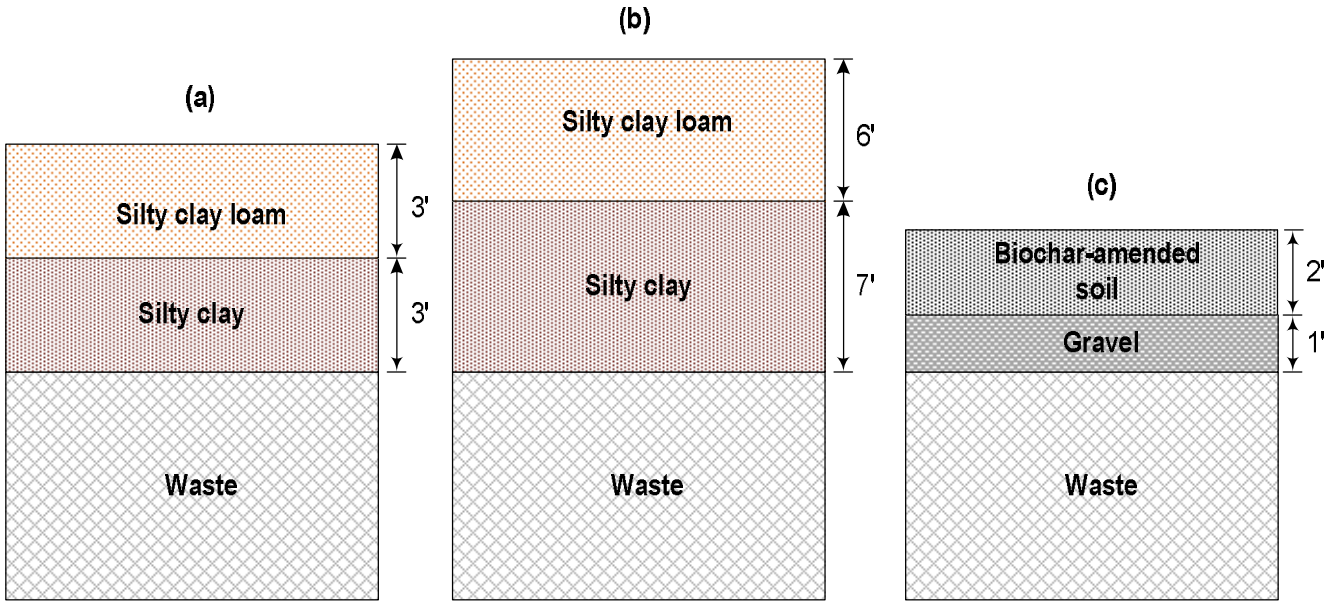


FIGURE 8-3: DESIGN OF FINAL COVER SYSTEMS BASED ON CALMIM: (A) IEPA MINIMUM REQUIREMENT FOR SOIL COVER WITHOUT GEOMEMBRANE (ANNUAL EMISSIONS = 912.7 KG CH_4); (B) SOIL COVER FOR 100% METHANE OXIDATION; (C) BIOCHAR COVER FOR 100% METHANE OXIDATION

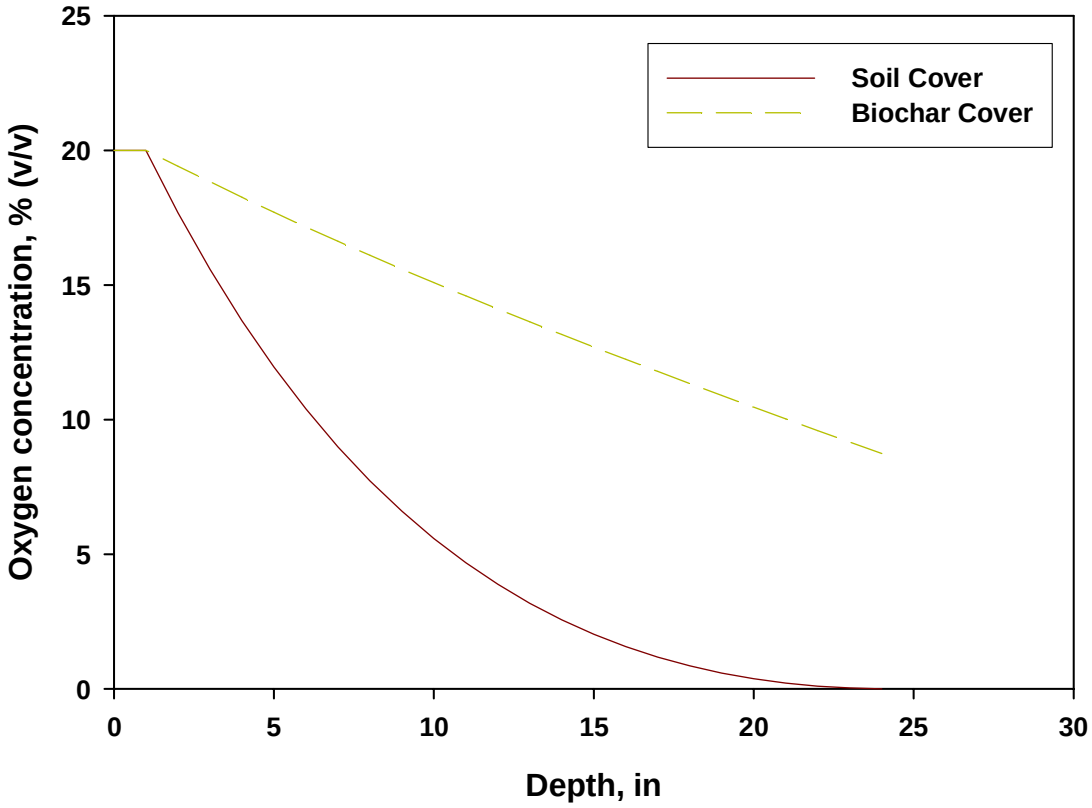


FIGURE 8-4: OXYGEN CONCENTRATION PROFILES IN THE TOP 2 FT. OF FINAL COVER SYSTEMS EXTRACTED FROM CALMIM OUTPUTS

8.4.2 Sustainability Assessment of Soil Cover and Biochar Cover System

8.4.2.1 LCA of Soil Cover and Biochar Cover Systems

The inputs for environmental sustainability analysis using SimaPro were determined from the type and quantity of cover materials required for the implementation of final cover designs and translated into values in terms of ton-km (i.e. product of material quantities and their corresponding transport distance) that can be used to model the resulting environmental impacts from the transport of the materials from source to the site using a truck. Additionally, the total volume of

the cover materials that need to be excavated and spread over 1 acre of the cover area using an excavator/ hydraulic digger is entered to quantify the resulting environmental impacts of this process. The input parameters for comparing the environmental impacts incurred for the cover system boundaries are listed in Table 8-2. To model the effects of waste wood recycling in biochar cover, an additional input for the quantity of waste wood needed to produce the required amount of biochar is entered in the material assembly.

TABLE 8-2 INPUT PARAMETERS FOR LCA OF SOIL COVER SYSTEMS USING SIMAPRO

Cover type	Material	Thickness (ft)	acre-ft	Volume (cu-m)	density (kg/ cu-m)	Quantity (tons)	Distance (km)
Soil Cover	Silty clay	7	7	8634.36	1631.552	14087.41	1
	silty clay loam	6	6	7400.88	1682.538	12452.26	1
Biochar-Based cover	Gravel	1	1	1233.48	1600	1973.568	1, 25, 50 & 100 km
	20% AWP	2	2	2466.96	1427.608	3521.851	
	Silty clay	--	--	--	--	2817.481	1
	Biochar	--	--	--	--	704.370	1, 25, 50 & 100 km

The results for Life Cycle Impact Assessment (LCIA) using the endpoint method (Eco-Indicator 99) comparing the soil cover and biochar cover systems by assuming various transport distances for gravel and biochar are shown in Figure 8-5. The results for LCIA are expressed in

terms of kPt (kilo-point) for each cover system scenario that is being compared. One 'point' (Pt) is considered equivalent to a small fraction (i.e. 1/1000) of an average European's environmental impact over one year (Goedkoop et al. 2013). The endpoint method in Eco-Indicator 99 computes the environmental impact under eleven different sub-categories (Figure 8-5) which are grouped under a total of three damage categories including, human health, ecosystem quality and resources. The effects of climate change, ozone layer depletion, carcinogens, respiratory effects and ionizing (nuclear) radiation correspond are grouped under the damage caused to human health. The category of 'ecosystem quality' encompasses the combined effects from ecotoxicity, eutrophication, acidification and land-use while the remaining impact categories such as minerals and fossil fuels pertain to the effects on non-renewable resources.

The sum of all impacts for each scenario indicates that the option of biochar cover assuming that the materials are available on-site resulted in the least environmental impact while the highest impacts were observed if the biochar cover materials were assumed to be transported by a distance of 100 km (Figure 8-5). The impact of using soil cover system was five time higher than that of the biochar cover system (transport distance = 1km) and was almost equal to that of the biochar cover scenario which assumed that the cover materials were transported by a distance of 25 km. Based on the single score results, it is evident that the process of transporting the cover materials to the site caused a significant impact in the results. The highest level of contribution to the overall impact resulted from the category of 'fossil fuels', closely followed by 'respiratory inorganics. The relative impacts under all eleven categories for the cover system scenarios are quantified and compared in Figure 8-6. The cover system option that had the highest level of impact is assumed to be 100% and the relative contribution to each impact category are represented for all the other options (Figure 8-6) based on the Eco-Indicator (99) impact assessment method.

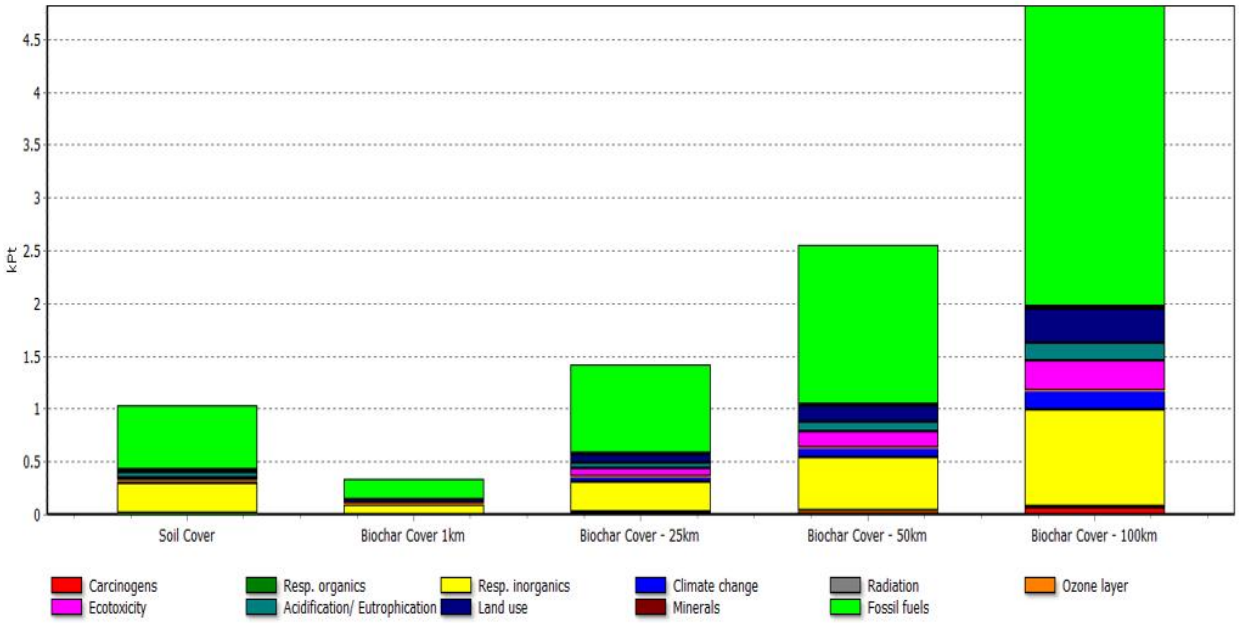
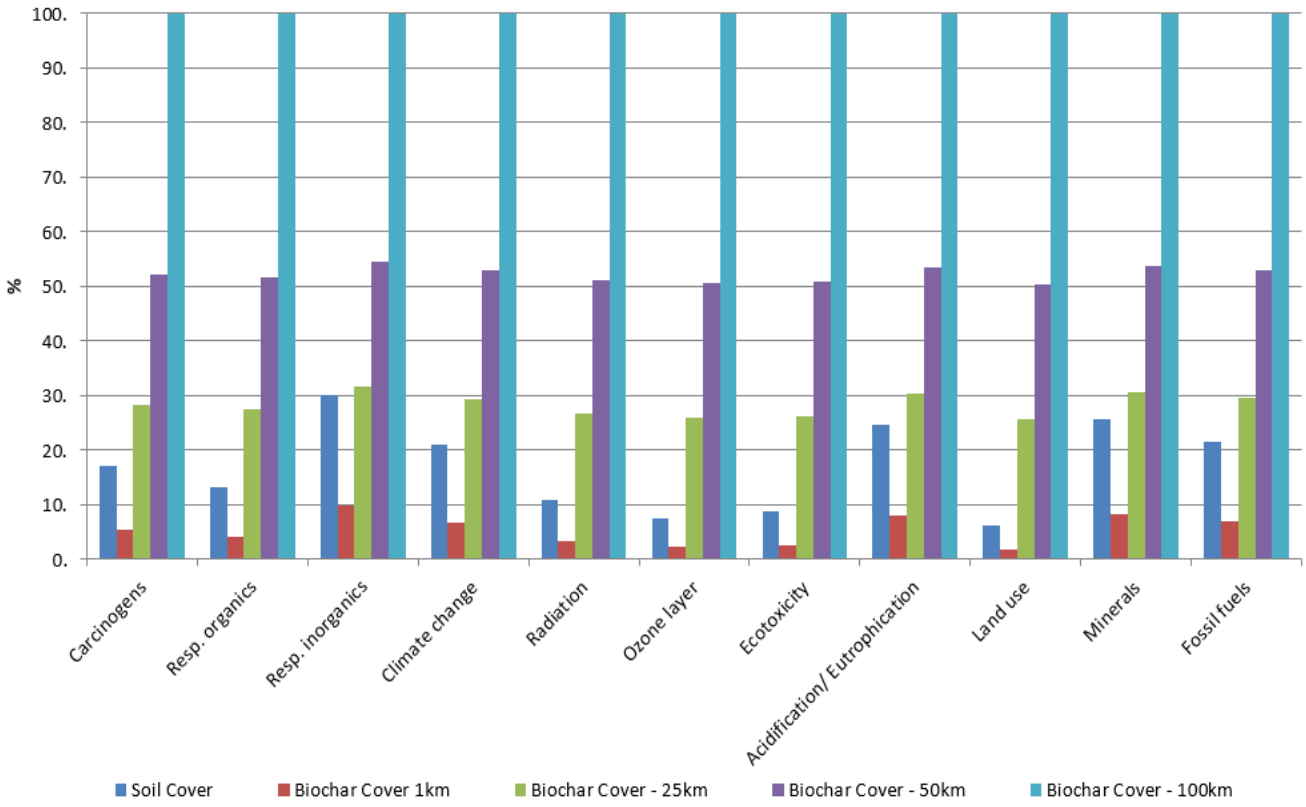


FIGURE 8-5: ECO-INDICATOR (99) SINGLE SCORE LCIA RESULTS FOR COMPARISON OF SOIL COVER AND BIOCHAR COVER SYSTEMS ASSUMING VARIOUS TRANSPORT DISTANCES FOR BIOCHAR COVER MATERIALS INCLUDING GRAVEL AND BIOCHAR

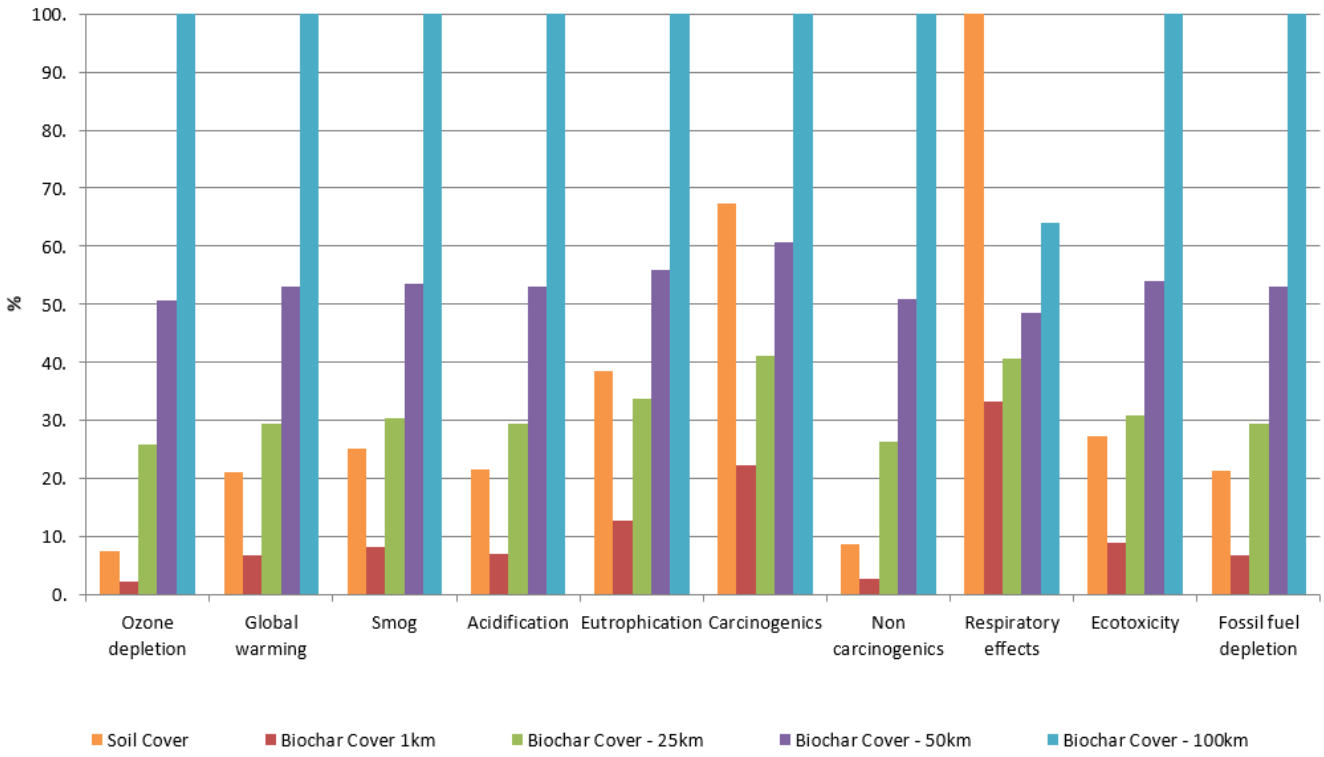


Sel	Impact category	Unit	Soil Cover	Biochar Cover 1km	Biochar Cover - 25km	Biochar Cover - 50km	Biochar Cover - 100km
☑	Carcinogens	DALY	0.000597	0.000191	0.000983	0.00181	0.00346
☑	Resp. organics	DALY	3.15E-5	9.95E-6	6.5E-5	0.000122	0.000237
☑	Resp. inorganics	DALY	0.0142	0.00464	0.015	0.0258	0.0473
☑	Climate change	DALY	0.00185	0.000597	0.00257	0.00463	0.00875
☑	Radiation	DALY	2.03E-5	6.34E-6	4.96E-5	9.48E-5	0.000185
☑	Ozone layer	DALY	4.79E-6	1.45E-6	1.68E-5	3.28E-5	6.47E-5
☑	Ecotoxicity	PAF*m2yr	3.24E3	996	9.72E3	1.88E4	3.7E4
☑	Acidification/ Eutrophication	PDF*m2yr	531	172	650	1.15E3	2.14E3
☑	Land use	PDF*m2yr	256	75.9	1.04E3	2.05E3	4.06E3
☑	Minerals	MJ surplus	221	71.9	264	465	865
☑	Fossil fuels	MJ surplus	1.71E4	5.52E3	2.35E4	4.22E4	7.97E4

FIGURE 8-6: ECO-INDICATOR (99) RELATIVE IMPACTS FROM CHARACTERIZATION OF LCIA RESULTS FOR COMPARISON OF SOIL COVER AND BIOCHAR COVER SYSTEMS ASSUMING VARIOUS TRANSPORT DISTANCES FOR BIOCHAR COVER MATERIALS

A sensitivity analysis was conducted by varying the impact assessment method in SimaPro and the results for LCIA using TRACI 2.1. are shown in Figure 8-7. TRACI 2.1. adopts the midpoint method to calculate the impact assessment and the results are categorized under ten different indicators. The option of soil cover causes maximum impact under the category of 'respiratory effects' closely followed by the level of impact under 'carcinogens. The overall characterization results indicate a relatively higher contribution of impacts to human health and eutrophication compared to other categories. The effects of recycling waste wood for the production of biochar in the case of biochar cover system is evaluated by assuming that the cover materials (gravel and biochar) are either available on-site or are obtained from off-site sources and compared to the impacts generated from soil cover system. The LCIA results indicate that considerable benefits are achieved by accounting for the avoided emissions otherwise incurred from the waste wood treatment and the use of forest products in the case of biochar cover systems (i.e. the logging and associated use of energy/ fuel from the chipping of wood). The maximum benefit of recycling is reflected for the avoided emissions under the category of fossil fuels. The overall impact generated by all the four biochar cover scenarios were lower than that of the soil cover system (Figure 8-8). This indicates that even if the biochar cover materials have to be transported to the site from off-site sources over a distance of 100 km, the net benefits of using biochar cover system for the landfill site out-weighs the environmental impacts generated from the use of soil cover system. It is to be noted that in this analysis no credit is given to the amount of CO_2 that is expected to be sequestered from the atmosphere after the placement of biochar cover on the landfill. The amount of CO_2 sequestration from the addition of biochar to soil is expected to 3 tons of CO_2 per ton of biochar amendment (Petelina et al. 2014). The characterization results indicate that there is considerable benefit of incorporating recycling of wood into the analysis

under the categories of respiratory organics, respiratory inorganics, climate change and fossil fuels (Figure 8-9).



Sel	Impact category	Unit	Soil Cover	Biochar Cover 1km	Biochar Cover - 25km	Biochar Cover - 50km	Biochar Cover - 100km
☑	Ozone depletion	kg CFC-11 eq	0.00597	0.0018	0.0209	0.0407	0.0804
☑	Global warming	kg CO2 eq	8.81E3	2.84E3	1.23E4	2.22E4	4.19E4
☑	Smog	kg O3 eq	2.25E3	729	2.72E3	4.79E3	8.94E3
☑	Acidification	kg SO2 eq	77.3	25	106	190	358
☑	Eutrophication	kg N eq	7.12	2.33	6.24	10.3	18.5
☑	Carcinogenics	CTUh	0.000285	9.42E-5	0.000174	0.000257	0.000423
☑	Non carcinogenics	CTUh	0.00167	0.000513	0.00501	0.00969	0.0191
☑	Respiratory effects	kg PM2.5 eq	7.79	2.59	3.17	3.78	4.98
☑	Ecotoxicity	CTUe	1.18E4	3.82E3	1.34E4	2.33E4	4.32E4
☑	Fossil fuel depletion	MJ surplus	1.69E4	5.45E3	2.34E4	4.21E4	7.96E4

FIGURE 8-7: TRACI 2.1. RELATIVE IMPACTS FROM CHARACTERIZATION OF LCIA RESULTS FOR COMPARISON OF SOIL COVER AND BIOCHAR COVER SYSTEMS ASSUMING VARIOUS TRANSPORT DISTANCES FOR BIOCHAR COVER MATERIALS INCLUDING GRAVEL AND BIOCHAR

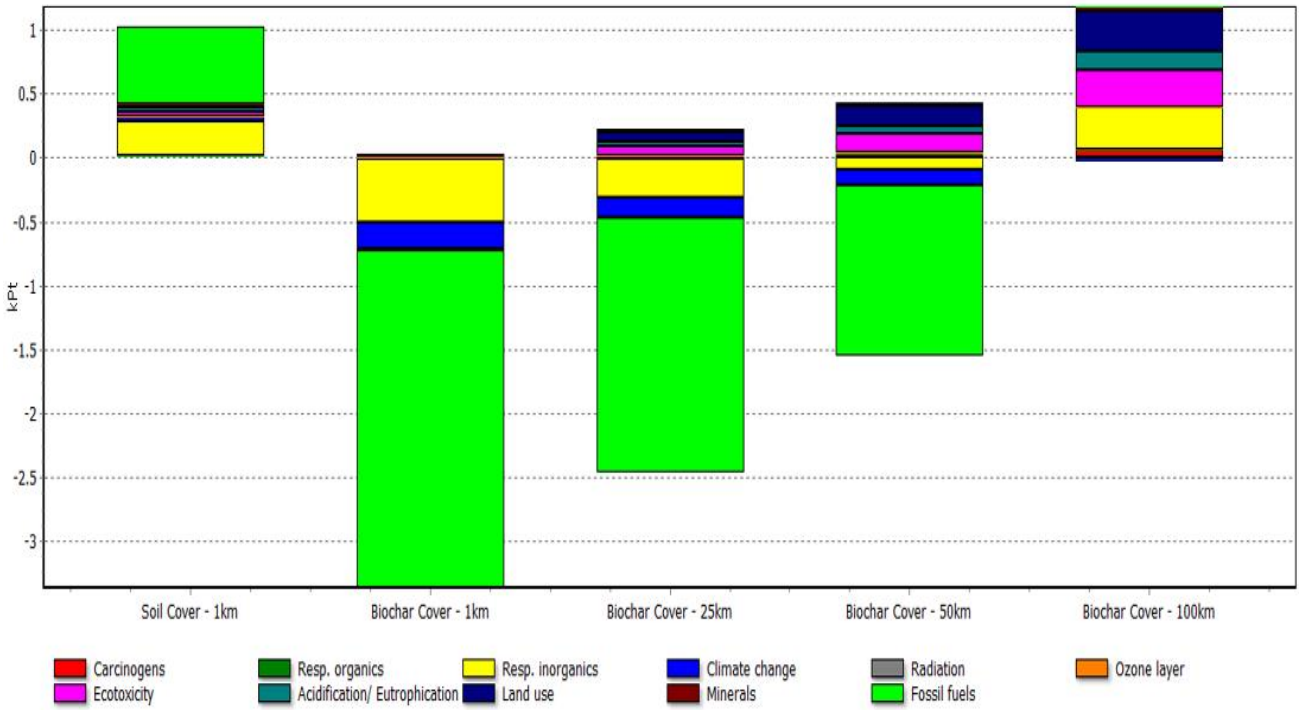
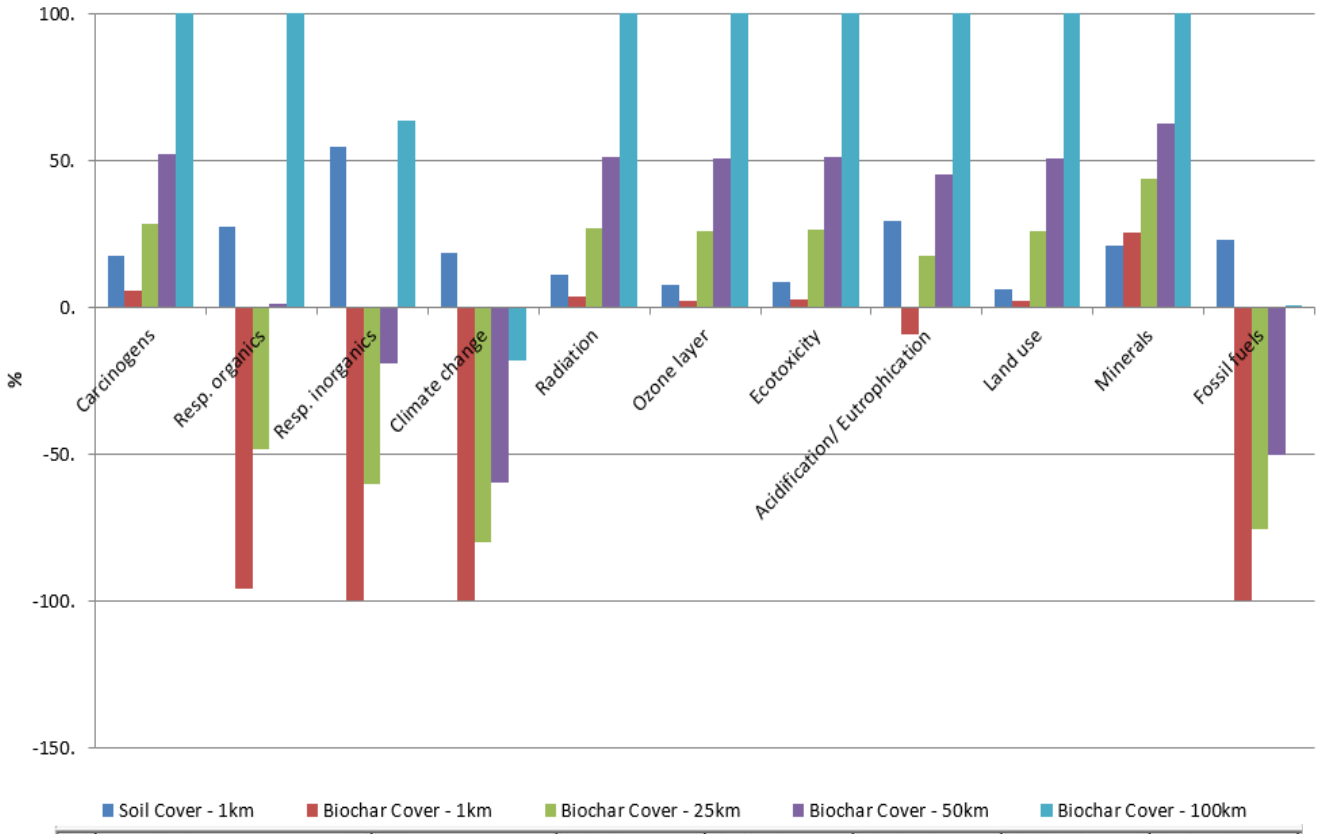


FIGURE 8-8: ECO-INDICATOR (99) SINGLE SCORE LCIA RESULTS TO EVALUATE THE EFFECTS OF RECYCLING WASTE WOOD TO PRODUCE BIOCHAR



Sel	Impact category	Unit	Soil Cover - 1km	Biochar Cover - 1km	Biochar Cover - 25km	Biochar Cover - 50km	Biochar Cover - 100km
☑	Carcinogens	DALY	0.000597	0.000191	0.000983	0.00181	0.00346
☑	Resp. organics	DALY	3.15E-5	-0.000111	-5.6E-5	1.41E-6	0.000116
☑	Resp. inorganics	DALY	0.0142	-0.0261	-0.0157	-0.00496	0.0166
☑	Climate change	DALY	0.00185	-0.00999	-0.00802	-0.00596	-0.00184
☑	Radiation	DALY	2.03E-5	6.34E-6	4.96E-5	9.48E-5	0.000185
☑	Ozone layer	DALY	4.79E-6	1.45E-6	1.68E-5	3.28E-5	6.47E-5
☑	Ecotoxicity	PAF*m2yr	3.24E3	996	9.72E3	1.88E4	3.7E4
☑	Acidification/ Eutrophication	PDF*m2yr	531	-163	314	811	1.81E3
☑	Land use	PDF*m2yr	256	75.9	1.04E3	2.05E3	4.06E3
☑	Minerals	MJ surplus	221	272	465	665	1.07E3
☑	Fossil fuels	MJ surplus	1.71E4	-7.41E4	-5.61E4	-3.74E4	53.8

FIGURE 8-9: ECO-INDICATOR (99) RELATIVE IMPACTS FROM CHARACTERIZATION OF LCIA RESULTS TO EVALUATE THE EFFECTS OF RECYCLING WASTE WOOD TO PRODUCE BIOCHAR

8.4.2.2 Economic Sustainability

An economic assessment was performed by accounting for the costs incurred from purchase and transport of the cover materials (if procured from off-site sources) along with the unit costs associated with the construction of the cover systems (Table 8-3).

TABLE 8-3: ECONOMIC SUSTAINABILITY ASSESSMENT

Cover system	Cover Material	Material Quantity (tons)	Transport Distance (Km)	Purchase[a] Cost	Transportation cost[a]	Unit Cost for construction (per cubic yard)	Total Cost per acre
Soil cover	Clay	14087.4	1	NIL	NIL	USD 30	USD 532,404
	Top soil	12452.3	1	NIL	NIL	USD 20	
Biochar cover (on-site)	Gravel	1973.6	1	NIL	NIL	USD 0.7	USD 97,930
	Biochar	704.37	1	NIL	NIL	USD 30	
	Clay	2817.48	1	NIL	NIL		
Biochar cover (off-site)	Gravel	1973.6	25 – 100	USD 4/ton	USD 0.1/km/ton	USD 0.7	USD 991,925 – 3,648,115
	Biochar	704.37	25 – 100	USD 1000/ ton	USD 50/km/ton	USD 30	
	Clay	2817.48	1	NIL	NIL		
Biowindow design (on-site)	Gravel	144	1	NIL	NIL	USD 0.7	USD 282,383
	Biochar	128.5	1	NIL	NIL	USD 30	
	Clay	12242	1	NIL	NIL		

[a] cost values were obtained from an ongoing field study of biochar cover systems at a Northeastern IL landfill site
[b] values obtained from 2012 Landfill Management Reserve Analysis Report for DuPage County, IL submitted by ARCADIS to the DuPage County Forest Preserve District

The total cost per acre of the landfill site for soil cover system is USD 532,404 and for biochar cover system is USD 97,930 if the cover materials are assumed to be available on-site. The purchase and transportation costs for the biochar cover materials (gravel and biochar) have been included based on the experience gained form an on-going field-scale study which aims at testing the performance of biochar cover systems at an active landfill site in Northeastern IL. The total cost per acre of the biochar cover system is much higher when the cover materials have to be purchased and transported to the site thereby making this option least economically preferable.

8.4.2.3 Social Sustainability

The results for social impact assessment for soil cover and biochar cover systems by assuming that the cover materials are either available on-site or acquired from off-site sources are listed in Table 8-4. Scores are assigned for each sub-category under five different stakeholder groups in order to evaluate the level of impacts using the social sustainability rating chart (Bennoit-Norris et al. 2011). The results indicate that the use of biochar cover system wherein, the materials are transported from off-site sources cause the highest level of negative social impact among all the three scenarios assessed. On the other hand, if the materials are assumed to be available on-site, then the biochar cover system appears to be the most socially favorable option compared to the soil cover system.

TABLE 8-4: SOCIAL SUSTAINABILITY ASSESSMENT

Stakeholder Group	Impact Category	Soil Cover (on-site)	Biochar Cover (on-site)	Biochar Cover (off-site)	Biowindow Design (on-site)
Workers	Freedom of Association and Collective Bargaining	0	0	0	0
	Child Labor	0	0	0	0
	Fair Salary	0	0	0	0
	Working Hours	-1	+1	-1	+1
	Forced Labor	-1	0	-1	0
	Equal Opportunities/Discrimination	0	0	0	0
	Health and Safety	-2	0	-1	+1
	Social Benefits/Social Security	0	0	0	0
Consumers	Health and Safety	0	0	0	0
	Feedback Mechanism	0	0	0	0
	Consumer Privacy	0	0	0	0
	Transparency	0	0	0	0
	End of life responsibility	0	0	0	0
Local Community	Access to material resources	0	0	-1	0
	Access to immaterial resources	0	0	-1	0
	Delocalization and Migration	-1	-1	-2	-1
	Cultural heritage	-1	-1	-1	-1
	Safe and Healthy Living Conditions	-1	-1	-2	-1
	Respect to indigenous rights	0	0	0	0
	Community engagement	0	+1	-1	+1
	Public commitments to sustainability issues	-1	+2	-2	+2
	Local Employment	+1	+1	+1	+1
	Secure Living Conditions	-1	-1	-2	-1
	Contribution to economic development	0	+1	+1	+1
Society	Prevention and Mitigation of Armed Conflicts	0	0	0	0
	Technology Development	0	+1	+1	+1
	Corruption	0	0	0	0
Value chain actors	Fair competition	0	0	0	0
	Promoting social responsibility	-1	+1	-2	+2
	Supplier relationships	0	+2	+2	+2
	Respect of intellectual property rights	0	0	0	0
Total Score		-9	+6	-11	+8

8.4.3 Uncertainty Analysis

An uncertainty analysis was performed using SimaPro to determine the extent of variation in the LCIA results for the soil cover and the biochar cover systems for a range of methane oxidation rates. The minimum cover depths required to achieve 100% methane oxidation at different rates of oxidation were determined based on emissions modeling for the landfill site using CALMIM (Figure 8-10). The results indicate that the cover depths were comparatively more sensitive to even slight changes that could be expected in the oxidation rates in the range reported from previous studies (200 – 500 μg CH_4 g^{-1} d^{-1}) for the soil cover system. On the other hand, the extent of variation in the biochar cover depths were not as prominent as that of the soil cover system within the expected range of variation (250 – 1150 μg CH_4 g^{-1} d^{-1}) reported to occur based on a previous study (Yaghnoubi, 2011).

An uncertainty analysis using SimaPro was conducted by entering the values of mean and standard deviation for the quantity of cover materials and assuming that the materials were available on-site for both the cover system. The inputs for SimaPro to conduct the uncertainty analysis are listed in Table 8-5. The Eco-Indicator (99H) method was used to perform the uncertainty analysis and the comparative characterization results indicating the expected range of variation in LCIA for both the cover systems are shown in Figure 8-11. The environmental impacts incurred by biochar cover was much lower than that of the soil cover under all the indicators. Overall, the uncertainty levels for soil cover represented by the coefficient of variation in the impact assessment results around the mean values ranged between 16 – 30% for all the indicators except for the subcategory, carcinogens in which a high level of uncertainty was noted (161%). The uncertainty levels for biochar cover were much lower than that of the soil cover and the values for the coefficient of variation ranged between 3 – 25%.

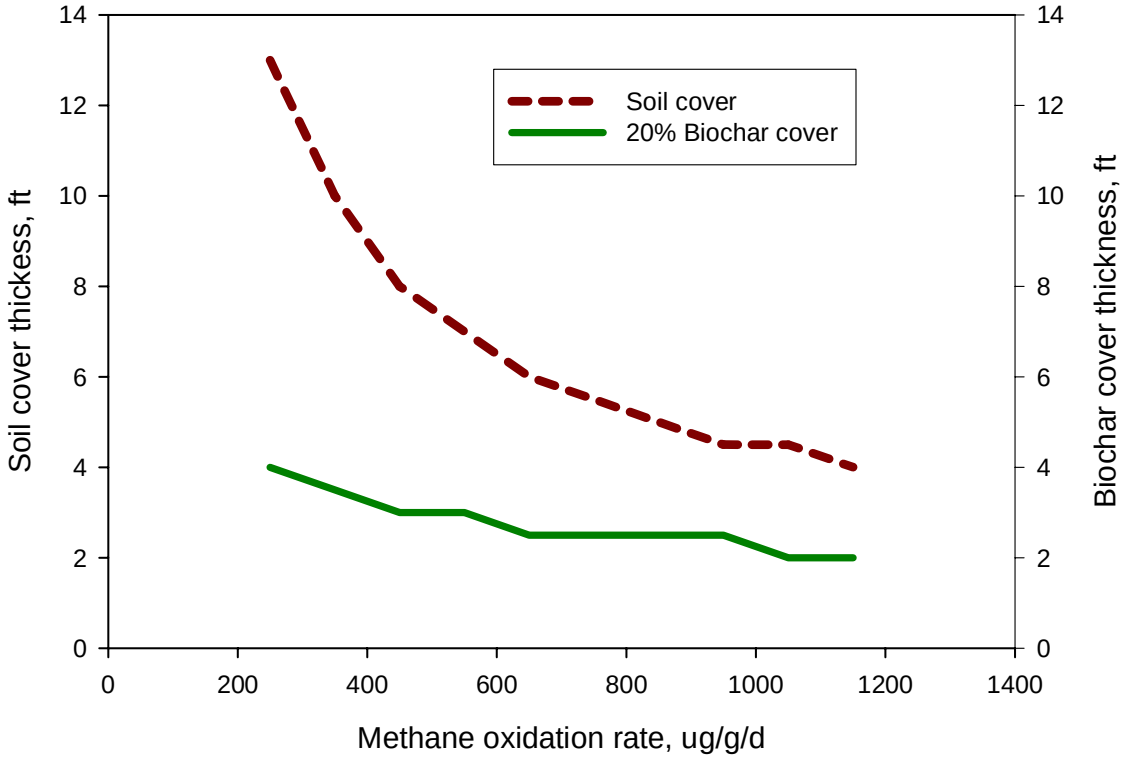


FIGURE 8-10: MINIMUM COVER DEPTHS REQUIRED TO ACHIEVE ZERO METHANE EMISSIONS AT VARIOUS METHANE OXIDATION RATES USING CALMIM

TABLE 8-5: INPUTS FOR CONDUCTING UNCERTAINTY ANALYSIS TO ASSESS THE VARIATION IN LCIA RESULTS WITH VARYING METHANE OXIDATION RATES USING SIMAPRO

Cover type	Processes	Mean value	Standard deviation
Soil Cover	Transport (tkm)[a]	22916.494	3944.541
	Excavation/ spreading (cu-m)	13842.4	2381.7
Biochar-Based cover	Transport (tkm)[a]	6571.541	806.720
	Excavation/ spreading (cu-m)	4454.23	536.85

[a] Cover materials are assumed to be available on-site (i.e. transport distance of 1 km)

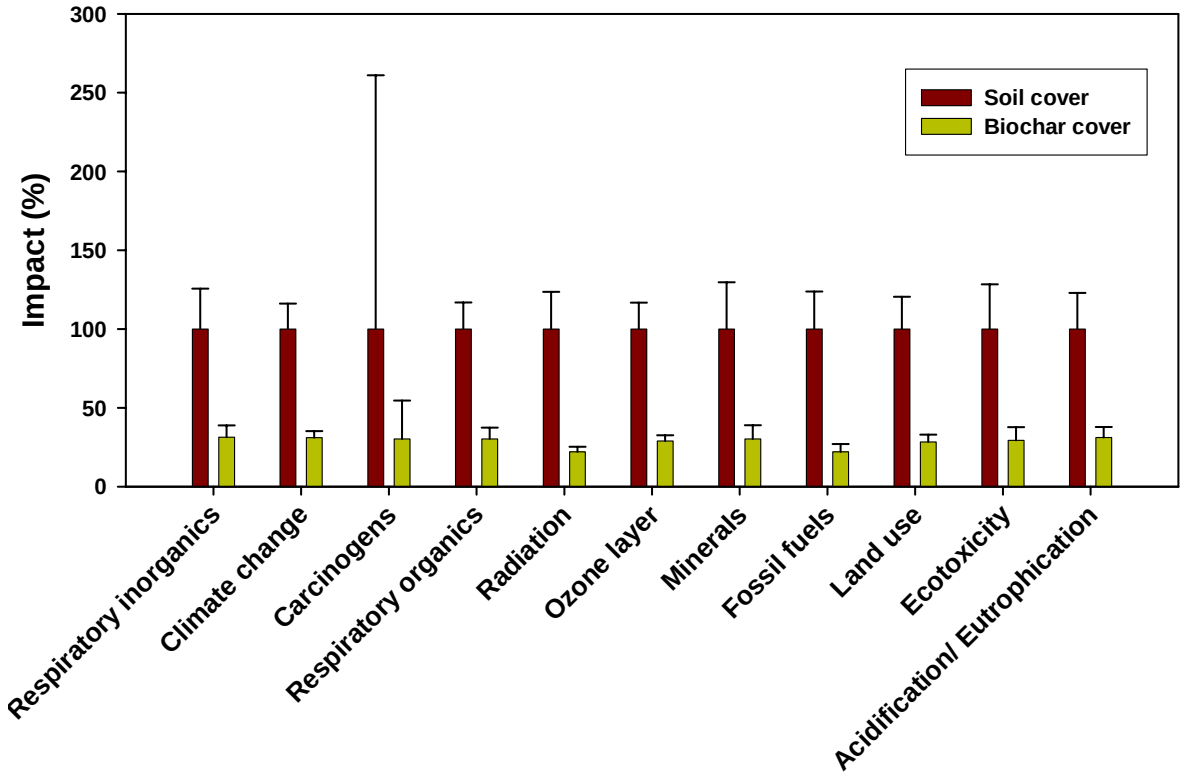


FIGURE 8-11: RELATIVE IMPACTS OF SOIL COVER COMPARED WITH BIOCHAR COVER FOR DIFFERENT INDICATORS. ERROR BARS REPRESENT 95% CONFIDENCE INTERVALS AS DETERMINED BY MONTE CARLO SIMULATIONS

8.4.4 Design of Biochar Cover System for Field-Application

The final cover configuration recommended for field application in of biochar-based systems in Northeastern IL landfills to achieve 100% methane oxidation is shown in Figure 8-12. The total baseline methane emissions over one acre of the landfill site that has an intermediate cover (i.e., prior to placement of the final cover system) based on CALMIM was found to be 73 kg CH_4 d^{-1}. The oxidation rate for 20% biochar amended soil based on laboratory results extracted from a

previous study (Yaghoubi, 2011) was found to range between 0.3 – 1.8 kg CH_4 m^{-2} d^{-1}. Thus, the minimum cross-sectional area of biowindow required for 1 acre of the landfill site was 250 m^2. However, the flux of methane entering the cross-sectional area of biowindow (q_{window}) would be much higher than the flux over the entire landfill area and this value was computed using Eqn. (2) which resulted in a flux value of 73 g CH_4 m^{-2} d^{-1}. Based on methane emissions modeling performed using CALMIM to mimic the expected bottom flux value (q_{window}) and the baseline site conditions prior to installation of the biowindow (i.e. for a site footprint of 100 m^2) indicated that a minimum biowindow cover depth of 2 ft. over 1 ft. of GDL was sufficient to achieve 100% methane oxidation. However, a total of three, 10m x 10m biowindows with a depth of 1.5m (5') overlying a GDL of 0.3m (1') thickness is recommended to be installed over 1 acre of the landfill site in order to achieve zero methane emissions in order to meet the regulatory criteria. The total depth of the soil cover surrounding the biowindow sections is 1.8m (6') which meets the minimum IEPA requirement for the thickness of final covers in Illinois except without the use of a flexible membrane layer.

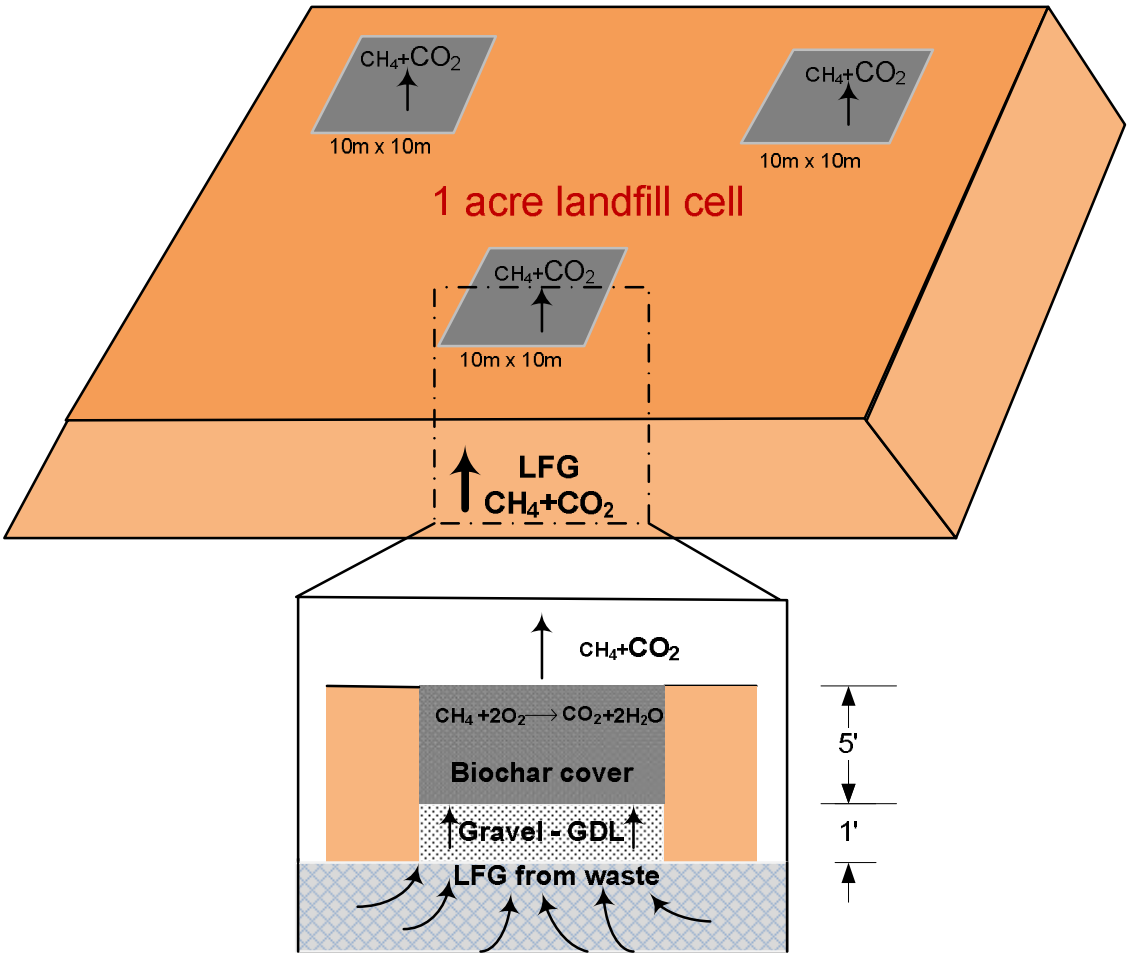


FIGURE 8-12: BIOWINDOW DESIGN CONFIGURATION RECOMMENDED FOR FIELD-SCALE APPLICATION OF BIOCHAR FINAL COVER SYSTEMS IN NORTHEASTERN IL TO ACHIEVE ZERO METHANE EMISSIONS

8.4.5 LCA Comparison of Biowindow Design, Soil Cover and Biochar Cover Systems

The resulting environmental impacts for biowindow design is less than half the impact generated from the use of soil cover system. However, the use of biochar cover system still resulted in the least value of impact (Figure 8-13). These results indicate that the placement of biochar-

based cover systems in the form of biowindows is more environmentally sustainable compared to the conventional soil cover system due to the lower quantity of materials needed to be handled during the cover construction thereby, considerably reducing the impacts generated from the use of excavators and transport trucks.

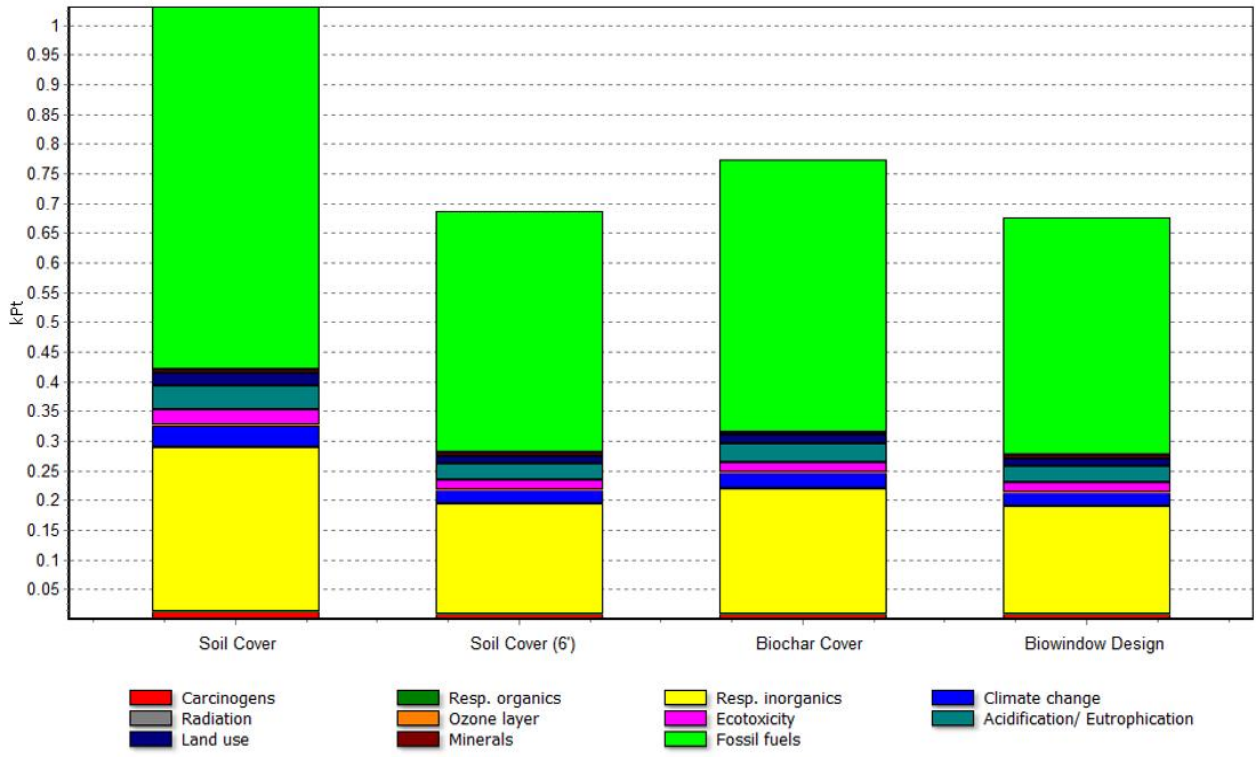


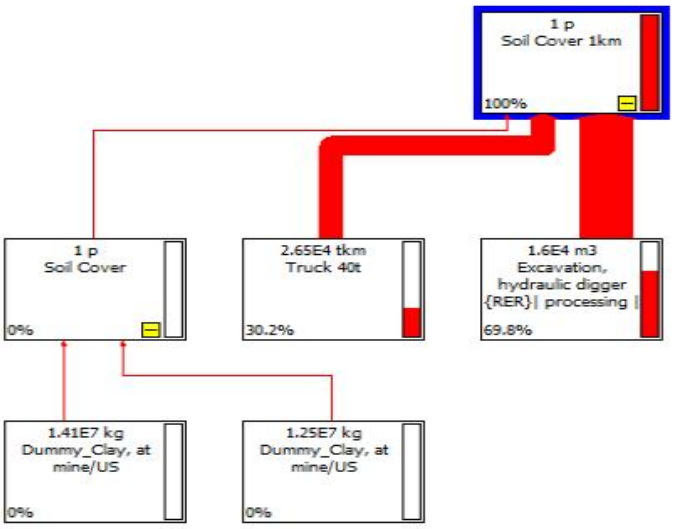
FIGURE 8-13: ECO-INDICATOR (99) SINGLE SCORE LCIA RESULTS FOR COMPARISON OF BIOWINDOW DESIGN, SOIL COVER AND BIOCHAR COVER SYSTEMS ASSUMING COVER MATERIALS ARE AVAILABLE ON-SITE

8.5 Discussion

8.5.1 Environmental Sustainability of Cover Systems

The breakdown of contribution levels to the overall impact from various materials/ assembly and processes for the soil cover and biochar cover systems are represented in the form of tree diagrams in Figure 8-14 assuming all the cover materials are available on-site. The thickness of the arrows provides the extent of contribution by any given product/ process in the materials assembly and their corresponding percentage levels of impact are shown for individual components. The results indicate that for the assumption of on-site availability of cover materials, the highest level of impact is associated with the use of hydraulic diggers for excavation and placement of the cover systems. The impacts resulting from the process of material transport is relatively lower. The relative impact assessment results using the TRACI method comparing the different cover system scenarios (Figure 8-7) indicated that a large extent of emissions resulting from soil cover caused damage to human health under the sub-categories of carcinogens and respiratory effects. To further evaluate this, the LCIA results were characterized based on the input products and processes for the soil cover system (Figure 8-15). A large percentage of contribution by the process of excavating and spreading the soil was found to have resulted in elevated levels of impact to human health under the two sub-categories. This can most likely be attributed to the much larger quantity of materials that need to be handled in the case of soil cover systems to achieve zero methane emissions (Table 8-2). The benefits of incorporating the effects of recycling waste wood to produce the required quantity of biochar in the biochar cover system scenarios indicated that the amount of emissions avoided due to the treatment of waste and the associated processing of forest products overshadowed the impacts resulting from the process of transportation, excavation and placement of the cover materials (Figure 8-16).

(a)



(b)

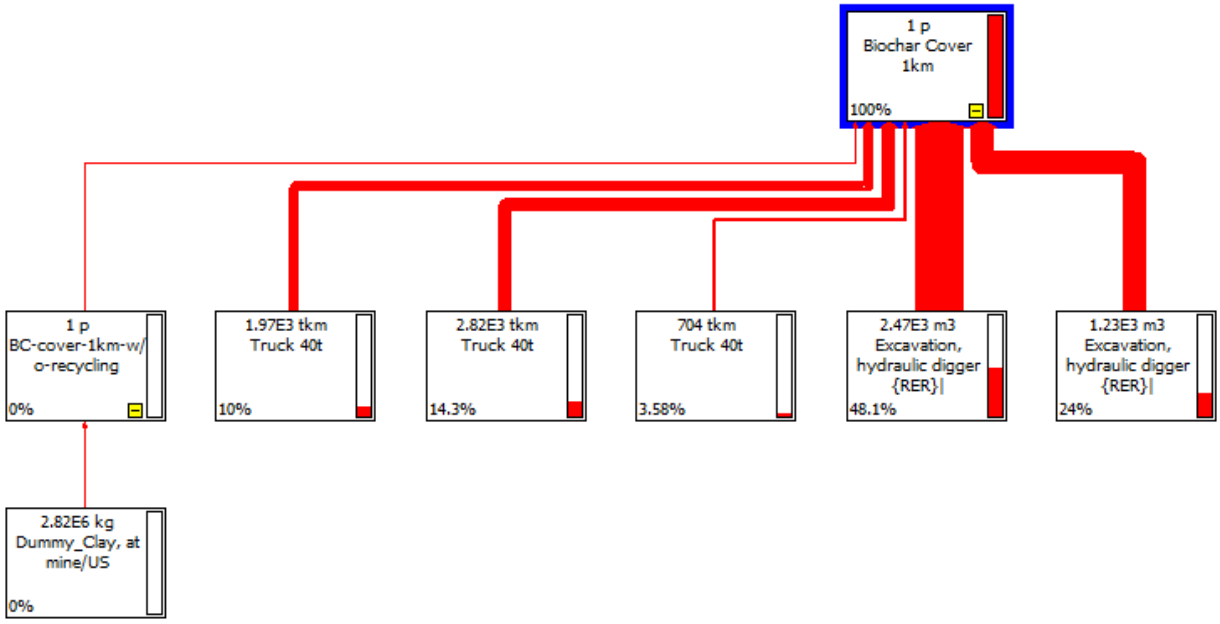
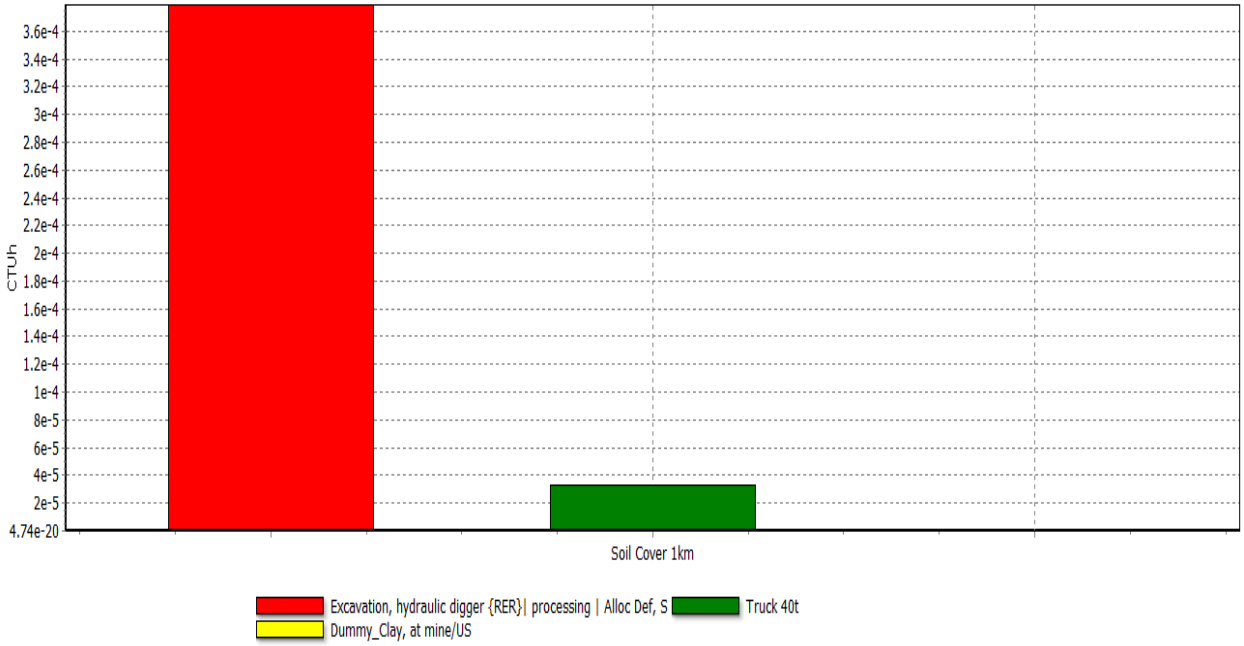


FIGURE 8-14: ECO-INDICATOR (99) SINGLE SCORE TREE DIAGRAM FOR (A) SOIL COVER AND (B) BIOCHAR COVER IF THE COVER MATERIALS ARE AVAILABLE ON-SITE

(a)



(b)

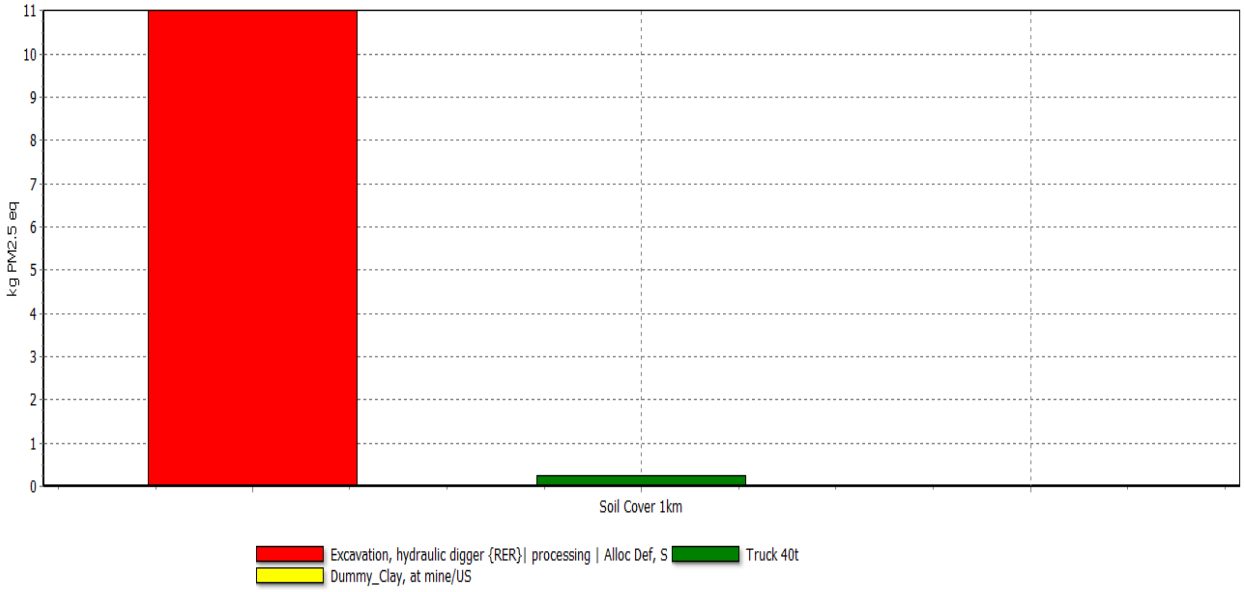


FIGURE 8-15: TRACI 2.1. LCIA RESULTS TO EVALUATE THE SOURCE CONTRIBUTIONS TO (A) CARCINOGENS AND (B) RESPIRATORY EFFECTS FOR SOIL COVER SYSTEM

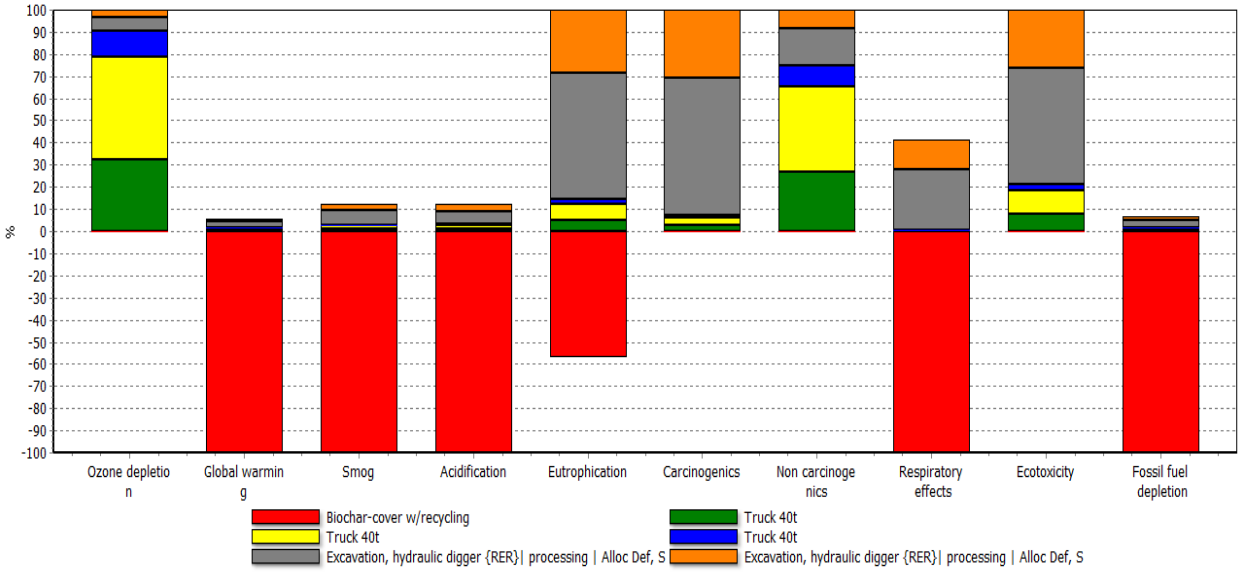
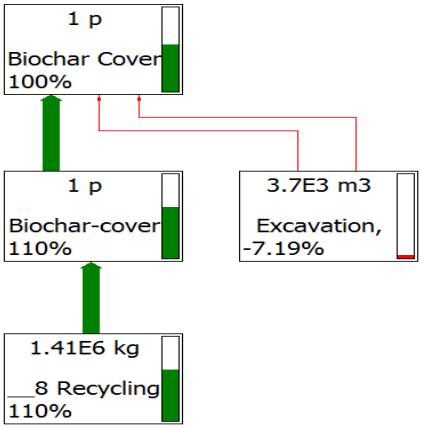


FIGURE 8-16: TRACI 2.1. LCIA RESULTS TO EVALUATE THE EFFECTS OF WASTE WOOD RECYCLING AND TO IDENTIFY THE SOURCE CONTRIBUTION TO OVERALL BENEFITS

The breakdown of the top processes and the specific sub-processes that resulted in an overall benefit in this case of biochar cover system has been presented in the form of a network diagram in Figure 8-17. Including the effect of recycling generates a net positive impact of 110% and a net negative impact of -7.19% from the process of transportation and cover placement. Further breakdown of the process tree specific to the contribution of positive impacts incurred from recycling indicated that a large portion of the benefit (180%) arises from the avoided emissions from forest products (i.e. the energy and resources spent on logging and chipping of forest wood). A small portion of the benefit (16.1%) arises from the avoided emissions which could have otherwise resulted from the treatment of waste wood.

(a)



(b)

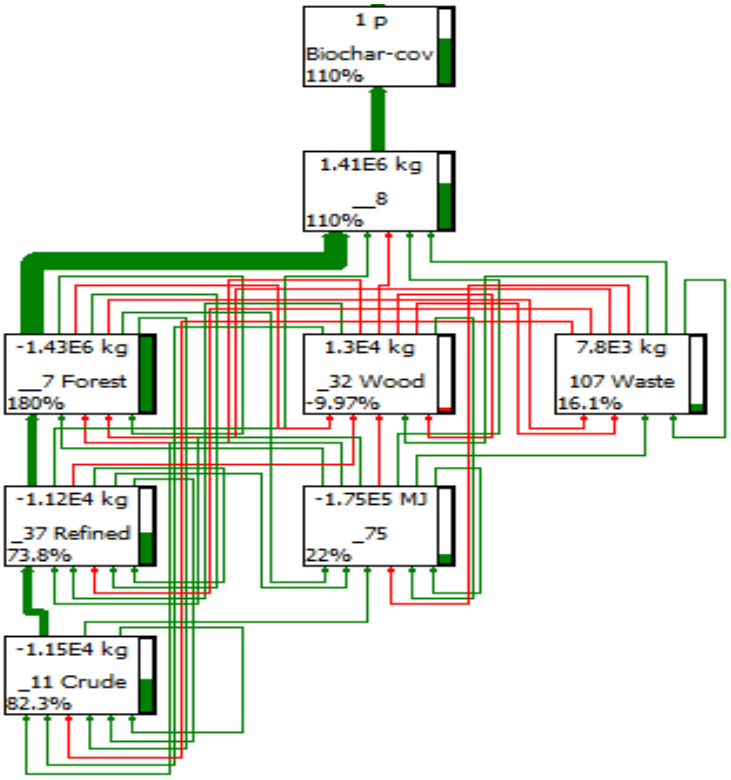


FIGURE 8-17: ECO-INDICATOR (99) SINGLE SCORE NETWORK DIAGRAM TO EVALUATE THE BENEFITS OF RECYCLING WASTE WOOD FOR (A) TOP PROCESSES AND (B) SPECIFIC SUB-PROCESSES CONTRIBUTING TO RECYCLING IF THE BIOCHAR COVER MATERIALS ARE AVAILABLE ON-SITE.

8.5.2 Economic Sustainability Cover Systems

The total costs incurred for the cover system scenarios compared in Table 8-3 does not account for the production cost for biochar if assumption is made that it is available on-site. However, it is to be noted that the production costs for biochar can be as low as USD 0.1/kg (Jiang et al. 2013). The use of a mobile, on-site reactor unit for biochar production has been highly recommended for use in sites where a large area of native soil needs to be amended with biochar for the purpose of remediation and/ or vegetation (Petelina et al. 2014). The total cost to cover 1 acre of the landfill site using the biowindow design including the cost for production of the biochar is still under USD 300,000 which implies that this option is more economically sustainable compared to the soil cover option. If the production costs for biochar are accounted for the biochar cover (option 2), then the total cost incurred would be approximately USD 170,000. However, due to the much larger quantity of biochar that needs to be produced for this option, there could be other additional costs incurred due to longer duration of the rental period for the mobile reactor and its associated operation and maintenance costs. The option of acquiring biochar from the market and transporting it to the site appears to be the least economically favorable.

8.5.3 Social Sustainability Cover Systems

The social impacts resulting from the different cover system scenarios were quantified by assigning scores for each sub-category under five different stakeholder groups (Table 8-4). The scores were assigned in the rating chart to assess the metrics for social impacts based on the following justifications:

- Under the category of 'workers', a total score of -4, +1, -3 and +2 was assigned to the options of soil cover, biochar cover (on-site), biochar cover (off-site) and biowindow design

respectively. Larger material quantities imply longer working hours spent in a landfill for cover construction. This impacts the welfare of the workers as they might be under the pressure of completing the landfill closure activities within a stipulated timeframe to meet the regulatory requirements (i.e. 180 days from the start of final cover installation without having to apply for further approval to extend this timeframe allowed by EPA). Transport of large quantities on biochar can cause longer driving times for the truck drivers impacting their welfare which is avoided in options 2 and 4 wherein, the biochar is assumed to be produced on-site. The handling of large quantities of soil in option 1 is likely to cause greater health effects on workers due to longer duration of exposure to dust from cover construction. For the option 3, the continuous movement of trucks transporting biochar from off-site sources to the construction site is likely to cause dusty atmosphere around the workers thereby resulting in probable health effects. In the case of biowindow design, the health effects can be very minimal due to on-site production and minimal amount of materials that need to be handled.

- Under the category of 'consumers', no impacts are thought to be caused.
- Under the category of 'local community', the health and safety impacts from the options 1 and 3 are likely to be negative due to large quantity of cover materials that need to be excavated and placed (option 1) and excessive truck traffic in the surrounding community (option 3).
- Under the categories of 'society' and 'value chain actors', the use of biochar-based cover systems can promote the supplier relationships and help with the growth of local businesses (for ex., biochar vendors, infrastructure and energy supply businesses for on-site biochar production, gravel and trucking companies if materials are acquired from off-site sources).

8.6 Conclusion

The 'triple bottom line' approach for sustainability assessment was systematically adopted in this study to quantify the environmental, economic and social metrics resulting from the use of soil cover and biochar cover systems that were designed to achieve zero methane emissions if implemented for closure of landfills in Northeastern IL. Based on the analysis, the following conclusions can be derived:

- The design of biochar-based final cover system resulted in more compact design configurations (i.e., lower values for cover depths) compared to conventional soil cover systems thereby, considerably reducing the overall quantity of materials that need to be handled on-site during the cover construction.
- The assumptions pertaining to whether or not the biochar cover materials are available on-site significantly affected the resulting environmental impacts; the process of transporting large quantities of biochar in the case of biochar cover systems resulted in much greater environmental impact and this option also proved to be economically as well as socially least favorable among the other options evaluated.
- The incorporation of recycling into modeling the environmental impacts resulted in a net environmental benefit of using biochar and considerably reduced the emissions to values lower than that of soil cover system even if the biochar cover materials were assumed to be transported by a distance of 100 km.
- The uncertainty analysis indicated that the variation in LCIA results using SimaPro is expected to range between 16 – 30% for soil cover system and 3 – 25% for biochar cover systems if the oxidation rates of the cover materials assumed during the design of cover configurations were varied to encompass the reported values from literature.

- The use of biowindow configuration for field application to achieve zero methane emissions resulted in the lowest levels of environmental and social impacts among all the cover system options evaluated; the most cost-effective option was the biochar cover system wherein the materials were assumed to be available on-site; however, for this option the hidden costs associated with the production of a much larger quantity of biochar can considerably impact this assessment. The results from this study are very specific to the system boundaries and the associated assumptions which have to be carefully noted. In the environmental impact analysis, no credit was assigned to account for the expected amounts of carbon sequestration in the long term for the biochar cover options and the emissions associated with the production of biochar was not considered. It should also be noted that social sustainability assessment is subjective, and it can vary among assessors based on their individual perception. A more methodical and definitive quantification tool to assess the social sustainability impacts need to be further developed to better incorporate this aspect of triple bottom line into future projects.

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9. OVERALL CONCLUSIONS AND FUTURE RECOMMENDATIONS

9.1 Overall Conclusions

The applicability of seven different types of wood-based biochars as cover materials to target the methane emissions in landfills was investigated in this study. The research was carried out systematically by characterizing the physical-chemical and engineering properties of the biochars and determining the changes to these properties when they are added to landfill cover soil. The physical-chemical characterization studies helped understand the suitability of biochar application to landfill cover soils from an environmental stand point (for ex. changes caused to pH of soil) while the engineering properties helped understand the feasibility of using biochars from the technical stand point of the overall strength and stability of the cover system (for ex. stability of slopes). Since biochars exhibited high porosity and surface area, adsorption of methane was expected to significantly contribute to the overall extent of methane reduction possible in biochar-based landfill cover systems. In order to quantify the amount of methane that can solely be adsorbed and transported through the biochars and biochar amended soils, a series of small-scale batch adsorption and column transport studies were designed to quantify the effects of different factors such as biochar type, varying moisture, temperature, selected biochar types to soil amendment ratios and exposed levels of methane concentrations on the overall methane reduction. The results from this study helped with the quantification of kinetic rate constants for methane adsorption and the maximum methane adsorption capacity in addition to the reactive transport parameters (i.e., dispersion coefficients). Further, the effects of biochar properties on their adsorption capacity were evaluated to determine the most significant properties of biochar that can favor the adsorption in order to aid the screening of biochars prior to use in landfill cover systems.

To further the understanding of the methane adsorption capacity by biochars, all the batch adsorption and transport tests were replicated using granular activated carbon (GAC) which is widely used as a common adsorbent for dealing with removal of both gas-phase and aqueous-phase contaminants. This can help with perceiving the adsorption capacity results obtained for the biochars in a more practical sense.

Further studies were conducted to evaluate the effects of adding biochars to pre-incubated landfill cover soil and determine the resulting changes to the overall methane reduction which occurs because of combined processes including adsorption and bio-chemical methane oxidation. The batch incubation studies were designed to quantify the effects of varying temperature (4C – 45C), moisture (25% WHC – 75% WHC), selected biochar types and biochar to soil amendment ratio (0%, 2%, 5% and 10% by weight). Finally, a sustainability assessment was performed to compare and evaluate the environmental, economic and social metrics for the soil cover and the biochar-based cover systems that were designed for field-scale implementation to achieve zero methane emissions in Northeastern IL landfill sites. The results based on life cycle analysis and evaluation of sustainability metrics provided a much deeper insight into addressing some of the practical challenges associated with the implementation of field-scale cover systems. The information presented in this study can guide the decision-making process relating to landfill closures and help the landfill owners take advantage of this technology with a well-rounded understanding of the associated technicalities and the long-term benefits which can be achieved using the biochar-based cover systems in place of the conventional soil cover systems. However, further understanding relating to the performance of the biochar-based cover system is needed through experimental field-scale trials over longer periods of time in order to capture its design specificity and incorporate critical considerations pertaining to dynamic field environments.

The general conclusions from this research is summarized below:

- The physical-chemical characterization of biochars indicated that they have inherent properties such as high porosity and surface area, high organic and carbon contents among others, which considerably enhanced the methane adsorption capacity as opposed to that observed in landfill cover soil.
- Certain physical-chemical properties of biochars were found to strongly influence the resulting methane adsorption capacity while some other properties had minimal impact; however, the conclusions that are derived from this study were only limited to biochars with elemental carbon content ranging from 20 – 83% d.w.
- Biochar amendment to soil increases the porosity, water holding capacity and organic matter and decreases the density and specific gravity of soil which consequently improves the overall soil physical quality.
- Biochars and biochar-amended soils exhibit higher axial strains as they are more compressible compared to soil and the values of constrained moduli for biochars and biochar-amended soils are presented in this study which can be used to compute the expected settlement to account for in the design of biocbar-based cover systems
- The shear strength of moist soil was considerably enhanced by the addition of biochars; the amendment of selected biochar types to soil at 10% amendment ratio, in the presence of 15% moisture, resulted in a decrease of cohesion and increase of frictional angle as compared to dry biochars.
- The factor of safety for stability of cover slopes was increased by about two times by amending biochars to cover soil under drained conditions.

- Sorption experiments indicated that the modeled dispersion coefficients for the biochars and GAC decreased with increasing levels of moisture content; the effects of moisture on the transport of methane through biochars were less pronounced than that was reported to occur in soil.
- The use of a simple, linear sorptive model was found to be sufficient to determine the transport characteristics of methane through the small-scale biochar columns; however, the non-equilibrium, non-linear behavior may be significant in determining the sorptive behavior of biochars in a transport-driven conditions, especially as the final covers are expected to be subjected to highly variable mass flowrates and concentrations of CH_4.
- The extent of CH_4 transport through soil (by accounting for adsorption) was two orders of magnitude lower compared to all biochar-amended soils.
- The amendment of even a small quantity of biochar (2% by weight) to soil dramatically increased the CH_4 transport and adsorption within the cover material by at least one order of magnitude implying the significant scale of impact that the addition of biochars can produce within a landfill cover system which can increase the adsorption of methane.
- Adding fresh, un-incubated biochars to landfill cover soil significantly inhibited the methane oxidation rates of the soil irrespective of biochar type, amendment ratio and the test conditions (i.e., moisture and temperature); the extent of inhibition in the methane oxidation rates were significantly different for different biochar types and consistently increased with increasing levels of biochar-amendment percentages; these results reflect the importance of pre-incubating the soil with biochar for sufficient amount of time under conditions that are expected to occur in landfill covers prior to estimating the maximum methane oxidation capacity for biochar-based cover systems; this is a critical finding

pertaining to the development of design guidelines for the application of biochar-based cover systems.

- The optimum conditions for methane oxidation in soil control and different biochar-amended soils occurred at a temperature range of 25 - 35°C and at a moisture content close to the water holding capacity of the cover materials (75% WHC) and these results agree with those ranges reported in the literature for compost and other biocover materials.
- The percent contribution to the extent of overall methane mitigation observed in the batch incubation chambers by rapid adsorption process was quantified against the combined adsorption and oxidation process; this is critical information which can be used to model the processes that control the migration of methane through biochar-based cover systems.
- Environmental sustainability analysis indicated that the use biochar-based cover systems resulted in much lower environmental impact compared to the soil cover systems (assuming that the cover materials were available for use on-site); the effect of recycling waste-wood in the form of biochar was accounted for in the LCA and indicated that this process produced significant positive impact on the environment compared to soil cover systems.
- A biowindow design configuration was recommended for field-scale implementation as it resulted in least levels of negative impacts compared to the soil cover design under all the three dimensions of sustainability assessment (i.e. environmental, economic and social); this indicated that the cover system can be designed and implemented as a biowindow as opposed to a biocover which minimizes the amount of biochar needed for the cover construction and also provides the room for increasing the biochar amendment levels to

soil during the design phase without compromising on the practical considerations pertaining to cost and ease of implementation.

9.2 Recommendations for Future work

Based on the general conclusions derived from this research, directions for future work is recommended with the aim of furthering the use of biochar-based cover systems and assist with the development of design guidelines to address the current knowledge gaps pertaining to large-scale design and field implementation. The following recommendations are suggested as a path forward in this field of research:

- This study was centered around characterizing and testing the feasibility of using biochars derived from waste wood (i.e. hardwood mixes of pine, fur and likewise) subjected to different conversion processes; however, in reality the use of locally available biochars from bioenergy crops would increase the probability of promoting this technology; thus, it is important to also test the feasibility of using biochars from different feedstock as potential landfill cover amendment for methane mitigation.
- The hydraulic properties of biochar-amended soils must be further evaluated in order to understand their potential impact on minimizing the amount of water percolation through the cover systems (i.e. in other words study the overall water balance of the field-scale biochar-based cover systems and understand the effects of using this technology from the standpoint of leachate generation).
- Long-term column experiments have to be conducted to evaluate the synergistic effects of methane adsorption and oxidation in simulated landfill cover environments; the effects of varying cover configurations such as the placement depths of the biochar-amended soil or

the biochar solely as a thin layer sandwiched between two cover soil layers have to be evaluated prior to making design recommendations for field-scale application of biochar-based cover systems.

- Detailed microbial analyses must be performed in the biochar-amended soils extruded from the long-term column oxidation tests in order to understand the changes to the microbial community structure and population of methane oxidizing bacteria resulting from the addition of biochar.
- Field-scale studies must be conducted in order to understand the effects of spatial, temporal and seasonal variation in the performance of biochar-based cover systems and capture any possible challenges associated with the large-scale implementation.
- Additional tests need to be conducted to further evaluate the observed inhibition in the rates of methane oxidation during the pre-incubation stages and identify if any specific inhibiting compounds are being produced that directly or indirectly affects the growth and activity of methane oxidizing bacteria.
- A comprehensive 1-D numerical model needs to be developed and validated by accounting for the effects of moisture and temperature on the diffusion and biochemical methane oxidation processes that occur within the biochar-based cover system

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