**Effects of biochar and wood pellets amendments added to landfill cover soil on microbial methane
oxidation: A laboratory column study**

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1 **ABSTRACT:** Alternate landfill covers designed to enhance microbial methane (CH₄) oxidation and
2 reduce the negative impacts of landfill gas emissions on global climate have recently been proposed and
3 investigated. In this study, the use of biochar as a soil amendment is examined in order to assess the
4 feasibility and effectiveness for enhanced CH₄ removal in landfill covers when incorporated under high
5 compaction conditions and relatively low soil moisture. Four different cover configurations were tested
6 in large soil columns for ~510 days and potential CH₄ oxidation rates were determined following long-
7 term incubation in small batch assays. Cover designs tested include: a thin biochar layer at 15 to 18 cm;
8 2% mixed soil-biochar layer at 20 to 40 cm; 2% mixed soil-uncharred wood pellets at 20 to 40 cm; and
9 soil obtained from intermediate cover at an active landfill site. The placement of a thin biochar layer in
10 the cover significantly impacted moisture distribution and infiltration, which in turn affected CH₄
11 oxidation potential with depth. An increase in CH₄ removal rates was observed among all columns over
12 the 500 day incubation period, with steady-state CH₄ removal efficiencies ranging from ~60 to 90% in
13 the final stages of incubation (inlet load ~80 g CH₄ m⁻² d⁻¹). The thin biochar layer had the lowest
14 average removal efficiency as a result of reduced moisture availability below the biochar layer. The
15 addition of 2% biochar to soil yielded similar CH₄ oxidation rates in terminal assays as the 2%
16 uncharred wood pellet amendment. CH₄ oxidation rates in terminal assays were positively correlated
17 with soil moisture, which was affected by the materials' water holding capacity. The high water holding
18 capacity of biochar led to higher oxidation rates within the thin biochar layer, supporting the initial
19 hypothesis that biochar may confer more favorable physical conditions for methanotrophy. Ultimate
20 performance was apparently affected by soil type and CH₄ exposure history, with the highest oxidation
21 rates observed in the unamended field soil with higher initial methanotrophic activity.

22

23 **Keywords:** Greenhouse gases; Climate change; Methanotrophy; Biocovers; Landfill gas emissions

1. Introduction

Methane (CH₄) generated from landfills is a serious concern for both society and the environment due to its high global warming impact (~25 times greater than CO₂ over a 100-year time period; IPCC, 2013). Biocovers have been identified as a key mitigation strategy to target low-level methane emissions that would not otherwise be captured by landfill gas (LFG) extraction systems and have thus been the subject of recent research investigating alternative landfill covers for enhanced methane removal via microbial oxidation (Sadasivam and Reddy, 2014). The majority of these alternate landfill covers involve the amendment of cover soils with organic-rich materials (e.g. compost) either over large areas (i.e. biocovers) or in targeted zones of high gas emissions (i.e. biowindows/biofilters), requiring significant changes to current cover construction and monitoring practices. A number of studies have investigated the use of organic amendments to landfill cover soils as a means of promoting microbial activity and biotic methane oxidation (e.g. Barlaz et al., 2004; Bogner et al., 2010; Scheutz et al., 2011), though our laboratory is the first to investigate the use of charred organic matter (biochar) as a possible soil amendment in biocovers and biofilters (Yaghoubi, 2011; Reddy et al., 2014; Sadasivam and Reddy, 2015a, b).

Biochar is produced via the pyrolysis or gasification of organic matter in environments with low or zero oxygen (Reddy et al., 2014). This process yields three products – biogas, bio-oil and biochar - the first two of which are commonly used for sustainable energy generation (Laird, 2008). The solid product (biochar) contains a more stable form of carbon than the initial feedstock, prompting interest for its use as a sink for atmospheric CO₂ (Spokas and Reicosky, 2009). Because biochar is composed of more recalcitrant forms of carbon than alternative cover amendments, such as compost, biochar may be more suitable for long-term applications due to lower rates of biodegradation of the cover material. Biochar also has a number of favorable characteristics – such as a high internal porosity, specific surface area,

1 and high water-holding capacity – that also contribute to improving soil cover conditions for microbial
2 CH₄ oxidation (Reddy et al., 2014; Yargicoglu et al., 2015). Studies investigating biochar application to
3 agricultural and natural soils have also reported positive impacts on soil fertility, including increases in
4 soil pH, nutrient retention and availability, and cation exchange capacity (e.g. Glaser et al., 2002; Chan
5 et al., 2007; Mukherjee et al., 2014). Thus biochar amendment may also be suitable for use in vegetated
6 final covers on landfills.

7 Biochar has a long lifetime in soils, with some reports of biochar having a half-life in soil on the
8 order of several hundred days to years (Steinbess et al., 2009; Bolan et al., 2012). Biochars are able to
9 store soil carbon effectively over long timescales, and thus have recently been investigated as soil
10 amendments to enhance carbon sequestration (e.g. Spokas and Reicosky, 2009) in addition to their use
11 in landfill cover soils (Reddy et al., 2014; Sadasivam and Reddy, 2015a, b). Other alternative covers
12 evaluated in previous studies have utilized materials that would require special design considerations not
13 compatible with current practice (e.g. compost biocover; Barlaz et al. 2004). As a result, many of these
14 designs may not be easily incorporated into current landfill cover configurations, potentially limiting
15 their widespread use. In addition, the methane oxidation removal of these materials in laboratory studies
16 may not adequately reflect their expected performance when constructed in the field, generally with
17 relatively high degrees of compaction.

18 The present study investigates biochar-amended soil covers under field-relevant conditions using
19 biochar amendment applied either to small sections of the cover depth or to the entire depth profile. In
20 order to investigate the performance of biochar-amended soils as alternate landfill covers, two sets of
21 large soil column tests were conducted in conjunction with a field study performed at an active landfill
22 site in northeast Illinois (Yargicoglu, 2016). This paper compares the results obtained from monitoring
23 four columns under simulated landfill cover conditions. One column (C5) was constructed with biochar

1 applied only at 15 to 18 cm depth in order to compare the performance of biochar applied in
2 concentrated layers versus homogenous soil-biochar mixtures applied over larger depth zones (i.e. 20 to
3 40 cm depth). The second column (C6) was constructed with 2% biochar amended to 20 to 40 cm depth;
4 fine ash was retained in the biochar before adding to soil in order to evaluate the impact of higher ash
5 content on the methane removal efficiency over time. A third column (C7) was constructed in the same
6 manner as C6 using the raw, uncharred wood pellet feedstock used by the vendor to produce the pelleted
7 biochar investigated in this study in order to examine the impact of charring biomass on its effectiveness
8 as a soil cover amendment. The fourth column (C8) was an unamended soil (no biochar added) utilizing
9 sieved soil obtained from an intermediate cover area at the site of related field tests ([Yargicoglu, 2016](#))
10 in order to establish the expected performance of unamended cover soil and facilitate comparisons
11 between performance in field trials and laboratory tests.

12 Specific objectives of these column tests were to: (1) evaluate biochar-amended cover performance
13 under high compaction conditions at an initial moisture content lower than the optimal moisture content
14 (OMC) in terms of standard geotechnical engineering practice; (2) determine the performance of
15 unamended soil cover using sieved field soil from an active intermediate landfill cover in order to assess
16 variability among field and laboratory studies due to differences in soil type; (3) compare performance
17 of biochar-amended soil with soil amended with uncharred pinewood pellets (i.e. raw feedstock) to
18 investigate the impact of charring organic amendments prior to adding them to cover soils. It was
19 hypothesized that the high water holding capacity and internal porosity of biochar would promote the
20 growth of methane-oxidizing bacteria more readily than wood pellet amendment or unamended soil.

21

22 **2. Research Methodology**

23 *2.1 Column setup and design configurations tested*

1 A column test employing acrylic columns (1 m height; 18.4 cm ID) was performed to simulate
2 landfill cover conditions and evaluate the performance of each cover under controlled CH₄ input using
3 synthetic landfill gas (60% CH₄, 40% CO₂). Atmospheric air was passed through an in-line filter and
4 humidification tank and fed into the headspace of each column in order to provide sufficient O_{2(g)}
5 necessary for CH₄ oxidation to proceed. Inlet and outlet flow rates were monitored continuously using a
6 series of three-way valves and rotameters placed at the inlet and outlet lines of each column. Soils were
7 sieved through a 2-mm sieve and homogenized prior to adding moisture to ~6 to 7% dry wt. basis and
8 added to the columns in ~5 cm layers above the gas distribution layer, which was the same thickness (60
9 cm) for all column tests. Due to the large quantity of soil required for the column experiments and
10 concerns regarding removing excess soil cover from an active landfill, our research team was not
11 permitted by the landfill operators to obtain sufficiently large quantities of soil directly from the
12 intermediate cover for all column tests. Instead, we were permitted to take soil for further experiments
13 from the stockpile immediately adjacent to the active landfill, which was of the same soil type currently
14 in use for soil cover at the DeKalb site. As a result, two soil types obtained from different landfill sites
15 were employed: in C5, C6 and C7, silty clay soil from the DeKalb landfill (DKLF) used in prior column
16 tests was used. The soil used in C8 (ZLF) was obtained from the site of a related field trial (Zion, IL) for
17 comparison of laboratory and field studies. However, the extent of prior methane exposure, and thus the
18 extent of colonization and activity of methane oxidizing bacteria within the soil from the stockpile
19 (DeKalb) and the intermediate cover soil (Zion) likely differed significantly.

20 A 30 cm thick gas distribution layer composed of clean pea gravel retained on 4.75 mm sieve was
21 placed below the amended soil columns to allow uniform flow of synthetic landfill gas to the base of the
22 columns. A schematic of the cover profiles tested is shown in **Figure 1**. Cover soils were compacted to
23 bulk densities of ~1.51 to 1.62 g/cm³ in the columns using a 7-lb tamping rod during setup. These

conditions are not expected to be ideal for CH₄ oxidation, as compaction reduces the total porosity and air-filled porosity of the cover. However, it was determined that the laboratory columns should be constructed in a manner reflective of typical field conditions (i.e. high degree of compaction applied) in order to evaluate the practical use of alternative landfill cover designs without significant alterations to current construction practices.

2.2 Determination of methane removal efficiency in long-term column tests

A mass balance approach was used to calculate the amount of CH₄ removed by each column as has been done in prior work on landfill covers employing column incubation tests (e.g. [Kightley et al., 1995](#); [Rachor et al., 2011](#); [Gebert et al., 2011b](#)). Methane removal efficiency (MRE, %) was calculated based on a methane mass balance as shown in **Equations 1** and **2**. Influent and effluent gas flow rates from the columns were monitored via NIST-certified calibrated digital mass flow meters (Aalborg Model No. GFM-17A-VDL6-B0). Additional rotameters (Cole-Parmer, Model No. PMRI-010874) were also employed following an in-house calibration against the calibrated digital mass flow meters, allowing for simultaneous measurement of inlet and outlet flows to the entire system and each individual column. Inlet flow rates were checked and manually adjusted as needed throughout the experiment. In addition to calibration of the flow meters used to control the inlet flow of synthetic landfill gas and headspace air, uniform flow among the columns during the experiment was verified through the use of soap-film rotameters. Additional independent verification of uniform air flow to the columns was performed by checking the pressure in the headspace of each column using Setra Model 264 ultra-low pressure differential pressure transducers. These measurements confirmed that the air flows into each column were maintained at equal levels.

Outlet flow rates were measured out of each column separately during measurement of headspace gas concentrations in order to determine the outlet flux (J_{out}) from each column according to **Eq. 1** below:

$$J_{out} = \frac{Q_{out} \times C_{out}}{A} \quad (1)$$

where Q_{out} = outlet flow rate of gas exiting the column, ml/min; C_{out} = CH_4 concentration, mol/m³; and A = cross-sectional area, m².

Methane removal efficiency (MRE, %) was determined from the following equation:

$$MRE = \frac{(J_{out} - J_{in})}{J_{in}} \times 100\% \quad (2)$$

where J_{in} is the inlet methane flux (mol CH_4 d⁻¹ m⁻²) and J_{out} is the outlet methane flux (mol CH_4 d⁻¹ m⁻²). This methodology to estimate methane removal from soil columns has been used and validated by a number of prior studies investigating landfill covers (e.g. [Rachor et al., 2011](#); [Gebert et al., 2011b](#)).

Gas samples were withdrawn from sampling ports installed along the sides of the columns and in the headspace using a luer-lock syringe and analyzed using gas chromatography (GC). CH_4 was detected using either an HP 6890 GC equipped with a flame ionization detection (FID) and GS-Carbon Plot column for low concentrations (< 1%) or using an SRI 9300 GC equipped with a thermal conductivity detector (TCD) and CTR-1 column capable of separating N_2 and O_2 for simultaneous analysis of CO_2 , CH_4 , O_2 and N_2 [CH_4 detection limit $\geq$ 1%]. A calibration curve was constructed using ultra-high purity CH_4 standards (AirGas™, Elk Grove, Illinois) at concentrations ranging from 0.1% to 50% v/v in order to calculate CH_4 concentrations from the peak areas detected on the GC. The SRI GC equipped with a TCD was calibrated using standards ranging from 1% to 50% CH_4 and standards ranging from 5% to 50% CO_2 . Calibration curves for CH_4 and CO_2 were constructed from a minimum of 3 points.

2.3 Characterization and monitoring of physicochemical properties in cover materials

Physical and chemical properties characterized at setup were limited to water content (ASTM, 2010); organic matter content (ASTM, 2014); soil pH, oxidation-reduction potential and electrical conductivity (ASTM, 2007a); and particle size distribution (ASTM, 2007b). A data acquisition system (Campbell Scientific™ CR1000 Data Logger equipped with an AM16/32 B multiplexer) was used to continuously collect and record physical parameters at depth within the column substrate. Data was recorded every 15 seconds and averaged every 4 hours, allowing continuous monitoring of key soil parameters. Measurements of soil matric suction were recorded at 25 cm depth in each column using a Soil Measurement Systems™ column tensiometer. Prior to installation, the tensiometers were calibrated using an adjustable vacuum pump fitted with a vacuum gauge at several different pressures ranging from 0 to -100 kPa. Following calibration, the sensors were soaked in water for one day to fill the tensiometer cup; during the experiment the cup was refilled with sterile deionized water as needed. Volumetric water content, temperature, and electrical conductivity (EC) were monitored at three depths in each column (20, 35 and 50 cm bgs) using time-domain reflectometry (TDR) sensors (CS655-L, Campbell Scientific™).

2.4 Long-term column incubation and performance monitoring

Due to time and equipment availability restrictions, performance of the soil columns was monitored on a periodic basis and detailed monitoring was limited to 2 of 4 experimental stages (Stage I and III) outlined in **Table 1**. These stages were defined by the CH₄ load applied and the time elapsed since initial exposure to synthetic landfill gas. Prior to increasing the methane load in Stage I, an in-place pre-incubation stage was applied to acclimate the methane-oxidizing bacterial communities within the cover soils for ~65 days. During this time an inlet flow rate of ~7 ml/min of 1% or 0.1% CH₄ and 99 to 99.9%

N₂ gas was continuously applied to the base of the columns ($J_{in} \sim 1.5 - 2.5 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) and the headspace of each column was flushed with filtered atmospheric air at ~5 to 10 ml/min.

The initial methane load applied in Stage I was selected based on that expected for intermediate landfill covers ($<100 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$), and was increased incrementally in order to observe the performance of the columns at higher CH₄ loads during Stage II. A slightly lower CH₄ load was applied in the latter stages III and IV as it was observed that none of the columns achieved 100% CH₄ removal efficiency at the higher loads applied ($> 100 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$). LFG incubation was continued at a low CH₄ load (~3 to 5 ml/min or ~65 to 100 g CH₄ m⁻² d⁻¹) for several months in order to determine whether removal efficiency would improve over time. Inlet air was humidified and flushed the headspace continuously at flow rates ranging from 10 to 20 ml/min. Precipitation events (50 ml H₂O per event) were simulated by applying sterile deionized water to the tops of the columns via a syringe at a rate of ~2.5 ml/min. The columns were evaluated again after ~300 days under continuous LFG incubation and results were averaged over a period of 47 days for Stage III (Days 426 to 474). Detailed monitoring was conducted after the system stabilized in Stages I and III and checked periodically during Stage II to ensure the system was operating properly. Due to limited data obtained during Stage II, only Stages I and III are evaluated and discussed in detail. The experimental stages of column testing are summarized in **Table 1**. Total test duration was approximately 510 days before the columns were exhumed and sampled.

2.5 Terminal sampling and characterization of exhumed column soils

Following long-term incubation with synthetic landfill gas, the columns were exhumed and terminal characterization of key physical (moisture content, grain size analysis) and chemical properties (pH, organic matter content) was performed using the same procedures as for initial characterization at

10, 30 and 50 cm depth. Soil samples were taken from freshly exhumed columns at these three depths for terminal batch incubation assays to determine the CH₄ oxidation potential of the cover substrates. Additional samples obtained from the biochar layer at 16 to 18 cm depth from C5 were subjected to the same tests as all other samples. Samples were taken throughout the column profile during exhumation for moisture and organic content determination. Samples (~30 g) for microbial batch assays were collected with sterile spatulas from the center of the columns at each depth targeted and collected in sterile glass vessels, homogenized, and immediately placed into sterile 125 ml glass vials. Vials were then pre-incubated for 72 hours in the presence of 5% CH₄ and 5% CO₂ prior to beginning batch assays. All sterilization was performed via autoclaving for a minimum of 2 cycles (1 hour at 121°C and ~1.5 bar) using a Napco™ Model 8000-DSE autoclave in order to prevent cross-contamination of the microbial test units.

2.6 Determination of terminal reaction rates and data analysis

For batch assays, a known quantity of methane was placed in the vial headspace after removing an equal volume of gas and its rate of degradation was monitored over time by sampling 1 ml of headspace gas periodically until all of the CH₄ was consumed. CH₄ oxidation rates were determined from the linear slope of CH₄ versus time as zero-order reaction kinetics was observed in all samples. CO₂ production and O₂ consumption rates were also determined based on linear regression of the degradation curves. All batch assays were performed in duplicates and the results averaged, with the exception of 2 sets of soils ($n = 4$; sampled from 30 and 50 cm in C5) with very low rates of CH₄ oxidation and soil respiration in Trial 1. In order to attain maximum oxidation rates and to avoid the possibility of excessively long lag phases due to methane deprivation, 30 grams of freshly exhumed soil samples were pre-incubated in 5% CH₄ for 72 hours inside sterile 125 ml serum vials (Wheaton Glass, Millville, NJ) sealed with red butyl

rubber septa (Grace, Deerfield, IL) after replacing 10 ml of headspace gas with 50% CH₄/50% CO₂ prior to initiating the first trial. The same procedure of pre-incubating the test units for 72 hours with a vial headspace of 5% v/v CH₄ was also performed following Trial 1 prior to initiating Trial 2 in order to maintain microbial activity and estimate the maximum potential oxidation rates. Statistical analysis of batch test results (t-tests for equivalency of sample means; $\alpha = 0.05$) was performed using OriginPro™ (version 9.1) software.

3. Results

3.1 Physical properties of soil and biochar-amended soil columns

The initial physical properties of the cover substrates are summarized in **Table 2**. All columns were compacted to bulk densities of ~1.5 to ~1.6 g/cm³, resulting in initial estimated air-filled porosities of ~30 to 33%. Initial moisture content was set to ~30% of the materials' water holding capacities, or ~6.5% gravimetric water content in Columns 5, 6 and 7. A higher initial gravimetric water content was achieved in C8 due to its higher water holding capacity (~53% dry wt. basis), compared to only ~20.9% dry wt. for the sieved DeKalb landfill cover soil.

Grain size distributions of the cover materials are illustrated in Figure S-1, Supplemental Information. The biochar layer had a much higher fraction of gravel-sized (~19.4% > 4.75 mm) and sand-sized (~73% between 0.075 to 4.75 mm) particles than both types of unamended cover soils included in this study. The USCS soil classification for the DeKalb landfill cover soil (DKLF) used in C5, C6 and C7 is a silty clay (CL-ML), containing ~38 to 40% sand, ~22 to 27% clay, and ~31 to 39% silt. Atterberg limits for the DKLF soil indicated it was a low-plasticity clay (PL = 11.5%; LL = 17.7%; PI = 6.2). The ZLF soil in C8 contained ~19% sand, 28.7% silt and ~52.2% clay; USCS classification for this soil is a lean clay (CL) based on Atterberg limits (PL = 19.4%; LL = 32.5%; PI = 13.1).

Differences in soil texture also impacted the void ratios of the columns after compacting into soil columns, with average overall void ratios in C5, C6 and C7 of 0.74, 0.73, and 0.67 respectively, while in C8, the void ratio was significantly higher (0.98). Air-filled porosities were roughly equal among all columns (~30 to 33%) due to the proportional addition of water relative to the materials' water holding capacities.

Volumetric water contents recorded by the TDR sensors were lower than anticipated based on initial gravimetric water contents and dry densities of the cover materials, ranging from 2 to 2.7% vol. in C5; from 1.8 to 3.1% in C6; from 2.0 to 4.4% in C7; and from 4.9 to 6.5% in C8. Increases in volumetric water content were observed in most depths and columns over time, partly due to water production as a result of methane oxidation, as well as the application of sterile water during simulated precipitation events applied on seven different occasions (Day 64, 76, 146, 147, 161, 162 and 351) and continuous exposure to humidified air being passed over the tops of the columns. With the exception of increased temperatures on days 165 to 265 as a result of building renovations, temperature remained fairly consistent among the columns and over time, and was generally 23 to 24°C throughout all stages. Average values of volumetric water content, temperature, and electrical conductivity for each stage and depth are given in Table S-1, Supplemental Information.

Descriptive statistics of the tensiometer data for each column after removing erroneous values are given in Table S-2 in Supplemental Information. The data indicates that all columns were below field capacity and exerted matric suctions above the 50 kPa reported to be optimal for methanotrophy in landfill soils ([Spokas and Bogner, 2011](#)). Because of the high proportion of clay in the cover soils tested and unsaturated conditions, average soil suction values were relatively high, averaging from ~250 to 400 kPa. Generally higher matric suction values were recorded in C5 at 25 cm (average of ~400 kPa) relative to C6 and C7, reflecting the lower availability of moisture below the thin biochar layer. C8 had higher

average soil matric suction values (-375 kPa) than C6 (-292 kPa) and C7 (-251 kPa) despite its higher water content due to the soil having a higher proportion of hydrophilic clay particles (~52%).

The terminal soil moisture profiles at the time of exhumation and terminal sampling are illustrated in **Figure 2**. The placement of the biochar layer in C5 significantly impacted the distribution of soil moisture with depth by limiting downward infiltration of water below the biochar layer. The high water holding capacity of biochar itself (~33 % total mass; [Yargicoglu et al., 2015](#)) led to a concentration of water within the thin biochar layer, such that average water contents at the end of incubation within the biochar layer were ~21 % dry wt. as compared to soil moisture contents of ~5.3% to 6.2% dry wt. in the underlying soil (~18 to 60 cm depth). The soil above the biochar layer in C5 also had higher water content (~9.4 – 10.9% dry wt. at exhumation) relative to the lower depths as a result of reduced infiltration through the biochar. In the other columns, soil moisture was much more uniform with depth. Average gravimetric soil moisture was very similar among C6 and C7, ranging from ~8.8 to ~6.9% dry wt. at 0 to 5 and 50 to 60 cm depth in C6, respectively. In C7, average soil moisture in the upper depths was ~8.9% dry wt. and decreased to ~7.3% dry wt. in the lower depths of the column (50 to 60 cm depth) as shown in **Fig. 2**. Higher overall average soil moisture was maintained in C8 throughout testing and at exhumation, soil moisture ranged from ~13.1 to 13.5% dry wt..

Electrical conductivity increased over time in all columns and depths considered. Initial values were highest in C8 (0.013 dS/m at 50 cm up to 0.036 dS/m at 20 cm). Lower values were initially observed in C5, C6 and C7, though increases over time were observed, most significantly in C6 and C7. Average values in C6 increased from 0.0151 to 0.0203 dS/m at 20 and 50 cm, respectively, to 0.0357 and 0.035 dS/m by Stage III. In C7, electrical conductivity at 20, 35 and 50 cm depth increased from 0.0297 to 0.0501 dS/m, 0.0273 to 0.041 dS/m, and 0.0192 to 0.0372 dS/m, respectively. Lowest increases over time were observed in C5, with values increasing from 0.012 to 0.02 dS/m at 20 cm,

0.0175 to 0.0194 dS/m at 35 cm, and remaining relatively stable at 50 cm with average value of ~0.01 dS/m from pre-incubation through Stage III.

3.2 Chemical properties of cover materials

The chemical properties of the different cover materials used in column testing are summarized in **Table 3**. Organic matter content of the soil was increased by the addition of biochar and uncharred wood pellets as expected, with initial organic matter contents ranging from ~2.84% dry wt. in the 2% biochar-amended layer in C6 to ~3.62% dry wt. in the wood pellet-amended layer in C7. In C5, C6 and C7, the soil layers had much lower organic matter content compared to the treatment zones (20 to 40 cm bgs), ranging from ~0.7 to 0.9% organic matter per gram dry soil. In C8, however, the overall organic content was higher (average of ~2.62% dry wt.).

Terminal organic matter contents of soil and biochar-amended soil layers were not significantly different than those measured in initial samples, though slight increases in organic matter content were observed in the upper soil layers (i.e. 0 to 10 cm depth) of C5 (1.302% dry wt. $\pm$ 0.37) and C7 (1.441% dry wt. $\pm$ 0.21) as compared to initial contents of approximately 0.7 to 0.9% dry wt. Slight increases were also noted in the lower unamended soil layers (40 to 60 cm depth) of all columns, with average terminal organic matter contents of ~1.03% in C5, 1.46% in C6, 0.84% in C7, and 2.72% in C8. The greatest relative increase in organic content in the lower soil layers occurred in C6, increasing 49.6% on average relative to initial levels (0.98 $\pm$ 0.08% dry wt.) Increases in organic matter content in the upper and lower soil layers could reflect the proliferation of bacterial cells over time, as has been the case in prior column studies investigating soil amended with compost (e.g. [Pawlowska et al., 2011](#)). The thin-biochar layer in C5 did not degrade significantly over the experimental period (> 500 days), as the terminal organic matter content (~95.1% dry wt.) was comparable to the initial value of ~96.0% dry wt.

By contrast, the uncharred wood pellets placed in C7 did show obvious signs of microbial or fungal degradation, namely browning and physical disintegration of the wood pellets.

Soil pH was found to decrease slightly with the addition of uncharred wood pellets, with an average initial pH of 6.5 observed in the 2% wood pellet-amended soil added to C7. This compares to an average pH near neutral for un-amended cover soil of ~7.3 for both DeKalb and Zion cover soils (**Table 3**). Because the pH of the cover materials are all near neutral values, which are generally optimal for methanotrophic bacteria ([Hanson and Hanson, 1996](#)) it is not expected that pH differences will have a significant impact on the observed results. Moreover, terminal pH testing of the cover substrates following exhumation indicated all cover materials had fairly similar pH values by the end of the experiment, ranging from 7.5 to 7.8.

3.3 Methane removal efficiencies over time

Initial differences in the methane removal efficiency of the soil columns were observed during the pre-incubation phase (days 1 to 67) and immediately after increasing the methane load in Stage I (days 70 to 130; inlet load of $\text{CH}_4 \sim 90 \text{ g m}^{-2} \text{ d}^{-1}$). In general, the lowest methane removal efficiency was observed in C5 during the pre-incubation stage (average removal efficiency of ~24.4%) and the highest removal efficiency was observed in C8 (~88%). Removal efficiencies in C6 and C7 were 53.3% and 67.6%, respectively, during this period. Average and standard deviations for the outlet fluxes during each monitoring stage and during the pre-incubation stage are given in **Table 4**.

Removal efficiency decreased in all columns upon increasing the inlet CH_4 load to $\sim 90 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Stage I) following pre-incubation for all columns, with the exception of C5. Average CH_4 removal efficiencies ranged from ~25.5% [C6] and ~33.9% [C7], to ~45.1% [C5] and ~45.3% [C8] during Stage I (days 70 to 130). This is interpreted to reflect the adaptation stage of the methanotrophic communities

1 in response to a dramatic increase in methane concentrations within the soil from very low
2 concentrations, which is typical for methane-oxidizing bacteria in landfill covers (Spokas and Bogner,
3 2011). Further decreases in removal efficiency were observed when the inlet CH₄ load was increased to
4 > 100 g CH₄ m⁻² d⁻¹, with removal efficiencies dropping to < 5% in some cases immediately following
5 increases in the CH₄ load during Stage II (data not shown). Such observations are consistent with prior
6 studies that have found a significant inverse relationship between the CH₄ load and the CH₄ oxidation
7 capacity of a cover (e.g. Stein and Hettiaratchi, 2001; Rachor et al., 2011). C5 typically had the lowest
8 CH₄ removal efficiency by the end of the experiment, and C8 typically had the highest removal
9 efficiency in all stages, ranging from ~45% [Stage I] up to ~89.6% removal [Stage III].

10 Although removal efficiencies increased among all columns over time, the relative performance
11 among the columns did not change significantly, as illustrated in **Figure 3**. By Stage III, average CH₄
12 removal ranged from ~56.5% in C5 to ~89.6% in C8, representing an increase of ~11.4% to ~44.3% in
13 CH₄ removal efficiency relative to Stage I for C5 and C8, respectively. Average CH₄ removal efficiency
14 in C6 and C7 also increased substantially in Stage III compared to Stage I, with relative increases of
15 27.6% and 35.3% for C6 and C7, respectively. The increase in removal efficiency over time was greatest
16 for C8, possibly reflective of the fact that this soil was obtained from a landfill cover with more
17 exposure to active filling and higher ambient CH₄, as well as higher portions of organic matter relative
18 to the DKLF soil. Such an observation is consistent with prior studies on soil and compost-based covers,
19 wherein higher CH₄ oxidation rates were achieved in ‘hot spot’ locations with higher degree of prior
20 CH₄ exposure (e.g. Scheutz et al., 2011; Gebert and Perner, 2015). Box plots of average CH₄ removal
21 efficiencies during Stages I and III are shown in **Figure 4** and illustrate the relative performance of each
22 column over time. As illustrated by these figures, C7 and C8 displayed generally higher CH₄ removal
23 efficiencies towards the end of the incubation period [Stage III] than C5 or C6.

3.4 Initial and terminal gas profiles

Gas profile data was averaged over the initial and terminal monitoring periods (Stages I and III) and is presented in **Figure 5**. From these figures we see clear differences beginning to develop among the columns in terms of the distribution of CH₄, CO₂ and O₂ with depth in the covers. As CH₄ is being applied to the columns at 1.5 times the rate of CO₂, one would expect CH₄ concentrations to be elevated relative to CO₂ concentrations throughout the depth profile if little CH₄ oxidation is occurring. Because CH₄ oxidation results in conversion of CH₄ to CO₂, decreases in the ratio of CH₄:CO₂ in landfill cover soils have been related to the extent of methane oxidation in prior studies (e.g. [Rachor et al., 2011](#); [Gebert et al., 2011a, b](#)). It should be noted that interpretation of gas profiles can be complicated by the presence of other transport or transformation processes affecting the migration of CH₄ and CO₂ through soil (e.g. dissolution in soil pore water; sorption onto soil and biochar particles), and thus must be considered only as qualitative indicators for CH₄ oxidation activity.

From the Stage I profiles, we can infer that less CH₄ oxidation is occurring in the initial stages of the experiment in all columns as compared to the latter stages by the fact that the CH₄ and CO₂ profiles maintain roughly the same relative concentrations as the inlet gas throughout the column profiles, most significantly in C5, C6 and C7 (see **Fig. 5**). The relative ratio of CH₄ to CO₂ during Stage I at all depths ranged from ~1.3 to 1.44 in C5 and C6, and from ~1.26 to 1.43 in C7, reflecting only minor change from the ratio of 1.5 in the inlet LFG. Average CH₄ concentrations 10 cm below the soil within the gas distribution layers were ~14.85%, 17.7% and 17.2% in C5, C6 and C7 respectively. CO₂ concentrations at the same depth (70 cm bgs) in C5, C6 and C7 were 10.7%, 12.5%, and 12%, respectively; slight increases in CO₂ content were also noted at the interface between the gas distribution layer and the base of C6 and C7 at 60 cm depth. C8 had slightly lower average CH₄ concentrations within the gas

distribution layer (~14% v/v), possibly reflecting some CH₄ oxidation was occurring within the gravel layer itself. C8 appears to have higher initial methanotrophic activity based on the fact that in this column, CO₂ production was significant enough to impact the gas profiles of CH₄ relative to CO₂, which maintained almost equivalent concentrations with depth in the soil during Stage I (ratio of CH₄:CO₂ of ~1.05 to 1.36). This indicates that likely some of the CH₄ was being converted into CO₂.

In addition, gas profile data indicates elevated CO₂ concentrations at depth in C7 and C8 throughout the cover profile in Stage III, likely as a result of microbial oxidation of CH₄ into CO₂. Using this measure, further evidence of greater oxidation in C7 and C8 relative to C5 or C6 is observed: average ratios of CH₄:CO₂ within the soil during Stage III in C7 ranged from 0.67 to ~0.97, and in C8 ratios as low as 0.2 to ~0.67 were observed. The lowest ratio of CH₄:CO₂ was observed at 15 cm depth both in C7 and C8, possibly indicative of the zone of maximum oxidation. In the biochar-amended columns C5 and C6, CH₄:CO₂ ratios were generally higher in the final stages of incubation, likely indicating only partial oxidation was occurring. In C5, CH₄:CO₂ ratios ranged from ~1.14 to 1.18 in the gas distribution layers – possibly reflecting methane oxidation that is occurring at depth below the soil cover – decreasing slightly to ~0.98 to 1.29 throughout the soil profile. Similar ratios were observed in C6 within the soil cover (10 to 50 cm depth), ranging from ~1.05 to ~1.3. This is also illustrated by the fact that CH₄ and CO₂ maintain similar proportions relative to each other throughout the depths of the profiles in C5 and C6, with consistently higher CH₄ concentrations relative to CO₂ (see **Fig. 5b**). In C7 and C8, CH₄:CO₂ ratios were generally lower than those in C5 and C6 at all depths during Stage III, indicating greater CH₄ oxidation throughout these columns. All columns remained fairly well-aerated throughout the experiment, with average O₂ concentrations typically ranging from ~15 to 16% in the headspace of the columns during Stage III, such that O₂ availability was likely not a limiting factor.

Thus it is possible that the amendment of biochar to these soils did not significantly improve the conditions for growth of methane-oxidizing bacteria under the experimental conditions applied.

3.5 Potential CH₄ oxidation and CO₂ production rates in batch assays

A summary of the average rates of CH₄ oxidation, CO₂ production, and O₂ consumption determined from batch assays is given in **Table 5**. Average oxidation rates are plotted as a function of depth in the soil columns for Trials 1 and 2 in **Figure 6a** and **6b**, respectively. Overall it was observed that the soils from C8 (100% sieved Zion cover soil, or ZLFS) had the highest rates of CH₄ oxidation and soil respiration: average rates of CH₄ oxidation ranged from ~42 to ~54 µg CH₄ (g-soil)⁻¹ day⁻¹ in Trial 1 to ~67 to ~79 µg CH₄ (g-soil)⁻¹ day⁻¹ in Trial 2. Initially higher rates of CH₄ oxidation were observed in soils from the lower depth (50 cm bgs) in C8, though by the second trial all depths in C8 (10, 30 and 50 cm bgs) showed relatively uniform rates of CH₄ oxidation. This data, in conjunction with gas profiles observed during monitoring, likely indicates that the entire 60 cm depth of soil was active in CH₄ removal throughout the column incubation period. Rates of CO₂ production in C8 soils ranged from ~87 to 101 µg CO₂/day/g-soil during Trial 1 and increased to ~150 - 168 µg CO₂/day/g-soil during the second trial, with the highest rates of respiration observed in the upper depths of soil (10 cm bgs). O₂ consumption rates were also high in C8 soils, ranging from ~90 to 100 µg O₂/day/g-soil in Trial 1 and ~127 to 132 µg O₂/day/g-soil in Trial 2.

Rates of CH₄ oxidation in C5, C6 and C7 were all significantly lower than those observed in C8, perhaps due to differences in soil type and potential microbial activity among the two cover soils examined. Among the columns using DKLF soil (C5, C6, C7), potential oxidation rates at 10 cm were not statistically significantly different from each other ($p > 0.82$), though all were significantly lower than those in C8 at the same depth (Tukey's Test comparing means; $p < 0.001$). The same trend was

observed at 50 cm also, likely reflective of the fact that all these samples were composed of 100% DKLF soil and originated from the same soil stockpile.

In C5, CH₄ oxidation rates were highest in the upper ~18 cm due to the presence of the thin biochar layer, which restricted downward infiltration of soil moisture applied during precipitation events below the biochar layer and resulted in much higher water contents within the biochar layer (~25 to 28% dry wt. at exhumation). Rates of CH₄ oxidation in the biochar layer of C5 were higher than in any other zone of C5, C6 or C7, with average oxidation rates in Trials 1 and 2 of ~25.4 and ~51 µg CH₄/day/g-dry soil, respectively. An additional three trials were performed on the biochar layer test units in order to estimate the maximum potential for methane oxidation within the biochar layer itself due to the dramatic increase in oxidation rates observed from Trial 1 to 2 (total of 5 trials performed on 2 replicates; data shown in Supp. Information, Fig. S-2). Increases in CH₄ oxidation were less dramatic in subsequent trials, with a maximum oxidation rate of 116.6 µg CH₄/day/g-dry soil. Soil above the biochar layer in C5 was significantly wetter than soil below the biochar layer at the time of exhumation, and this led to much lower CH₄ oxidation rates in soils sampled at 30 cm and 50 cm depth in C5 (average of ~4 µg CH₄/day/g-dry soil at a moisture content of ~7% wet wt.). It is likely that the overall lower rates of CH₄ oxidation during long-term incubation in C5 relative to C6 and C7 is a reflection of reduced microbial activity at lower depths due to water limitation given the lower soil moisture content in C5 below the biochar layer relative to the other columns. Thus, it can be concluded that a thin layer of biochar within the cover soil is capable of supporting an active methanotrophic community within a relatively narrow depth zone.

In C6, CH₄ oxidation rates in Trial 1 showed a clear trend with respect to depth in the column, with the highest oxidation rates at 10 cm depth (~19.25 µg CH₄/day/g-dry soil) and the lowest at 50 cm depth (~8.41 µg CH₄/day/g-dry soil). Increases in oxidation rates in the second trial were observed across all

depths, during which highest oxidation rates were observed at 30 cm depth (2% biochar with ash; average oxidation rate $\sim 28.85 \mu\text{g CH}_4/\text{day/g-dry soil}$), such that the initial trend with respect to depth was no longer observed. The upper and lower soil layers at 10 and 50 cm depth, respectively, had average methane oxidation rates of ~ 24.25 and $19.78 \mu\text{g CH}_4/\text{day/g-dry soil}$ in Trial 2. The greatest increase in methane oxidation rate from Trial 1 to 2 was observed in C6 at 50 cm, with an average increase in oxidation rate of 135% relative to trial 1 – higher than the relative increase in oxidation rate from trial 1 to 2 observed among all other terminal batch assays ($n = 26$). By comparison, methane oxidation rates in soils from C6 increased by 26% at 10 cm and 67.4% at 30 cm in trial 2 relative to trial 1, respectively.

Rates in C7 were only slightly higher than those observed in C6 in both trials conducted. In Trial 1, oxidation rates in C7 soils ranged from ~ 13 to $23.7 \mu\text{g CH}_4/\text{day/g-dry soil}$, with the highest rate observed at 30 cm within the 2% wood-pellet amended treatment zone. Rates increased most dramatically in the lower soil at 50 cm depth, similar to the trend observed in C6, from ~ 13.03 in trial 1 to $22.91 \mu\text{g CH}_4/\text{day/g-dry soil}$ in Trial 2. Interestingly, rates in soils from 10 cm depth above the treatment zone did not increase significantly from trials 1 to 2 (average oxidation rates of ~ 18.7 and $18.9 \mu\text{g CH}_4/\text{day/g-dry soil}$, respectively). This may indicate that differences in cell abundance and/or affinity for CH_4 (e.g. due to differences in methanotrophic populations) were present at the start of batch assays in the lower soil layers relative to those at 10 cm depth, which were generally wetter and better aerated than soils in the mid and lower depths of the columns, leading to higher growth rates in terminal assays for the 30 cm and 50 cm depth samples. CO_2 production rates ranged from 19.0 to $45.4 \mu\text{g CO}_2/\text{g-dry-soil/day}$ in Trial 1 and from 32.9 to $52.8 \mu\text{g CO}_2/\text{g-dry-soil/day}$ in Trial 2. Highest CO_2 production rates in both trials were achieved at 30 cm in the mid-depth of the treatment zone (2% wood pellets).

4. Discussion

4.1 Effect of cover properties on methane removal efficiency

Prior work has established the importance of soil cover textural properties on the gas diffusivity and overall aeration of cover soils, which governs the extent to which methane can be oxidized to CO₂ as it travels upward through the cover profile (Gebert et al., 2011c; Scheutz et al., 2011). Adequate diffusion of atmospheric oxygen into the interior pores of soil is critical to maintaining high oxidation rates, as O₂ is required for the microbial oxidation of CH₄ to proceed. It is well established that higher degrees of soil compaction reduce soil porosity and can have negative impacts on the diffusion of gases through a cover due to a reduction in unsaturated voids (Rachor et al., 2011). The water content at compaction is also significant, as this will impact the soil structure and initial air-filled porosity.

The high extent of compaction and low initial moisture content applied in these tests is thought to have negatively impacted methane removal efficiency of the cover materials. Overall lower methane removal efficiencies were observed during this study as compared to earlier column trials compacted at a higher initial water content (Yargicoglu, 2016), and this may be related to the fact that soil was compacted at a lower moisture content. This design consideration reduced the formation of fissures in the soil cover due to desiccation, but resulted in a lower initial moisture content below the 10 to 20% gravimetric water content considered optimal for methane oxidation in landfill cover soils (Huber-Humer et al., 2008). This possibility is supported by prior work that has found that soil wetting history may have a significant impact on the potential methane oxidation capacity and its response to changes in soil moisture (Spokas and Bogner, 2011). While the interaction among soil moisture and pre-incubation history remains complex and not fully understood, Spokas and Bogner observed that soils that were initially wet and subjected to drying had the capacity for methane oxidation at lower soil moisture thresholds (i.e. soil tension up to 1500 kPa) than if soils were first dry and then slowly wetted (threshold

increased to ~600 kPa). This observation is consistent with the results of this study, wherein higher oxidation capacities were achieved in soils with higher initial soil moisture.

Soils were set to an initial moisture content equal to approximately 30% of the materials' water holding capacity at the start of the experiment to minimize any volume change in the soil over time due to drying and shrinkage. The higher water holding capacity of the Zion cover soil likely affected the results, as it was found that higher gravimetric water contents were positively correlated with overall methane removal efficiency in the final stages of LFG incubation (Stage III, $R^2 = 0.90$). Moreover, the ZLF soil had a higher void ratio than the DKLF soil in general, allowing a higher water-filled porosity to be maintained without reductions in air-filled porosity. An even higher R^2 value was found for the relation between volumetric water content in Stage III and overall methane removal efficiency ($R^2 = 0.98$), indicating that moisture availability is a key controlling factor on methane oxidation in the column tests. This result is corroborated by the strong positive correlation observed in terminal batch assays of soils from C6, C7 and C8 between the potential oxidation rate in Trial 1 ($R^2 = 0.97$) and Trial 2 ($R^2 = 0.94$) versus the soil moisture content (% wet wt.) Because of the biochar layer absorbing significant amounts of water in C5 (without parallel increases in oxidation rates), this positive correlation between moisture content and potential oxidation rate in batch assays from C5 was not observed. In C5, it is likely moisture limitation below the thin biochar layer limited CH_4 oxidation rates in the lower soil layer. This is illustrated quite well in **Fig. 6**, which shows the potential oxidation rates as a function of depth in the column: in C5, highest rates were achieved in the thin biochar layer, with a sharp decline in rates along with soil moisture below this point.

4.2 Effect of Organic Matter on Methane Oxidation

1 Typically higher organic matter content is associated with higher CH₄ oxidation rates in landfill
2 covers soils and compost-based biocovers ([Huber-Humer et al., 2011](#)), primarily because organic matter
3 contains the bulk of nutrients present in soil, tends to have a higher specific surface area and internal
4 porosity, and also generally improves soil water holding capacity ([Scheutz et al., 2009](#)). The higher
5 organic matter content of the ZLF soil used in C8 improved soil moisture retention and possibly nutrient
6 content relative to the DKLF soil used in other columns, likely contributing to the higher oxidation rates
7 observed. The presence of additional organic matter in the form of biochar in C6 did not appear to
8 improve oxidation rates in the large columns significantly more than the organic matter in C7, perhaps
9 reflecting low bioavailability of the organic carbon contained within biochar, or alternatively, the
10 presence of some inhibitory factor associated with the biochar added to C6, which included a fine ash
11 fraction. Highest methane oxidation rates in C6 were achieved within the biochar-amended layer in
12 terminal batch assays, in spite of slightly higher moisture content in the upper soil layers of C6. Thus,
13 the addition of 2% biochar to C6 soils may have increased nominal oxidation rates of the unamended
14 soil slightly, e.g. by increasing available surface area for microbial colonization ([Pietikäinen et al.,](#)
15 [2000](#)). However, considering that similar CH₄ oxidation rates were achieved in batch assays of C7 at
16 similar moisture levels, this effect may have minimal significance. Moreover, the results obtained during
17 long-term column testing indicated that C7 generally had higher CH₄ removal efficiency than C6,
18 though soil moisture profiles were very similar.

19 In C5, the biochar layer apparently supported higher activity of methane-oxidizing bacteria as
20 indicated in batch assays, though the soil below the biochar layer appeared to be negatively affected as a
21 result of reduced infiltration and lower soil moisture. In these tests the overall organic matter content of
22 the un-amended soil used in C5, C6 and C7 was relatively low (~0.8% dry wt.); additional biochar
23 added to C5 in the thin layer only comprised ~2% of the total soil mass and was targeted to depths of

~15 to 18 cm bgs, while in C6 only 2% by weight of biochar was added to the middle 20 cm of soil. Lower organic matter contents in unamended soil layers were associated with lower soil moisture contents as well due to the positive relationship between organic content and water holding capacity, and thus differences due to organic content cannot be distinguished from the role of soil moisture. Additional research is warranted on the topic of nutrient mobility from biochars over long timescales and its resultant impact on soil microbial communities.

4.3 Effect of prior landfill gas exposure on material performance

Differences in performance among the columns during long-term incubation appeared to diminish with time, though C8 consistently performed better than the other columns. The reason for this may be related to the initial abundance of methane-oxidizing bacteria in the Zion soil: higher oxidation rates were observed in Zion soil as compared to DeKalb soil in small-scale batch tests performed on 20 gram subsamples of the sieved soils without any pre-incubation (avg. oxidation rates of 16.76 versus 1.72 $\mu\text{g CH}_4 \text{ d}^{-1} \text{ g-soil}^{-1}$). Also, a much shorter lag phase was observed during batch assays in the un-incubated Zion soil (< 70 hrs) upon rewetting to 10% water content as compared to the DeKalb soil (~12 days), indicating a more robust methane-oxidizing community was likely present. It is hypothesized that the greater inherent microbial activity of the Zion soil is related to its methane exposure history and the extent of mixing and interaction with waste layers, which likely contributed some of the organic matter content in the Zion cover soil. Because this soil was obtained from the intermediate cover within an active filling area in the landfill, it likely has been regraded and reused as soil cover many times, and may have been exposed to higher and/or variable levels of CH_4 throughout this process.

Thus, these results suggest that ultimate performance and CH_4 removal capacity is soil-specific, and soils without significant prior methane exposure may require longer pre-incubation periods at higher

methane loads prior to achieving optimal performance. This is consistent with findings of a comprehensive study on methane oxidation in different landfill covers across a range of soil moisture potentials and temperatures conducted by [Spokas and Bogner \(2011\)](#). In that study, a 60-day pre-incubation period at soil moisture levels near field capacity (33 kPa) and 5% CH₄ in the headspace was found to eliminate differences in CH₄ oxidation rates among landfill cover soils from different depths and cover types. Little or no prior CH₄ exposure was associated with the longest lag phases and lowest initial oxidation rates in controlled batch assays ([Spokas and Bogner, 2011](#)). They concluded that the primary factors governing oxidation rates *in situ* were soil moisture and microclimate, along with CH₄ exposure history.

4.4 Effect of amendment type on biocover performance

The effect of amendment type on biocover performance was examined by comparing the performance of C6 and C7. Overall higher CH₄ removal rates during the column tests were observed in C7 (2% uncharred wood pellets) relative to C6 (2% wood pellet biochar with fine ash retained). The long-term monitoring data indicated higher CH₄ removal efficiency was achieved in C7 relative to C6: average steady-state CH₄ removal efficiency for C7 (~70%) was nearly 20% greater than C6 during Stage III (~53%). The uncharred wood pellets added to the treatment zone in C7 may have provided more readily available carbon and nutrients to the microbial communities in cover soils compared to the recalcitrant organic fraction in biochar, possibly stimulating CH₄ removal and soil microbial activity. It is unclear whether these positive impacts will be sustained on timescales of several years to decades considering the considerable amount of physical degradation of the wood pellets over the 500 day incubation. Furthermore, in terminal batch assays, potential oxidation rates in the treatment zone (30 cm depth) of C6 and C7 were not significantly different from each other based on a two-sample t-test of

sample means ($p = 0.67$), indicating that the two treatments did not lead to significantly different rates of potential CH₄ oxidation. Thus it does not appear that uncharred wood pellets are superior to pelleted biochar under the specific test conditions of this column study.

Prior work utilizing the same cover soil and biochar (wood pellet with fine ash; CE-WP1) by [Sadasivam \(2015\)](#) may provide some insight on the expected performance of biochar-amended soil in C6: [Sadasivam \(2015\)](#) observed inhibition of methane oxidation rates in biochar-amended soils of the same type was higher when fine ash was retained with the pelleted biochar fraction. In Col. 6, fine ash was retained with biochar and amended at 2% w/w. The presence of organic molecules (e.g. catechol, furan, ethylene, acetylene) sorbed onto fine ash particles in biochar has previously been implicated as a possible cause for reduced microbial activity ([Lehmann et al., 2011](#); [Spokas, 2013](#)) and thus may be related to the relatively low methanotrophic activity of C6 soils. Moreover, this may explain the discrepancy between the high oxidation rates observed (up to ~116 µg CH₄/g-dry soil/day) within the biochar layer in C5 - which had the fine ash removed prior to setup - and the much lower oxidation rates observed in C6 soils composed of 2% biochar-amended soil (average oxidation rate of 28.9 µg CH₄/g-dry soil/day in Trial 2). [Spokas \(2013\)](#) also observed significant differences in both greenhouse gas production and removal from biochar-amended soils depending on the extent of ageing and physical weathering of the biochar, with reductions in methane oxidation rates observed when ‘fresh’ biochar was applied and no statistically significant impacts on CH₄ emissions if field-aged biochar (> 3 years) was applied. Though the presence of fine ash particles is not directly analogous to biochar ageing, the incorporation of ash is typically higher in freshly produced biochars, and biochar weathering typically reduces the amount of organic compounds that may act as microbial inhibitors sorbed to the surface, in addition to potentially high mineral salt concentrations leached from ‘fresh’ biochars ([Spokas, 2013](#); [Quilliam et al., 2013](#)). Thus the higher portion of fine ash in C6 may have contributed to the lower

1 maximum methane oxidation rates observed relative to C7 and earlier column trials wherein fine ash
2 was removed prior to mixing with soil ([Yargicoglu, 2016](#)). Additional investigation on the organic
3 compounds associated with these particular biochars, especially those in the fine ash fraction, is required
4 to fully understand possible surface interactions among microbial activity and potential inhibitory
5 compounds.

6 7 **5. Conclusions**

8 A series of column tests were performed to assess the performance of several types of biochar-
9 amended soil covers under conditions designed to replicate typical field and construction conditions.
10 From these tests the long term performance of soil columns in terms of methane removal efficiency was
11 assessed to compare the effects of different amendment types and environmental conditions imposed.
12 The results of this work indicate that the design configuration and amendment type are both significant
13 considerations for the design and implementation of a biochar-amended soil cover intended to enhance
14 microbial methane oxidation and removal. Based on the relationships observed between soil moisture
15 availability and CH₄ oxidation capacity in column and batch tests, the primary factors governing
16 methane removal efficiency of these covers appears to be available soil moisture and initial activity of
17 methane oxidizing bacteria. It was hypothesized that the addition of biochar would improve the physical
18 environment of the soil by increasing water-holding capacity and internal porosity, which would in turn
19 improve activity of methanotrophic bacteria. The high rates of CH₄ oxidation observed within the thin
20 biochar layer in C5 appear to support this hypothesis, though additional study should be undertaken with
21 regards to biochar toxicity due to the possible presence of microbial inhibitors within the ash fraction of
22 biochar. The addition of biochar strongly impacts the distribution of soil moisture with depth, and its
23 amendment to cover soils may lead to higher oxidation rates by retaining moisture in the oxidative zone.

Additional study on thin-biochar layers and highly concentrated biochar layers as landfill cover amendments is recommended to better understand the impact on leachate production, nutrient availability, and effects on cover soil moisture retention and erosion susceptibility.

From this column incubation study, the following conclusions can be drawn:

- Design configurations with thin biochar layers instead of mixed soil-biochar layers had lower average methane removal efficiencies in laboratory column tests, as the concentrated biochar layer absorbed significant quantities of water and restricted water infiltration to deeper zones of soil. This led to reduced methane oxidation rates below the biochar layer due to moisture limitations and overall lower methane removal efficiency during column tests.
- Uncharred wood pellets added at 2% w/w ratio yielded statistically similar mean oxidation rates as compared to 2% biochar amendment, indicating that charring of biomass may not equate to higher oxidation rates on short timescales (<500 days).
- Soil type and prior methane exposure are key factors governing the ultimate methane removal capacity of a soil cover regardless of the presence of biochar or uncharred wood pellet.
- In addition to methane exposure history, available soil moisture also governs methanotrophic activity. With the exception of the thin biochar layer, methane oxidation potential in batch assays of soils and amended soils was positively correlated with soil moisture ($R^2 \geq 0.94$).

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22

Table Captions

Table 1. Experimental stages of the column tests.

Table 2. Initial physical properties of the columns at setup.

Table 3. Chemical properties of soil column substrates tested.

Table 4. Average outlet methane fluxes ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) from C5-C8 during pre-incubation and monitoring stages (I and III).

Table 5. Average rates of CH_4 oxidation, CO_2 production, and O_2 consumption observed in trials 1 and 2 of terminal batch assays. Standard deviations shown after average rates ($n = 2$) for each trial.

1 **Table 1**

2 Experimental stages of the column tests.

Stage	Days	Avg. CH ₄ Load $\pm$ SD (g m ⁻² d ⁻¹)
Pre-incubation	1 to 67	1.5 $\pm$ 1.1
LFG Incubation, Stage I	70 to 130	90.0 $\pm$ 8.9
LFG Incubation, Stage II	131 to 425	~25 to ~100
LFG Incubation, Stage III	426 to 473	76.9 $\pm$ 11.4
LFG Incubation, Stage IV	474 to 510	79.8 $\pm$ 10.4

3

1 **Table 2**

2 Initial physical properties of the columns at setup.

Property	Col. 5	Col. 6	Col. 7	Col. 8
Bulk density, ρ (g/cm ³)	1.51	1.57	1.62	1.52
Dry density, ρ_d (g/cm ³)	1.43	1.47	1.52	1.37
Specific Gravity, G_s	2.48	2.55	2.56	2.68
Void Ratio, e	0.74	0.73	0.67	0.98
Total Porosity, n	0.42	0.42	0.40	0.49
Air-filled Porosity ¹ (%)	32.4	32.9	29.6	33.1
Water-filled Porosity ¹ (%)	8.3	9.4	10.7	16.4
Gravimetric Water Content ² (%)	5.83	6.40	7.01	12.08
Volumetric Water Content ² (m ³ /m ³)	0.023	0.023	0.032	0.055

3 ¹ Based on phase relationships established using initial gravimetric water content and material specific
4 gravity and bulk density

5 ² Reported values of gravimetric and volumetric water content are averages across all layers at the time
6 of setup.

Table 3

Chemical properties of soil column substrates tested.

Property	Zion field soil	Sieved DKLF soil	2% BC + 98% DKLF soil	2% Wood Pellet + 98% DKLF soil	CE-WP1 biochar
Organic Matter Content (%)	2.62	0.77	2.84	3.62	96.0
pH	7.36	7.30	7.40	6.50	6.24
Oxidation-Reduction Potential (mV)	-32.42	-35.9	-37.5	12.3	35.1
Electrical Conductivity (mS/cm)	0.348	0.321	0.310	1.6	4.15

Table 4

Average outlet methane fluxes ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) from C5-C8 during pre-incubation and monitoring stages (I and III).

Stage	Days	Avg. inlet flux ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$)	Avg. Outlet CH_4 Flux ($\text{g m}^{-2} \text{ d}^{-1}$) $\pm$ SD			
			C5	C6	C7	C8
Pre-incubation	1 to 67	1.5	0.74 ± 0.80	0.48 ± 0.62	0.25 ± 0.21	0.19 ± 0.35
Stage I	70 to 130	90.0	50.0 ± 15.4	68.7 ± 13.0	59.2 ± 18.8	49.7 ± 24.9
Stage III	426 to 473	76.9	36.3 ± 13.5	39.0 ± 11.5	23.7 ± 15.6	9.0 ± 8.2

Table 5

Average rates of CH₄ oxidation, CO₂ production, and O₂ consumption observed in trials 1 and 2 of terminal batch assays. Standard deviations shown after average rates ($n = 2$) for each trial.

	Depth (cm)	MC (% dry wt.)	OC (% dry wt.)	CH ₄ oxidation rate ($\mu\text{mol g-dry-soil}^{-1} \text{d}^{-1}$)		CO ₂ production rate ($\mu\text{mol CO}_2 \text{ g-dry-soil}^{-1} \text{d}^{-1}$)		O ₂ consumption rate ($\mu\text{mol O}_2 \text{ g-dry-soil}^{-1} \text{d}^{-1}$)	
				Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
C5	10	9.5	1.11	1.39 $\pm$ 0.06	1.55 $\pm$ 0.07	1.26 $\pm$ 0.04	1.13 $\pm$ 0.05	1.48 $\pm$ 0.05	1.59 $\pm$ 0.15
	15 to 18	29.4	89.61	1.65 $\pm$ 0.10	3.18 $\pm$ 0.08	1.74 $\pm$ 0.09	1.48 $\pm$ 0.11	3.53 $\pm$ 0.02	4.04 $\pm$ 0.46
	30	7.8	1.06	0.30 $\pm$ 0.00	ND	0.15 $\pm$ 0.00	ND	0.23 $\pm$ 0.01	ND
	50	7.1	0.95	0.22 $\pm$ 0.00	ND	0.09 $\pm$ 0.01	ND	0.15 $\pm$ 0.01	ND
C6	10	9.98	0.90	1.20 $\pm$ 0.03	1.49 $\pm$ 0.04	0.91 $\pm$ 0.14	1.38 $\pm$ 0.00	0.99 $\pm$ 0.02	1.28 $\pm$ 0.05
	30	9.12	2.47	1.15 $\pm$ 0.10	1.83 $\pm$ 0.11	0.62 $\pm$ 0.02	1.42 $\pm$ 0.08	0.79 $\pm$ 0.01	1.53 $\pm$ 0.08
	50	8.21	0.97	0.52 $\pm$ 0.02	1.23 $\pm$ 0.11	0.27 $\pm$ 0.01	0.76 $\pm$ 0.10	0.42 $\pm$ 0.02	1.25 $\pm$ 0.33
C7	10	10.4	1.23	1.16 $\pm$ 0.02	1.19 $\pm$ 0.04	0.98 $\pm$ 0.06	0.87 $\pm$ 0.06	1.08 $\pm$ 0.12	1.20 $\pm$ 0.01
	30	9.65	2.72	1.48 $\pm$ 0.02	1.71 $\pm$ 0.16	1.03 $\pm$ 0.03	1.20 $\pm$ 0.01	1.42 $\pm$ 0.16	1.55 $\pm$ 0.03
	50	8.98	0.86	0.81 $\pm$ 0.05	1.44 $\pm$ 0.03	0.43 $\pm$ 0.01	0.75 $\pm$ 0.14	0.67 $\pm$ 0.01	1.30 $\pm$ 0.04
C8	10	14.74	2.59	3.15 $\pm$ 0.15	5.04 $\pm$ 0.02	2.64 $\pm$ 0.16	4.86 $\pm$ 0.66	3.25 $\pm$ 0.07	5.23 $\pm$ 0.52
	30	15.3	2.79	3.52 $\pm$ 0.03	4.89 $\pm$ 0.09	2.66 $\pm$ 0.08	2.41 $\pm$ 0.02	3.60 $\pm$ 0.15	4.61 $\pm$ 0.02
	50	15.8	2.74	4.00 $\pm$ 0.32	5.72 $\pm$ 0.14	2.64 $\pm$ 0.44	4.01 $\pm$ 0.07	3.71 $\pm$ 0.30	4.63 $\pm$ 0.09

Figure Captions

Fig. 1. Diagram of cover configurations evaluated during column testing.

Fig. 2. Average moisture content with depth at the end of column testing following exhumation.

Fig. 3. Average methane removal efficiencies observed during pre-incubation and monitoring stages I and III.

Fig. 4. Box plots showing median, lower quartile and upper quartiles of average methane removal efficiency during Stages I and III. Whiskers correspond to minimum and maximum values.

Fig. 5. Average gas profiles for each column during Stage I (Day 70 to 130) and Stage III (Day 426 to 473).

Fig. 6. Average CH₄ oxidation rates versus sampling depth: (a) observed in Trial 1 of batch assays; (b) observed in Trial 2 of batch assays.

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(a)

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(b)

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(a)

(b)

Fig. 6. Average CH_4 oxidation rates versus sampling depth: (a) observed in Trial 1 of batch assays; (b) observed in Trial 2 of batch assays.