Biocovers at Landfills for Methane Emissions Reduction

Demonstration

CalRecycle

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Contractor's Report

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Acknowledgments

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Executive Summary

Introduction

The largest anthropogenic source of methane greenhouse gas (GHG) emissions is from landfills which accounted for 5.62 million metric tons of carbon dioxide equivalent (MMTCO$_2$E) in 2004, according to estimates from the California Air Resources Board. Decomposition of organic material in landfills accounts for most anthropogenic methane emissions in California. Cover soils provide some oxidation of fugitive methane as it travels through the landfill surface. Methanotrophic microorganisms (the bacteria responsible for oxidizing methane) are present in most soils. Recent work has sought to increase the oxidation of fugitive methane by placing a biocover consisting of compost, mulch, green waste, or mixtures thereof over the surface of a landfill. However, limited research exists on the long-term performance and maintenance requirements of biocovers. In addition, California has many small, closed landfills which would benefit from installing a biocover to mitigate fugitive methane as an alternative to installing a comprehensive gas collection system. As such, a demonstration project that would address both questions of long-term performance and widespread application using a suitable and readily available biocover material would be useful to provide landfill operators with additional information to evaluate and implement this option.

Project Objectives

Compost and compost-woodchip mixtures are known to be good biocover materials, but there are few data to evaluate how long their methane oxidizing capacity is maintained, particularly under different climatic conditions (e.g., rainy versus dry seasons). Alternatively, readily available green material feedstock from residential yard waste and other collection programs (as defined in Title 14, California Code of Regulations, Section 17852(21)) might be a satisfactory biocover medium, but no data are available to substantiate performance or longevity as a treatment medium. Initially, biodegradation of green material will likely out-compete methanotrophic microorganisms for oxygen, but this material may quickly decompose and be an appropriate substitute for compost and compost-woodchip mixtures.

Research is needed to evaluate the effectiveness of aged and fresh green material as a biocover medium. In particular, data are needed to quantify the ability of these materials to support methanotrophic bacteria over different seasons and climatic conditions. Such data must include field tests using controlled cells where methane oxidation can be easily quantified for large representative samples of the media, laboratory tests to quantify gas and water flow properties, and laboratory tests to quantify material stability and the influence of temperature and moisture on methane oxidation. To aid in the analyses of these data, numerical simulations of both gas transport and methane oxidation during various seasons are needed.

The main objective of this demonstration project was to assess the performance of the green material as biocover over an 18-month period and to link the observed performance to both material properties (e.g., thickness) and climatic conditions (e.g., temperature).

Because of the limited funding and grant time limit, the focus of this research was on fresh and aged green material as biocover and not on end-product compost produced through facility composting processes. Research results for fresh and aged green material in this study are compared with applicable properties and standards for compost. The authors concluded that, under the stated limitations of this grant, fresh and aged green material as biocover is an area of particular research need whereby this study could significantly contribute toward the science and practical application of biocovers. Furthermore, it is important to note that for the purposes of this study landfill alternative daily cover using green material is not considered biocover, and the methane oxidation and emissions aspects of landfill alternative daily covers is beyond the scope of the study.

Project Results

The results of the project are summarized as follows.

a) While fresh and aged green material created from yard waste had low pH and P, but high NO_2-N when compared to recommended ranges, both materials could oxidize CH_4 at very high rates—up to 100-200 g CH_4/m^2/day.

b) Fresh and aged green material, while classified as "very stable" according to the California Compost Quality Council (2001) based on respiration tests, consumed O_2 at rates greater than that recommended for landfill biocovers: fresh and aged green material consumed 11.8 and 44.7 mg O_2/mg organic matter for 7-day tests, while Huber-Humer, et al., (2009) recommended less than 8 mg O_2/mg organic matter.

c) When biocover test cells were operated with high CH_4 loadings (500-700 g CH_4/m^2/day), both fresh and aged green material generated significant CH_4 in winter months. CH_4 generation was reduced significantly, though, when the loading was reduced to 200-250 g CH_4/m^2/day. In this case the green material oxidized 50-70 g CH_4/m^2/day.

d) When both biocovers were operated at this smaller loading rate (200-250 g CH_4/m^2/day) for several months, the aged green material performed reasonably well with measured CH_4 removal rates matching independent model predictions. The same was not true for the fresh green material, though, where it appeared that CH_4 continued to be generated and the biocover performance was always significantly less efficient at removing CH_4 than model predictions.

e) The rates of CH_4 oxidation in the fresh and aged green materials are similar to those reported for other composts exposed to similar CH_4 loading. The decrease in CH_4 oxidation rate observed with the green material through time in our field tests was also observed for composts in laboratory experiments.

f) Laboratory tests quantified the resistances to gas diffusion and advective gas flow in the fresh and aged green material. The Troeh model was best for describing gas diffusion, and this model was used in computer modeling to predict CH_4 oxidation with changing season.

g) Laboratory and field tests for water flow in the green material indicate that they contain macropores and may be best described as dual domain porous media. Future modeling of water flow through these materials should account for this behavior.

h) The TMVOCBio computer code was modified to describe CH_4 oxidation in the fresh and aged green material over the period of this study. This modeling confirmed the impact of CH_4 generation on CH_4 emissions, and model results suggest that the biocovers would perform better if they were significantly thinner. Modeling also indicated that temperature was the most important environmental factor affecting CH_4 oxidation during the 18-month operation of the test cells.

i) The effect of thinning the biocovers was tested in the field (July 2010). Green material biocover thicknesses were reduced from 61 cm to 51 cm and 48 cm for aged and fresh green material biocover, respectively. For the aged green material, before thinning CH_4 was generated within the cover, while after thinning CH_4 was oxidized. For the fresh green material, before thinning between 1-9 percent of the CH_4 was removed, while after thinning approximately 17 percent was removed. Clearly, a thinner biocover made of these materials would reduce or eliminate anaerobic zones, reduce CH_4 generation, and thus promote overall removal of CH_4 within each material. However, these measurements were made for short periods after thinning. Longer-term tests of thinner materials are needed to extrapolate these results for longer times.

j) The biocover test cells that were designed and constructed for this study are useful tools for evaluating landfill cover materials for oxidizing CH_4. The unique use of a gas tracer to quantify and then correct for gas leakage from the cells was an innovative feature that we recommend for similar field tests in the future.

Conclusions and Recommendations

The following recommendations are made based on the results from this project:

a) Green material derived from yard waste should be aged at least one year before placement on a landfill. It is further recommended that respiration tests be used to quantify the stability of the green material and that, if possible, the green material be allowed to age until the stability characteristics proposed by Huber-Humer (Huber-Humer et al., 2009) are satisfied.

b) Initial green material biocover thicknesses of ~ 90 cm were used in this study, which were shown to be too large. Further field study and computer simulations should be conducted to develop recommended biocover thickness, which may vary depending on climatic conditions (e.g., ambient temperature, rainfall and variations in barometric pressure) and landfill gas loading.

c) The Michaelis-Menton kinetic parameters measured and/or estimated for methanotrophic activity in this study were reasonable for modeling CH_4 oxidation in biocovers derived from similar source materials and for similar ages.

d) We recommend that the Troeh model be employed in the California Landfill Methane Inventory Model (CALMIM) (Bogner, et al., 2010) and other similar codes for describing gas diffusion in green material.

e) The results from this study demonstrate that green material derived from yard wastes can serve as effective landfill biocovers, if they are sufficiently stable. What is not known, though, is how effective this material will be when placed on all or part of a landfill. Will emissions occur through cracks and thus bypass treatment zones? Since some CH_4 emissions are correlated with wind or barometric pressure changes and since these biocovers are very permeable, will CH_4 emissions be significantly worse when biocovers are used rather than less permeable soils on windy days or during periods of rapid changes in barometric pressure? Field tests are required to address these questions, where it seems likely that measurements of whole landfill CH_4 emissions will be needed before and after biocover placement to verify that indeed the addition of this material reduces CH_4 emissions.

f) For old and small landfills that produce low levels of methane, further study is needed to compare the effectiveness of landfill biocover placed over the entire surface as compared to designing a passive gas system where landfill gas collected is directed through a biofilter constructed from green material derived from yard waste. Long-term performance of such a system must be evaluated for methane destruction efficiency.

g) Our study adds to the growing body of knowledge on the performance of biocovers by adding information on the utility of green material. However, an important limitation of our study and others employing biocovers is the long-term performance of these media. Compost and green material are less stable than soils and will likely exhibit greater changes in physical structure, e.g., porosity and bulk density, than soils as they age. These physical changes will alter each medium's ability to retain moisture and support methanotrophic bacteria. While studies similar to ours have been employed to evaluate compost biocovers over a few years, we are unaware of studies for longer time period, e.g., in the range of 3-15 years. Such studies are needed to assess the long-term performance of compost and green material biocovers and, if necessary, the need to refresh these materials to maintain their capacity to oxidize methane. Such studies should include a variety of climatic conditions.

h) Finally, we recommend future work to develop best management practices for the design, construction, and maintenance of biocovers. Such practices must necessarily address the economics of biocovers, which include the cost of the materials and any need to "refresh" the materials as they age. Rather than cover an entire landfill with an engineered biocover, it may be more economical and perhaps just as effective to construct biocover "windows," where fugitive landfill gases are directed to biocovers constructed on small sections of a landfill via a passive gas collection system. Such a design may be a particularly attractive option for older landfills without active gas collection systems.

Introduction

A landfill biocover is a porous medium in which biological activity is significant enough to reduce methane concentrations appreciably before landfill gas (LFG) reaches the atmosphere. Naturally occurring biocovers have been around for a long time. Whalen, et al., (1990) was arguably the first study to acknowledge CH_4 oxidation in soils covering landfills.

By definition, biocovers should support and maintain meaningful methanotrophic microbial populations that convert CH_4 to CO_2 while LFG diffuses or advects through the cover. Materials rich in organic matter, e.g. compost and compost/woodchips mixtures, might enhance CH_4 oxidation when compared to traditional clay soil covers (Barlaz, et al., 2004; Abichou, et al., 2006; Stern, et al., 2007). In addition to this function, a compost layer overlaying a low permeability soil cover with significant clay can decrease dehydration of clay, thus increasing resistance to vertical gas flow. This, in turn, decreases the amount of CH_4 entering a biocover (Stern, at al., 2007; Abichou, et al., 2009).

Research on the oxidation of CH_4 in landfill cover soils including compost materials has been conducted for more than 15 years. There have been numerous laboratory and field studies quantifying processes controlling CH_4 oxidation, and these are well understood. However, there are several questions that have not been completely addressed:

- Can organic materials created from yard waste function effectively as biocovers after relatively short periods of stabilization?
- What is the long-term performance of biocovers, particularly those where the source material was yard waste? Will performance degrade through time as these materials age, and can this be readily predicted?
- Given the recent development of the CALMIM model (Bogner, et al., 2010) to describe CH_4 emissions from landfill cover soils, what are the appropriate model parameters describing gas diffusion and CH_4 oxidation that must be included in CALMIM to describe diffusion through cover soils and CH_4 oxidation?
- Is CALMIM or similar approximate modeling approaches sufficient for predicting CH_4 emissions from landfill cover soils, or are more sophisticated modeling approaches needed?

The research conducted here addressed all but the last question. Here, we developed a predictive model to describe CH_4 oxidation in biocovers and used this model to help us interpret data from field tests. Future work is needed to examine the significance of the simplifying assumptions in the CALMIM model and the need (or lack thereof) for more comprehensive modeling approaches.

Design, Construction and Testing

Biocover Cell Design and Construction

Two biocover cells were constructed near a landfill module where landfill gas could be diverted to each biocover cell. Each biocover cell foot print was 2.4 m by 1.8 m by 1.2 m height. Prior to installation of the base liner system, the sub-grade soil was compacted. The side of each biocover cell was constructed from chain link fencing (see Figure 2) to support the liner system. The bottom of each biocover cell was graded to drain to the lowest point of the cell. An 8 mil reinforce polyethylene liner was installed to enclosed the entire inner area of each biocover cell (see Figure 3). A leachate drain system was installed to allow excess water to drain through a 0.3 m thick layer of gravel (Figure 1).

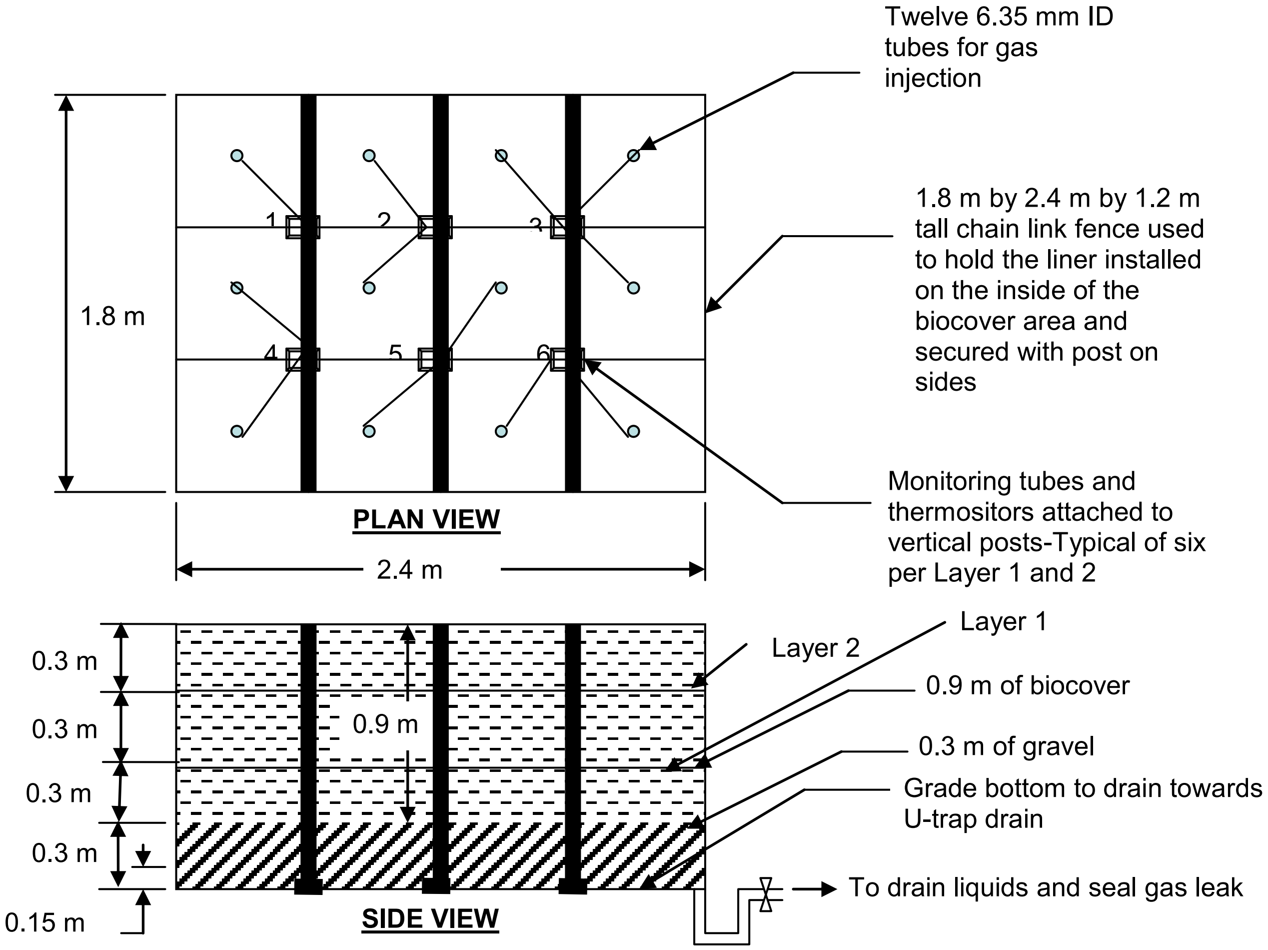

Figure 1. Layout design for each bicover test cell.

Figure 2. Chain link fencing used as structure for biocovers.

Figure 3. Interior of biocover cells lined with 8-mil reinforced polyethylene liner.

Gas Distribution System

After placement of 0.3 m of gravel, at the bottom of the each biocover cell a dozen 6.35 mm ID tubes were installed for landfill gas injection and distribution. Each gas injection tube was connected to a needle valve so that the flow rate through each tube could be adjusted. The manifold with 12 needle valves per biocover is shown in Figure 6 below. The gas is supplied to these injection tubes using a diaphragm pump.

Figure 4. Biocover cell with metal rods inserted for support of sensors and tubing.

Figure 5. Overhead view of tubing used to distribute gas flow in base gravel layer.

Biocover Operation, Gas Sampling and Composition Measurement

The two biocover test cells were operated from May 2009 to July 2010, when landfill gas was injected into the gravel gas distribution layer at the bottom of each cell. Landfill gas flow rates were varied during the tests to explore the impact of methane loading on biocover performance. The two loading rates used were 500-700 g CH_4/m^2/day and 200-300 g CH_4/m^2/day. These two loading rates span the range of loading rates used in laboratory experiments testing compost performance (Scheutz et al., 2009; Wilshusen et al., 2004).

Gas composition within the biocover was monitored on layer 1 and 2 (Figure 1). On each layer six 2.0 mm ID tubes were installed for gas sampling. These tubes were connected to an automatic gas sampling system during field monitoring. The automatic gas sampling system was connected to the Supervisory Control and Data Acquisition (SCADA) system to monitor the gas composition automatically. It consisted of a sampling pump (Model 35.1.2TTP, KNF Neuberger, Trenton, N.J.), a programmable multi-position electronic actuator and rotary valve (Model EMTAMA-CE, Houston, TX), a gas conditioning and condensate removal system, and a non-dispersive infrared gas analyzer (California Analytical Instrument (CAI) L Series, Orange, CA.) to measure gas composition continuously. It was calibrated automatically daily against gas standards (100 percent N_2; 50 percent CH_4, 35 percent CO_2 and 15 percent N_2; 45 percent CO_2, 21 percent O_2 and 34 percent N_2).

The total gas flow rate to each of the biocover cells (see Figure 6) were measured using a positive displacement meter (Roots Meters Series B3, Model 5M175 Roots, Houston, TX). The gas composition for the supply gas to each of the biocover cell was monitored using the automatic gas sampling system as described above.

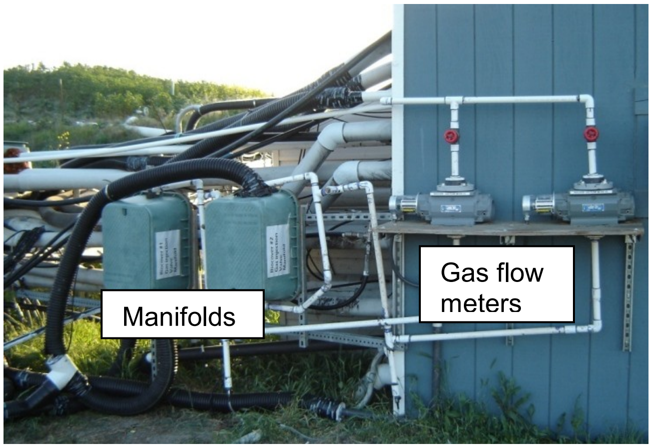

Figure 6. Gas flow meters and adjustment manifold boxes for each biocover cell.

Biocover Materials

Two types of biocover material were used (green material as defined in Title 14, California Code of Regulations, Section 17852(a) (21). The first biocover material was aged yard waste (aged green material-Biocover #1). This material was placed on outside landfill slopes for over a year and then removed for project use. The second biocover material was fresh yard waste (fresh green material-Biocover#2). This material was yard waste received at the landfill. Both aged and fresh green material biocover material were screened through a 76 mm screen. Biocover material was placed in each of the biocover cell at about 300 mm lifts and compacted manually (Figure 7). The final compacted height of biocover material was about 0.9 m in each biocover cell.

Figure 7. Filling biocover cell with aged and fresh green material.

Temperature Measurement

Total of six temperature sensors were installed within layers 1 and 2 to monitor biocover temperature. Horizontal temperature sensor spacing ranged from 0.85 to 1.2 m. The temperature sensors had a temperature range of 0 to 100°C (QT06005, Quality Thermistor, Inc., Boise, ID). Sensors readings were collected continuously using the on-site SCADA system.

Figure 8. Nearing the end of addition of biocover material. Sensors shown for layer 2.

Figure 9. Cells completed. Tubing and wires for temperature sensors connected to instrument shed in background.

Moisture Measurement

Moisture content of biocover samples were determined by drying samples at 105 °C for 24 hr (APHA 1985). Moisture content was expressed on a wet weight basis (mass water/wet mass).

Weather Station On-Site

A weather station (Vantage Pro2, Davis Instruments, Hayward, CA) was installed near the biocover cells to monitor ambient conditions. The parameters monitored and recorded automatically were: ambient temperature and humidity, barometric pressure, rainfall, solar radiation, wind speed, and wind direction.

Solids Sampling and Testing

Organic matter, total carbon, and total nitrogen were measured to chemically characterize biocover material samples. Optimum ranges for organic matter and the C/N ratio have been proposed for optimal methanotrophs growth (Wilshusen, at al., 2004, Dever, et al., 2007). Also, organic matter and C/N ratio can be used to determine the zone at which active methane oxidation occurs within biofilter systems (Im, et al., 2009, Huber-Humer, et al., 2009). In addition to these measurements, samples were analyzed for NH_4, NO_3, NO_2, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, elemental S, and Zn. All analyses were conducted by the University of Delaware Soils Testing Program.

Respiration Testing

Biocover samples were measured from samples collected in June 2009 and February 2010 from biocover #1 (aged green material) and biocover #2 (fresh green material) at two depth ranges: 0-12 inches, and 12-24 inches. Liquid was added to all samples to achieve gravimetric moisture contents of approximately 50 percent. Approximately 75 dry grams of each mixture were placed into 250-ml reactors for microbial activity studies at the time of arrival (May and VanderGheynst 2001). Reactors were aerated continuously with humidified air at approximately 10 ml min^{-1} to avoid oxygen limitations. Reactors were maintained at 35^{o}C for the duration of each experiment (see appendix A).

Carbon dioxide concentration was measured using an infrared CO_2 sensor (Vaisala, Suffolk, UK) and mass flow rate was measured using a mass flow meter. Mass flow rate and carbon dioxide data were recorded every five hours using a data acquisition system (VanderGheynst et al. 2002). Carbon dioxide evolution rates (CER) were calculated from mass balances on each reactor according to the following equation:

$$CER = F(CO_{2_{OUT}} - CO_{2_{IN}}) \qquad \text{Eq. (1)}$$

where F is the air flow rate (mg air day^{-1} gdw^{-1}), $CO_{2,OUT}$ and $CO_{2,IN}$ are the concentrations of carbon dioxide in the effluent and influent air, respectively (mg CO_2 mg air^{-1}), and $O_{2,IN}$ and $O_{2,OUT}$ are the concentrations of oxygen in the influent and effluent air, respectively (mg O_2 mg air^{-1}). Cumulative evolution rates were calculated by integrating CER over the 157 hr incubation period. Stability was estimated from the average CER for time > 125 hr.

JMP v.7 (SAS Institute Inc. Cary, N.C.) statistical software was used to perform statistical comparisons. Respiration rates were plotted using KaleidaGraph v. 4.0 (Synergy Software, Reading, PA).

Biocover Methane Oxidation Properties

While in-place field measurements were used to quantify overall biocover performance for CH_4 oxidation, laboratory measurements were needed to identify the parameters describing methane oxidation. Here, we followed the modeling approach by De Visscher, et al., (2003). Laboratory procedures were similar to those developed by others (e.g., Abichou, et al., 2009). Biocover samples incubated for 10 days in the laboratory were used to clarify the effect of temperature on rates of methane oxidation. Biocover samples collected from the field but not incubated were used to estimate the impact of moisture on methane oxidation and to estimate the Michaelis-Menton kinetic parameters used in the predictive modeling described below. The Michaelis-Menton kinetic parameters are needed to describe the utilization of CH_4 by methanotrophs in the numerical model.

Biocover Flow Properties- Infiltration and Gas Transport Testing

In order to both understand and then model the transport of gas, water and heat through fresh and aged green material as biocover, it is necessary to have constitutive models for fluid flow. Such models have been routinely measured for soils and are available for many soils in the literature. However, such models are lacking for biocovers. In particular, we are unaware of any constitutive models that have been tested for either gas diffusion or water flow in biocovers. Simply assuming models developed for soils can be used for biocovers may result in significant error.

The purpose of this portion of the work was to develop such models. While these constitutive models for fluid flow and diffusion will be used in the computer modeling to describe CH_4 oxidation in the biocover test cells, the constitutive relationships will be required in other models where CH4 oxidation is described. For example, the constitutive model for gas diffusion developed for biocovers can be employed in the California Landfill Methane Inventory Model (CALMIM) developed by Bogner, Spokas, and Chanton.

Biocover material used to fill each cell is shown in Figure 10 and 11 below. Visual examination of these samples reveals that fresh green material used on biocover #2 contained roots and branches of trees, while aged green material used on biocover #1 was mostly composed of leaves and fine shoots.

Figure 10. Aged green material used to construct biocover #1.

Figure 11. Fresh green material used to construct biocover #2.

In order to both understand and then model the transport of gas, water and heat through these biocovers, it is necessary to have constitutive models for fluid flow. Such models have been routinely measured for soils and are available for many soils in the literature. However, such data are lacking for biocovers. In particular, we are unaware of any constitutive models that have been developed for either gas diffusion or water flow in biocovers. Simply assuming models developed for soils can be used for biocovers may result in significant error. The purpose of this portion of the work was to develop such models, which are needed for the computer modeling to describe CH_4 oxidation in the biocover test cells.

Particle Size Distribution—The American Society of Testing Materials standard (ASTM 1963) was followed for conducting sieve analyses on biocover samples. All samples were oven-dried prior to sieving. Samples were sieved using eight screens with the following opening sizes: 19.050, 12.700, 2.000, 4.750, 10, 0.250, 0.106, and 0.075 mm Shaker used to perform sieve analysis is shown in Figure 12.

Figure 12. Shaker that was used to perform sieve analysis.

Air Permeability—Air permeability was measured using a steady-state method based on the application of Darcy's law (Ball, et al., 1981; Corey 1986). Biocover samples of different moisture content were placed on top of the gas chamber for air permeability tests. Air flow rates ranging from 0.4 to 18.5 L/min were used in the tests and measured with a flow meter (Cole-Parmer, No. EW-32458-46 and EW-32458-50). Pressure differences were recorded with a differential pressure meter (accuracy ± 0.1 mm H_2O) (Testo 506). Each measurement was repeated three times at each flow condition.

Diffusion—Effective gas diffusion coefficients were measured using the well-established Currie method (Dane 2002).This method is based upon the analytical solutions given by Currie (Currie 1960). In this method, the unsteady-state diffusion of a non-reactive gas is described by combination of Fick's first law and continuity equations. The experimental setup to measure diffusion coefficient and gas chromatograph (GC) to monitor tracer gas are shown in Figures 13 and 14.

The Troeh model was used to model tortuosity vs. air-filled porosity relationship. Troeh model is first proposed by (Troeh et al., 1982) and is presented below:

$$\tau = C(n - \varepsilon_{th})^{V} \qquad \text{Eq. (2)}$$

where τ is tortuosity (or ratio of gas diffusion coefficient in soil and free air), n is air-filled porosity, ε_{th} is the inactive pore space (below this value diffusion ceases to zero), V

is pore connectivity parameter, and C is a fitting parameter. C, V and ε_{th} are fitted to the measured diffusion data.

Figure 13. Experimental setup to measure gas diffusion coefficient.

Figure 14. Gas chromatograph used to measure tracer gas concentration.

Hanging Column Test—Hanging column test was performed to measure the pressure-saturation relationships for biocover samples for capillary pressure heads larger than -100 cm H_2O. Biocover samples were flushed with CO_2 at least for four pore volumes prior to complete saturation with deionized water under vacuum to assure all the pores were filled with water. Water was then drained out of samples by lowering the water level.

Small incremental changes of the water level in the outflow tubing were used to quantify the change in water saturation at each pressure step. Water saturation at each applied suction pressure was measured by using the final weight of sample, the total porosity, and the volume of water drained from the cell at each pressure step (Dane 2002).

Infiltration Test—Tension disk infiltrometry was used to measure saturated and unsaturated hydraulic conductivity of biocover samples in the field. Tension disk infiltrometry is a common field method that has been used on various soils to measure unsaturated hydraulic conductivity as a function of matric head (Baird 1997; Lin, et al., 1998; Holden, et al., 2001; Ramos, et al., 2006). A picture of a tension disk infiltrometer (Part# 2825K1, Soil Moisture Co., Goleta, CA) is shown in Figure 15.

Figure 15. Tension disk infiltrometer used to perform infiltration test.

A simple approach to analyze infiltration data on the soils was based on Wooding's relationship (Wooding 1968) further developed by (Clothier, et al., 1990; Ankeny, et al., 1991; Logsdon, et al., 1993). This method requires the measurement of steady-state infiltration rates at two pressures steps.

Field infiltration tests were performed in the two biocover cells. Pressure suction of -15, -6, -3 and 0 cm H_2O of water were applied to the disc filter.

Flux Box Testing and Measurement

Measurements of methane and carbon dioxide fluxes were made from the two biocover test cells in June 2009 and winter/spring/summer 2010. These tests involved the following steps:

1. Inject a tracer gas (sulfur hexafluoride, SF_6) into the influent LFG entering the bottom of each test cell. The tracer gas is injected at a fixed rate with a mass flow controller calibrated for SF_6. Wait for steady-state flow to be achieved.
2. Place the cover on top of the biocover test cell, creating an enclosed flux chamber for the entire cell.
3. Immediately turn on the fans mixing the air in the flux chamber.
4. Immediately begin sampling gas in the flux chamber by either (1) collecting gas samples in pre-evacuated sample vials, or (2) analyzing the gas for SF_6, CO_2, and CH_4 using a photoacoustic infrared spectroscope (PAS), (INNOVA Model 1312, Lumasense Technologies, Denmark).
5. Collect samples for approximately 30 minutes, after which the top cover is removed and the testing is repeated.

Preliminary tests showed that some gas entering the bottom of the biocover test cells leaked from the bottom of each test cell and thus did not flow through the biocover. In order to correct for this effect, the known mass flux of SF_6 was used to correct for any leakage. A photograph of the biocover with the top used for the flux tests is shown in Figure 16. The PAS used to measure gas concentrations is shown in Figure 17.

Figure 16. Biocover test cell with cover used for flux testing. The cover, propped up with pieces of wood in this photograph, is lowered onto the top of biocover and sealed during testing.

Figure 17. PAS (on right) used to measure SF_6, CO_2, and CH_4 in field for flux tests.

The first set of biocover flux tests outlined above was intended to determine the flux from the entire test cell. A second set of tests were conducted in Spring 2010 to evaluate emissions from different regions of the test cell. In this case, a 5-gallon bucket with the bottom removed was inverted, sampling tubing and fans were attached for mixing the gas inside the bucket, then this arrangement was placed at various locations on the top surface of the biocover to quantify the spatial variability of CH_4 emissions. Tests using this small-scale flux chamber were only conducted in Spring 2010. A photograph of the flux chamber is shown in Figure 18. The layout of the small-scale flux chambers across the surface of Biocover #1 and Biocover #2 is shown in Figure 19.

Figure 18. Small-scale flux chamber used to quantify the spatial variability of surface CH_4 fluxes from biocover test cells.

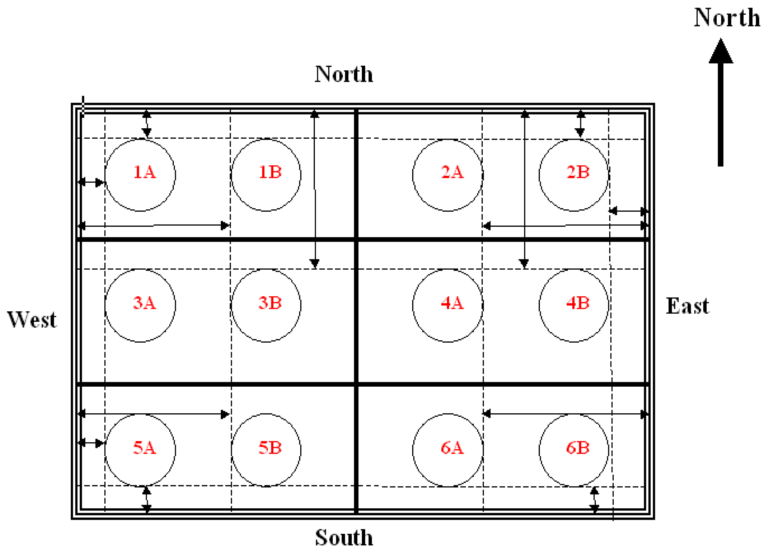

Figure 19. Layout of small-scale flux chamber tests shown on the top surface of each biocover test cell.

Stable Isotope Analyses

To further substantiate the measured removal of CH_4 from methanotrophs in each biocover, gas samples were used to determine the change in the stable isotope ratio for CH_4. The methodology for conducting these analyses is described in detail in Stern et al. (2007). Professor Jeff Chanton from Florida State University conducted these analyses.

Predictive Computer Modeling

Computer models can be a useful tool to assess the performance of biocovers through time and under different climatic conditions. Several models have been developed to simulate CH_4 oxidation in landfill cover soils with constant environmental conditions (Hilger, et al., 1999; Stein, et al., 2001; De Visscher, et al., 2003), and in compost biocovers with varying moisture content and temperature (Abichou, et al., 2009). Abichou, et al., (2009) used field measurements of moisture and temperature as input parameters to describe daily CH_4 oxidation. They were able to separate biological oxidation of CH_4 from blockage of LFG flow by the presence of compost biocovers.

While we plan to develop a computational tool that can simultaneously simulate CH_4 oxidation and the impact of climatic variations on temperature and moisture within biocovers, we took a simplified approach similar to that of Abichou et al., (2009) for this initial modeling. The data collected in the field (moisture content, temperature, atmospheric pressure, and flow rate and gas composition of LFG inflow) were used as initial and boundary conditions for model simulations. Several assumptions were made in the course of the model development. First, the structure of the biocover was assumed to be horizontally uniform. Second, water and gas flow in the biocover could be described with a single porosity model. Third, water movement is not significant over short periods, and therefore can be neglected during CH_4 oxidation simulations. With these assumptions, predictive computer modeling was conducted for different seasons to assess the impact of climatic effects on the long-term behavior of biocovers.

To simulate both gas transport of multiple gas constituents (CH_4, CO_2, O_2 and N_2) and CH_4 oxidation in the biocover, TMVOCBio (Aquater, 2002) was used. TMVOCBio is an extended version of TMVOC (Pruess and Battistelli, 2002), which is an integral finite difference simulator for multi-phase non-isothermal flows of multicomponent mixtures in porous media, with the capability of simulating biodegradation with a multiple Monod kinetic model. To compare with available field measurements such as gas composition and CH_4 oxidation rate, simulations were conducted for different seasons from June 2009 to August 2010. Simulation results were compared with field data to verify the model. The model was then used to help explain mechanisms affecting the efficiency of the biocovers to oxidize methane.

Model domain—A one-dimensional vertical model was developed for each biocover test cell constructed at Yolo County Central Landfill: Biocover #1 filled with aged green material (BC1) and Biocover #2 filled with fresh green material (BC2). The domain was 90 cm in depth. While the actual depth of BC1 and BC2 decreased by 13.2 and 24.4 cm, respectively, from Jan. 26, 2009 to July 8, 2009 due to settlement, the dimension of the domain was maintained constant, except for the simulation for August 2010, since the change of the biocover depth itself would not be the main factor affecting CH_4 oxidation. The settlement of the biocover would rather affect CH_4 oxidation by changing porosity, pressure-saturation relationship for water flow, and relative gas permeability function for gas flow. However, the relationships for water and gas flow cannot be simply predicted from the settlement data. Therefore, assuming settlement only resulted in the reduction of the void volume in the biocover, the bulk density and porosity were correspondingly reduced in the model in accordance with field measurements of changing biocover thickness.

In August 2010, the top half of the biocovers was removed and materials mixed with a shovel to mitigate the prevalent anaerobic condition of the biocovers and therefore improve the efficiency of CH_4 oxidation. To accommodate the model domain to this dramatic change, the depth of the domain was reduced to 50 cm. As a result, the temperature readings at Layer 1 were only used for this simulation, since Layer 2 sensors were now measuring atmospheric conditions.

Since water flow was neglected during the CH_4 oxidation simulations, the gravel layer only served as the gas distribution layer of LFG influx. Therefore, instead of simulating the gravel layer as a part of the model domain, a simple constant gas flux boundary condition was applied as the bottom boundary condition. The boundary conditions will be described later in detail. Figure 20 shows a schematic of the model domain.

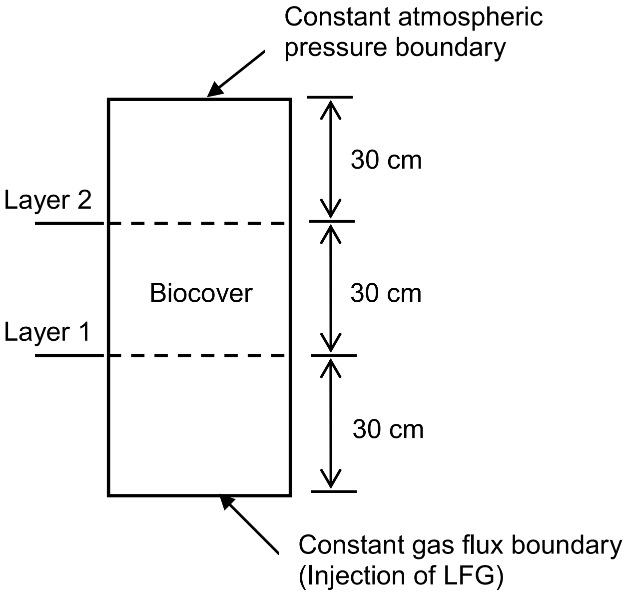

Figure 20. Schematic of model domain. Layer 1 and 2 indicate the location of monitoring tubes for temperature, moisture, and gas composition measurements.

Initial and boundary conditions—The volumetric water contents used in the model were calculated using the measured moisture content and dry bulk density of the biocover core samples:

$$M_c = \frac{\theta \rho_w}{\rho_b^d + \theta \rho_w} \qquad \text{Eq. (3)}$$

where M_c is the moisture content (mass of water/total wet mass of waste), θ is the volumetric water content ($L^3\ L^{-3}$), ρ_b^d is the dry bulk density of the biocover ($M\ L^{-3}$), and ρ_w is the density of water ($M\ L^{-3}$). The dry bulk density was estimated through time based on measurements from field cores and settlement data.

The temperature of the biocover was based on the temperature data collected at Layer 1 and 2 in each biocover. Since all field tests were conducted during the daytime, generally between 10 a.m. and 4 p.m., the temperature measured at 12 p.m. was used for simulations instead of the average daily temperatures. The temperature of the biocover between Layer 1 and 2 probes was assumed to be linearly changed, and the temperature above Layer 2 and below Layer 1 was assigned to be equal to the temperature at Layer 1 and Layer 2, respectively.

A constant atmospheric pressure was assumed at the top surface of the domain, and these data were obtained from the weather station at the site. The LFG injection flow rate was specified based on the field measurements, and was constant during each simulation. The temperature of the injected LFG was assumed to be equal to the average of the measured temperatures in Layer 1. The LFG was fully saturated with water vapor, and the corresponding vapor pressure at the temperature was calculated. The LFG was assumed to consist of CH_4, CO_2, N_2, and water vapor. The concentration of CH_4 and CO_2 were obtained from the field measurements, and the remaining balance, after excluding water vapor, was considered N_2.

Gas transport—Advective gas flux was computed by using Darcy's law, which accounts for relative permeability of the gas phase. Gas permeabilities were measured from the laboratory tests of intact cores taken from the field and were 3.91×10^{-10} m^2 and 5.03×10^{-10} m^2 for BC1 and BC2, respectively. Based on the laboratory tests, the gas permeabilities of the biocovers was invariant over the moisture contents measured in the field. Diffusive gas flux was described using Fick's law, and the effective gas diffusion coefficient was calculated by using the Troeh model (Troeh, et al., 1982) which was found to best describe diffusion in laboratory tests of intact cores taken from the field. The Troeh model describes the relationship between tortuosity and air-filled porosity and is:

Eq. (4)

where τ is tortuosity (or the ratio of the effective gas diffusion coefficient in soil to the gas diffusion coefficient in free air), n is air-filled porosity, ε_{th} is the inactive pore space, V is pore connectivity parameter, and C is a fitting parameter. The fitted parameters, C, V and ε_{th}, are provided in Table 1 along with other gas transport parameters obtained from laboratory experiments using intact cores from the field.

Table 1. Parameters for gas flow simulation.

Parameter	BC1	BC2
Gas permeability (m^2)	3.91×10^{-10}	5.03×10^{-10}
Porosity (m^3 m^{-3})	0.73	0.89

Troeh model	ε_{th} (m^3 m^{-3})	0.18	0.42
	V (-)	1.82	0.97
	C (-)	1.12	0.97

Methane oxidation-To describe CH_4 oxidation, the following equation was used, following the approach of De Visscher and Van Cleemput (2003):

$$\mathrm{CH_4} + 1.5\mathrm{O_2} \rightarrow 0.5\mathrm{CO_2} + 1.5\mathrm{H_2O} + 0.5\mathrm{CH_2O} \qquad \text{Eq. (5)}$$

where CH_2O represents biomass. The biological consumption of CH_4 was expressed as

$$r_{CH_4} = -V_{\max}\left(\frac{C_{CH_4}}{K_m + C_{CH_4}}\right)\left(\frac{C_{O_2}}{K_{O_2} + C_{O_2}}\right) \qquad \text{Eq. (6)}$$

where r_{CH_4} is the reaction rate (ppm min^{-1}) and V_{max} is the maximum reaction rate (ppm min^{-1}). K_m and K_{O_2} are the half-saturation constant (ppm) for CH_4 and O_2, respectively, and C_{CH_4} and C_{O_2} are CH_4 and O_2 concentration (ppm), respectively.

The effect of temperature on K_m and V_{max} was accounted for by introducing the temperature correction factor for K_m and V_{max}, and the approach described in De Visscher and Van Cleemput (2003) was used.

For the temperature correction factor for K_m, $f_{K,T}$,

$$f_{K,T} = \frac{0.143 + 0.207T}{0.143 + 0.207 \cdot 22}\,\frac{K_{H,22°\mathrm{C}}}{K_{H,T}} \qquad \text{Eq. (7)}$$

where T is the temperature in °C, and $K_{H,T}$ is the CH_4 solubility in M atm^{-1} at the temperature T. $K_{H,T}$ was expressed as follows (Sander, 1999):

$$K_{H,T} = 1.4 \times 10^{-3} \exp\left(1700\left(\frac{1}{T + 273.15} - \frac{1}{298.15}\right)\right) \qquad \text{Eq. (8)}$$

For the temperature correction factor for V_{max}, $f_{V,T}$,

$$f_{V,T} = \begin{cases} 2.8^{\frac{T - 22°\mathrm{C}}{10}} & , \ \text{if } T \geq T_j \qquad \text{Eq. (9)} \\ \frac{\ln 2.8}{10} \cdot 2.8^{\frac{1}{\ln 2.8} - 2.2} \cdot T, & \text{if } T < T_j \qquad \text{Eq. (10)} \end{cases}$$

$$T_j = 10/\ln 2.8 \qquad \text{Eq. (11)}$$

where T_j is a junction temperature where the temperature correction factors calculated with Eq. (9) and Eq. (10) have the same value.

The effect of moisture content on V_{max} was also considered. While there is no detrimental effect of water on CH_4 oxidation when water contents are sufficiently high, the reaction rate decreases as water contents lower (Abichou, et al., 2009). In this study, the water content dependence was described using a moisture content correction factor, $f_{V,M}$:

$$f_{V,M} = \begin{cases} 1 \ , & \text{if } \theta \geq \theta_{crit} \\ \frac{\theta - \theta_{0.1}}{\theta_{crit} - \theta_{0.1}}, & \text{if } \theta_{0.1} \leq \theta < \theta_{crit} \\ 0 \ , & \text{if } \theta < \theta_{0.1} \end{cases} \qquad \text{Eq. (12)}$$

where θ is the volumetric water content, $\theta_{0.1}$ is the volumetric water content corresponding with the moisture content of 0.1, and θ_{crit} is the critical volumetric water content corresponding with the critical moisture content, $M_{c,crit}$. That is, it was assumed that V_{max} decreases linearly for volumetric water contents between θ_{crit} and $\theta_{0.1}$, and that V_{max} becomes zero for volumetric water contents below $\theta_{0.1}$. The moisture content of 0.1 and $M_{c,crit}$ were determined based on laboratory measurements for CH_4 oxidation in this report, and $M_{c,crit}$ for BC1 and BC2 is shown in Table 2. All the correction factors were implemented in the TMVOCBio code.

Two assumptions were made to simplify simulations of CH_4 oxidation in the biocovers. First, no water production was considered. Water produced as a result of CH_4 oxidation has a very small effect on CH_4 transport and oxidation (Molins et al., 2008). This effect may increase, though, if initial water saturations are high and simulation times are long, but loss of water by evaporation may compensate for any water production (Molins et al., 2008). Second, biomass growth and decay were assumed to be in equilibrium, cancelling out the production of biomass in Eq. (5).

Unless stated otherwise, the parameters in De Visscher, et al., (2003) were used. Table 2 summarizes the model parameters for the CH4 oxidation simulation.

Table 2. Model parameters for the CH_4 oxidation.

Parameter	BC1	BC2
$V_{max,max}$ (µg g^{-1} hr^{-1}) at 22 °C *	85	
K_m (CH_4, ppm, gas phase) at 22 °C *	7207	
K_{O_2} (%, gas phase) †	1.2	
$M_{c,crit}$ *	0.18	0.25
θ_{crit} ‡	0.066	0.114

* Estimated from laboratory data in this report

† De Visscher and Van Cleemput (2003)

‡ θ_{crit} is automatically converted from $M_{c,crit}$ using the relationship in Eq. (3).

Results and Discussion

Solids Sampling and Testing

Results from the solids testing are shown below in Table 3 for samples collected from BC1 and BC2 in June 2009. Recommended parameter values for compost materials utilized in biocover construction are also shown from Huber-Humer, et al., (2009). The biocover material emplaced in BC1 and BC2 satisfy all recommended parameters with three exceptions, shown as shaded cells in Table 3: pH, NO_2^- - N, and P. The biocover material was slightly acidic, had somewhat elevated NO_2^- - N, which is an inhibitor of methane oxidation, and is slightly deficient in P.

As will be shown from our laboratory and field tests described below, though, these factors did not significantly limit methane oxidation in the field. Instead, environmental factors (temperature and soil moisture) dominated methane oxidation.

Table 3. Biocover solids testing data.

	Biocover #1 (Aged Green Material)		**Biocover #2 (Fresh Green Material)**		**Recommended (Huber-Humer, et al., 2009)**
Parameter	mean	Stdev	mean	Stdev	
pH	5.08	0.06	5.7	0.02	6.5-8.5
EC (mmhos/cm)	1.61	0.08	1.31	0.02	<4
Organic Matter (%)	37.7	1.51	61.0	1.0	>15
Total N (%)	0.96	0.12	1.04	0.09	>0.5
Total C (%)	28.79	2.07	21.03	3.76	
C/N Ratio	30.09	2.24	20.17	1.92	
NH4-N (mg/kg)	20.85		103.48		<400
NO3-N (mg/kg)	0.1		0.02		
NO2-N (mg/kg)	0.9		0.86		<0.1
Al (mg/kg)	17956		11385		
B (mg/kg)	41.34		100.56		
Ca (mg/kg)	16523		20813		
Cu (mg/kg)	53.73		32.83		
Fe (mg/kg)	22667		14201		
K (mg/kg)	4296		7566		
Mg (mg/kg)	11810		9506		
Mn (mg/kg)	647.57		410.2		
P (mg/kg)	1116		1129		>3000
S (mg/kg)	959		1126		

Zn (mg/kg)	173.69		99.77		

Respiration

Microbial activity was detected in all treatments, and example results are shown in Figure 21, where carbon dioxide evolution rates (CER) are plotted versus time. Final CER ranged from 1.26 to 3.54 mg CO_2 day^{-1} gdw^{-1} for samples collected in June 2009, and from 1.10 to 3.58 mg CO_2 day^{-1} gdw^{-1} for samples collected in February 2010. There were minimal changes in respiration rates between the two sampling events.

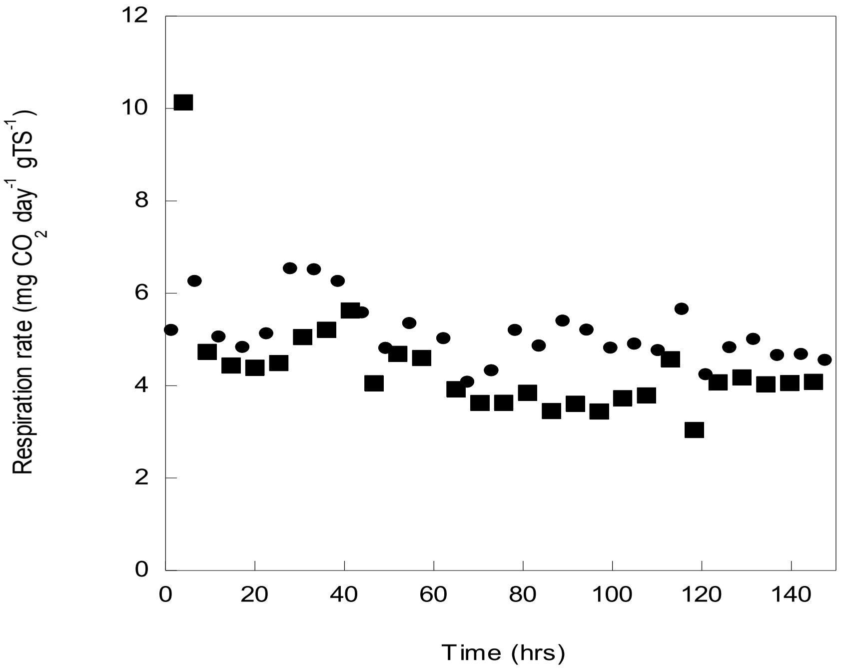

Figure 21. Respiration rates from samples collected from BC2-3 (5-23).

Table 4. Respiration results.

Sample	Average respiration mg CO_2 day^{-1} gTS^{-1}	Cumulative respiration mg CO_2 day^{-1} gTS^{-1}
June 2009		
BC1-1(0-16)*	1.26	16.04
BC1-1 (16-24)*	1.36	14.80
BC1-2 (17-24)*	1.50	17.29

BC2-1 (0-18)*	3.54	46.02
BC2-1 (18-24)*	2.61	31.98
February 2010		
BC1-3 (0-8) *	1.10	11.92
BC1-3 (8-18) *	1.35	16.44
BC1-3 (8-24) ***	1.89	21.37
BC2-3 (0-8) *	3.58	36.22
BC2-3 (8-15) *	3.42	36.51
BC2-3 (5-23) **	3.39	34.72

* n=3.
** respiration is the average of two samples
*** respiration is from only one sample

The results from all samples are reported in Table 4. BC1 (Biocover #1) samples and BC2 (Biocover #2) samples. Numbers in parentheses are the depths in inches over which samples were collected. The respiration rates of Biocover #2 samples are approximately two to three times larger than respiration rates of Biocover #1 samples, which is consistent with the younger age of Biocover #2 materials.

According to the California Compost Quality Council (2001), “very stable” composts have respiration rates < 2 mg CO_2-C/g organic matter/day. Converting the respiration rates reported in Table 4 to these units, the mean respiration rate for Biocover #1 was 1.02 mg CO_2-C/g organic matter/day, while the mean respiration rate for Biocover #2 was 1.48 mg CO_2-C/g organic matter/day. Thus, both aged and fresh green material were “very stable” composts based on respiration rates.

Huber-Humer, et al. (2009) recommended that composts used as biocovers should have respiration activity < 8 mg O_2/g organic matter for a 7-day test (OENORM S 2027-1, 2004). Assuming a respiratory quotient of one, the data reported in Table 4 were converted to these units. The mean respiration activity was 11.8 and 44.7 mg O_2/g organic matter for a 7-day test for Biocovers #1 and #2, respectively. Thus, the fresh and aged green material biocovers in this study do not satisfy the recommended stability requirements and may consume significant O_2 and/or generate unwanted CH_4 in the field. While the aged green material (BC1) is only slightly less stable than recommendations, the fresh green material (BC2) is expected to consume considerable O_2 in the field and potentially to generate appreciable CH_4 if anaerobic conditions occur.

Biocover Methane Oxidation Properties

Laboratory measurements were used to assess the impact of temperature and moisture content on methane oxidation. Results from experiments using biocover materials collected from the field and then incubated in the laboratory at different temperatures are shown below in Figure 22. Temperature clearly had a significant effect on the rate of methane consumption, with the effect more dominant in the aged green material for BC1 than the fresh green material in BC2. The reason for this difference is unknown. All samples had a uniform moisture content of 30 percent.

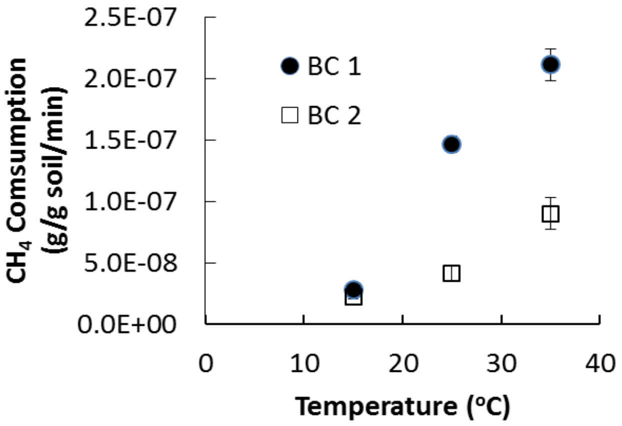

Figure 22. Effect of temperature on CH_4 removal in laboratory experiments.

The impact of moisture is illustrated in Figure 23. In this plot samples were analyzed at 25°C immediately after collecting them from the field from BC1 and BC2 in July 2010. The data suggest a significant impact of moisture content on methane oxidation. Here, it is important to note that because samples were collected at different locations and were not incubated, differences in microbial populations could have been associated not only with the availability of water but also the availability of oxygen in the field. Despite this confounding effect, the results indicate a significant correlation between moisture content and CH_4 oxidation. These data were used to estimate the critical volumetric water contents employed in the predictive modeling - Eq. 12 above.

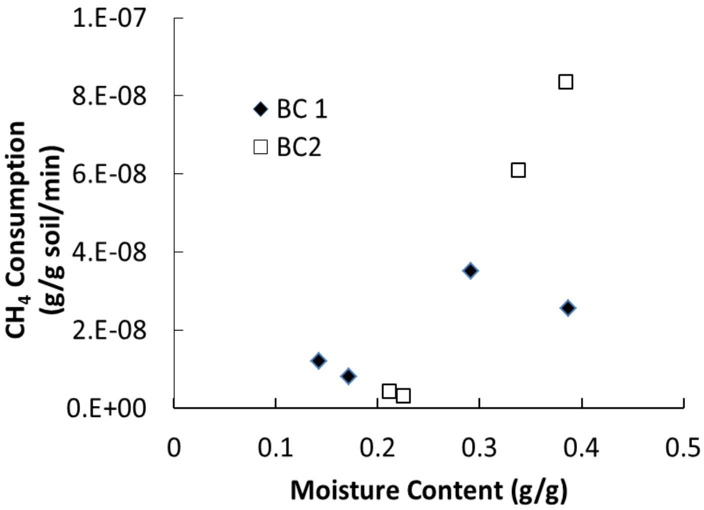

Figure 23. Effect of moisture content on CH_4 removal in laboratory experiments conducted with field samples.

Biocover Flow Properties—Infiltration and Gas Transport Testing

The biocover flow properties determined from laboratory and field tests are summarized below. These properties were needed to describe gas transport and CH_4 oxidation in the computer modeling. These properties can also be used in other types of models, e.g. the module for gas diffusion developed for biocovers here may be employed in the recently developed CALMIM model (Bogner, et al., 2010).

Particle Size Distribution—Two types of material were used in the construction of the biocover cell #1(aged green material) and #2 (fresh green material). Two large batches of 1.7 kg (aged) and 3.8 kg (fresh) were sieved and 270 g of aged green material and 759 g of fresh green material. These samples were then used to create repacked samples in the lab. The result of sieve analysis is shown on Figure 24 below.

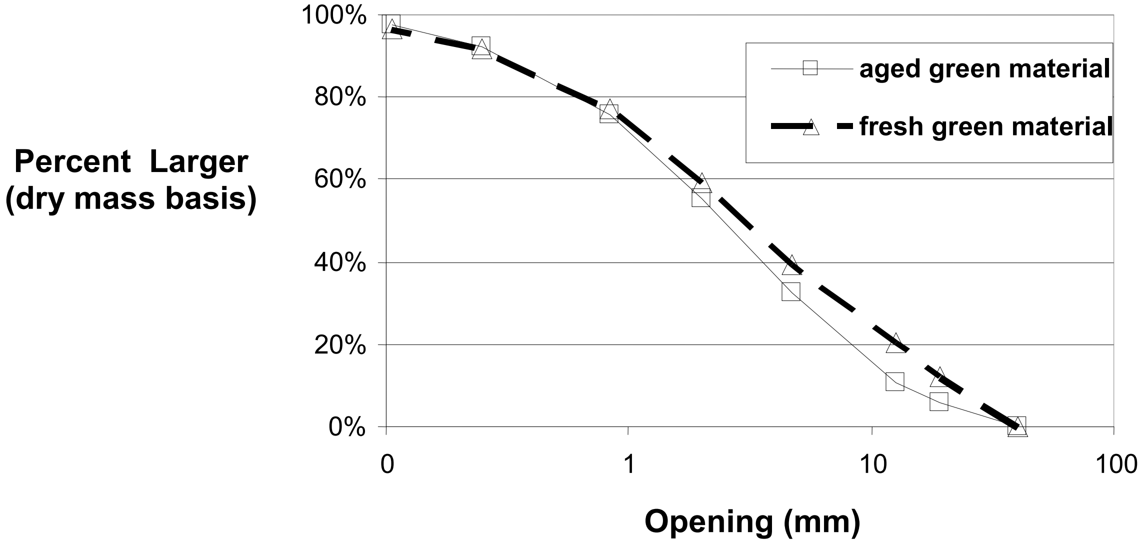

Figure 24. Particle size distribution of green material samples.

Fresh and aged green material samples had similar particle size distributions. The fraction of particles that had diameter larger than 2 mm were greater in fresh green material when compared to the aged green material sample. Fresh green material was composed of roots and leaves of trees that are not degraded, while aged green material had been already decomposed to some extent and was mostly composed of leaves. This may explain why fresh green material contained larger particles.

Air Permeability—Air permeability was measured for cores samples removed from biocover cells with aged green material (BC1) and fresh green material (BC2). The result of air permeability measurements are presented in Figure 25.

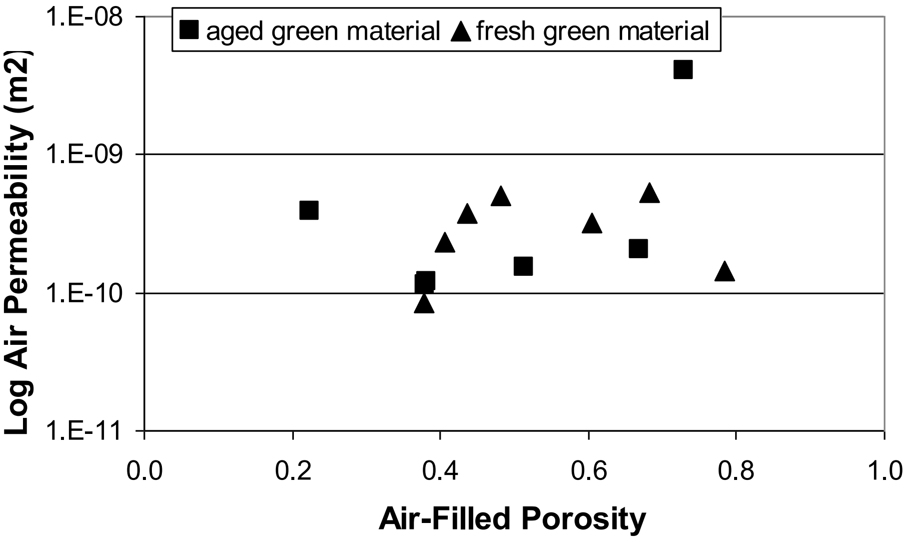

Figure 25. Log air permeability vs. air-filled porosity.

Air permeability was measured at the range of matrix potentials of -4 cm H_2O to dry for cores obtained from BC1 and BC2. We were unable to measure air permeability of BC2 at oven-dried condition due to its high value. Several researchers cited difficulties due to soil shrinkage from the walls and other experimental problems (Kawamoto, et al., 2006; Resurreccion, et al., 2007). Air permeability was generally constant at the range of our measurement (less than 2 and 1 order of magnitudes variations for BC1 and BC2 respectively).

Van Genuchten-Mualem (VGM) model was used to predict air permeability. This model is presented in the following equations 13 and 14:

$$S_e = \frac{S - S_r}{1 - S_r} \qquad \text{Eq. (13)}$$

$$k_a = k_{\text{int}}(1 - S_e^{0.5})(1 - (1 - (1 - S_e)^{1/(1-\frac{2}{n})})^{(1-\frac{2}{n})})^2 \qquad \text{Eq. (14)}$$

where S is water saturation, S_r is residual water content, k_{int} is intrinsic permeability, and n is van Genuchten model parameter which will be explained later (Hanging Column Data). The VGM model parameters were determined in the VGM model prediction of air permeability and measured values are plotted vs. water content at figures 26.

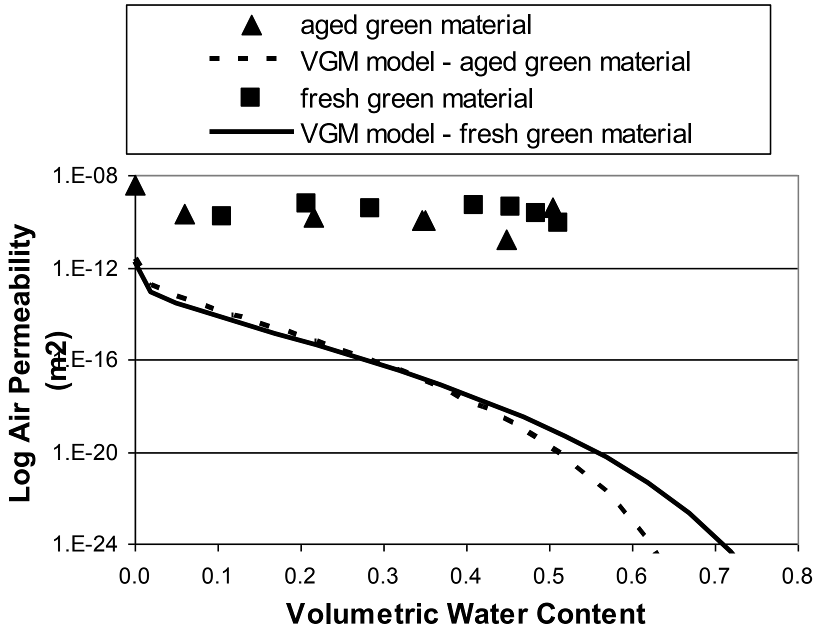

Figure 26. Log air permeability and VGM model predictions vs. water content.

VGM model always underestimates air permeability. The differences between VGM model predictions and measured values are larger for wet ranges. These data indicate that a VGM model developed from water flow measurements will be inadequate to describe gas flow in the fresh and aged green material.

Given the near constant air permeability over a wide range of volumetric water contents for both fresh and aged green material, the gas permeability was assumed to be constant and invariant with water content in the modeling reported below, as long as volumetric water contents did not exceed 0.5. This is not a typical result for soils and demonstrates the unique features of these materials, where very large water contents are needed in order for the largest pores that control gas flow to be affected.

Diffusion—The results of diffusion coefficient test on biocover materials are shown in following figures. The Troeh model (Troeh, et al., 1982) was the simplest model that provided an adequate fit to the measured data.

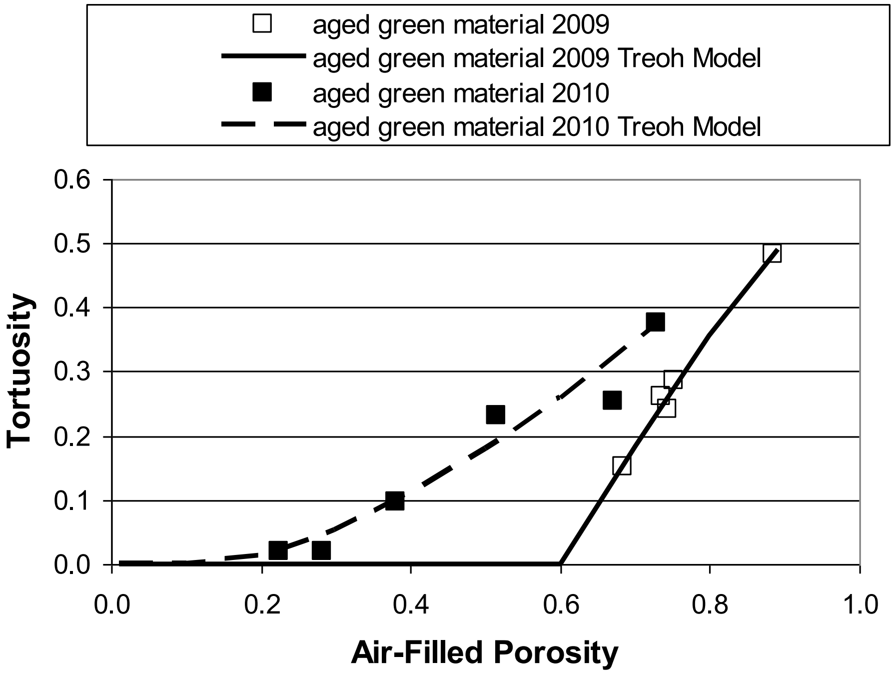

Figure 27. Tortuosity versus air-filled porosity (AFP) of aged green material (BC1). Solid lines represent Troeh model results.

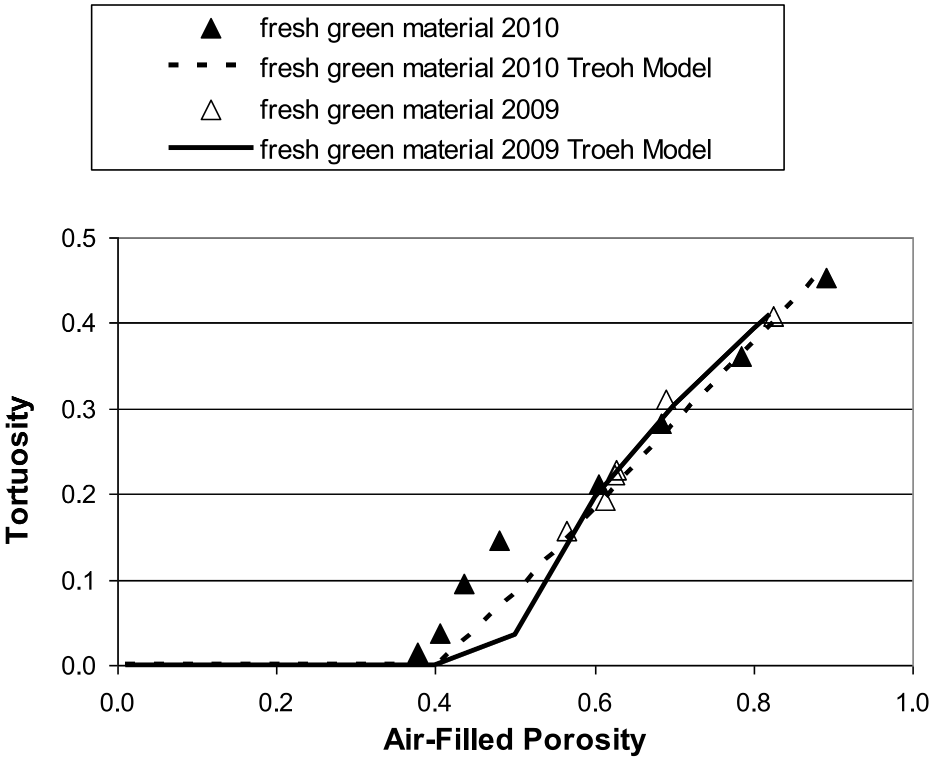

Figure 28. Tortuosity versus air-filled porosity (AFP) fresh green material (BC2) (Solid lines represents Troeh model).

The model parameter (C, V and ε_{th}) fitted to the data are presented in the following table:

Table 5. Troeh model parameters.

	C	V	ε_{th}
BC1-09	1.23	0.67	0.64
BC2-09	1.23	0.67	0.63
BC1-10	1.12	1.82	0.18
BC2-10	0.97	0.97	0.42

Air-filled porosity at which diffusion ceases to zero (ε_{th}) is usually considered as inactive pore space. As the biocover materials age, ε_{th} decreases for biocover samples. Also pore connectivity index is increased for both biocover samples as the materials ages. This means that diffusion occurs at higher rates as materials aging for the same air-filled porosities. This trend on the diffusion data was observed before for undisturbed soils samples and was related to the development of connected structures within undisturbed soil as they age (Moldrup, et al. 2005).

An important observation from our work is the inadequacy of the Millington-Quirk model to describe gas diffusion. The Millington-Quirk model is the standard model for describing diffusion in soils, but this model significantly over predicted gas diffusion in the fresh and aged green material. We recommend instead that the Troeh model be used to describe gas diffusion when a biocover is constructed of green material. Further testing in additional biocovers should be completed to verify the utility of the Troeh model for describing diffusion in biocovers from various source materials.

Hanging Column-The results of hanging column tests are presented in Figures 29 through 32.

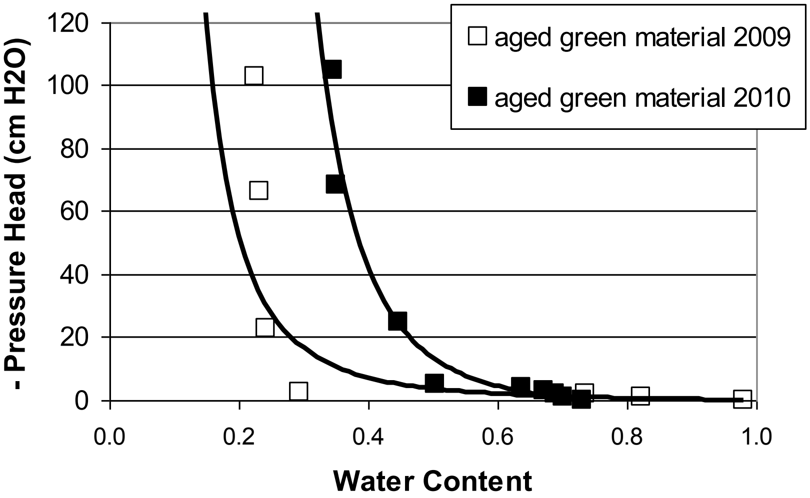

Figure 29. Pressure head versus volumetric water content for aged green material (BC1).

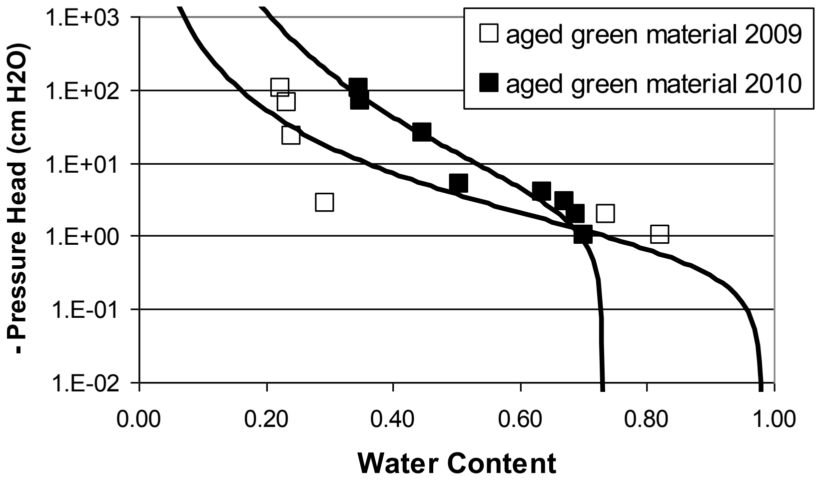

Figure 30. Log pressure head versus volumetric water content for fresh green material (BC1).

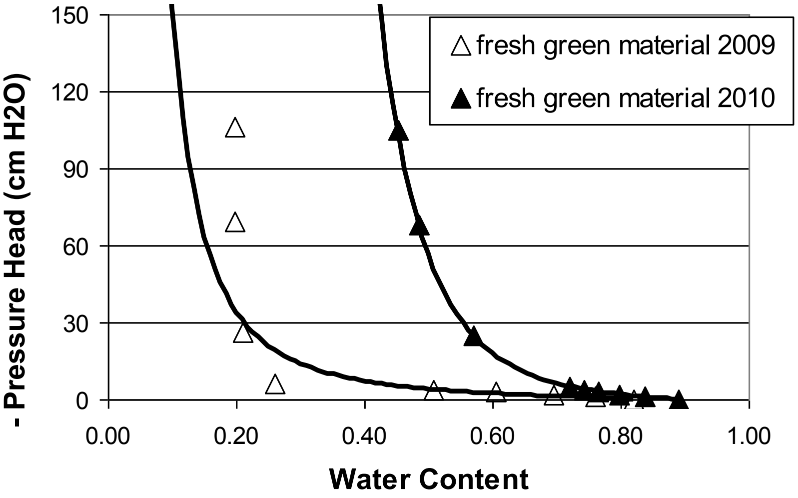

Figure 31. Pressure head versus volumetric water content for fresh green material (BC2).

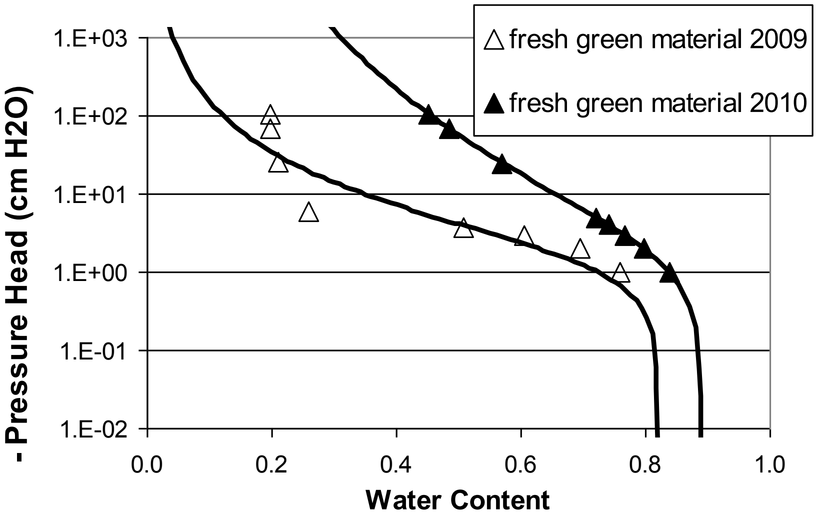

Figure 32. Log pressure head versus volumetric water content for fresh green material (BC2).

The Van Genuchten (VG) model was used to fit retention data and can be presented as follow:

$$S_e = \frac{1}{(1+(\alpha\,|\,h\,|^n)^{1-\frac{1}{n}}} \qquad \text{Eq. (15)}$$

where *h* is suction pressure.

VG model predictions are shown as lines on the graphs. Significant amounts of water drained at -4 cm H_2O suction pressure. This pressure is usually considered the boundary between fracture and matrix domain (Chen, et al., 1993; Holden, et al., 2001) and showed that a large volume of the fresh and aged green material are composed of easily drainable water (fracture volume). This volume decreases as time passes, probably due to compaction of biocover samples in both cells.

RETC, a package developed by USDA Salinity Lab to obtain retention model parameters from experimental data, was used to fit VG model parameters. The irreducible water content was set equal to 0.07, similar to that of silty soils. Saturated water content was fixed to the total sample porosity and *n* and *α* were fitted.

Table 6. VG model parameter for aged and fresh green material.

	aged green material 2009	aged green material 2010	fresh green material 2009	fresh green material 2010
α (cm^{-1})	1.73	0.40	0.62	0.57
n	1.35	1.21	1.46	1.17

Infiltration Test—Cumulative infiltrated water versus time of green material samples are shown in figures 32 and 34.

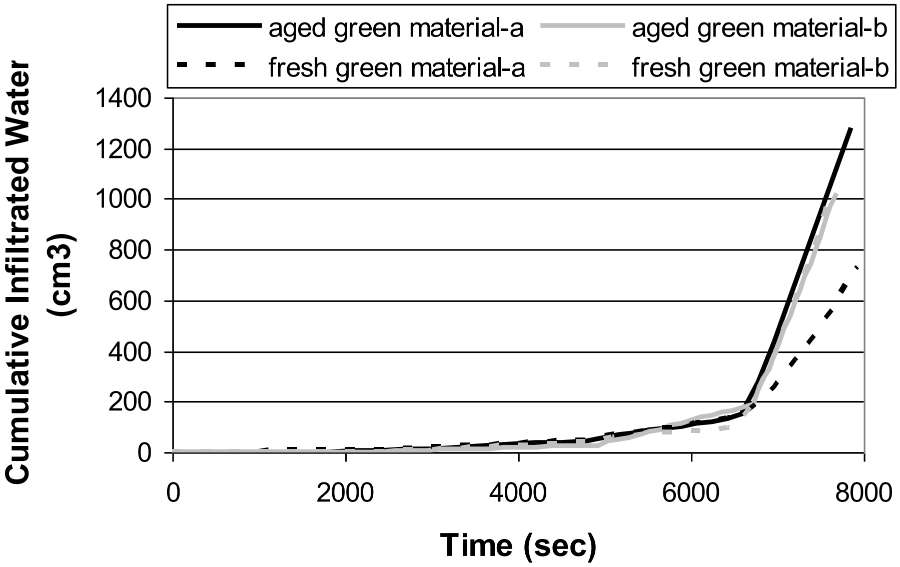

Figure 33. Cumulative infiltrated water versus time.

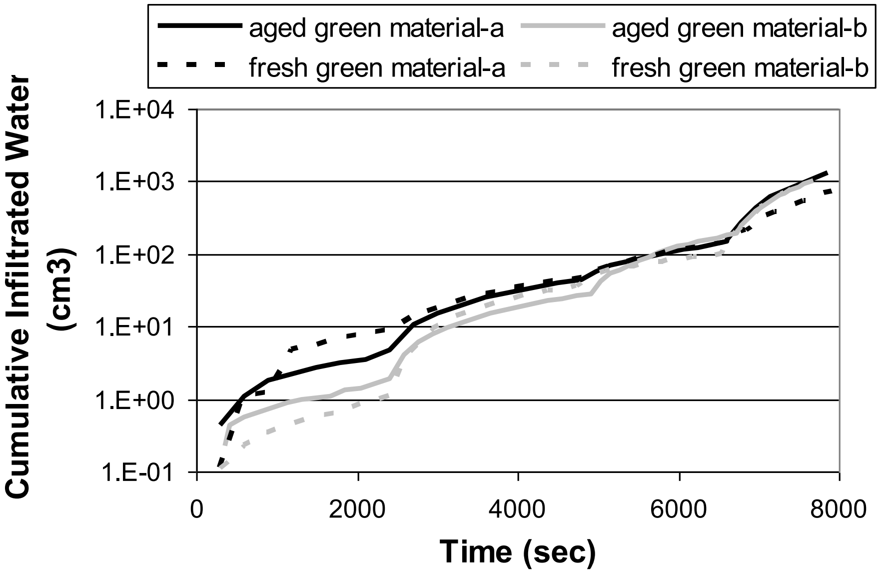

Figure 34. Log cumulative infiltrated water vs. time.

The Wooding approach (Wooding 1968) was used to analyze the infiltration data and to compute the saturated and unsaturated hydraulic conductivities at different applied suctions. The results of this analysis of the infiltration data are shown in Table 7.

Table 7. Wooding analysis results.

	Saturated and unsaturated hydraulic conductivity (cm/sec)			
Applied Pressure (cm H_2O)	**BC1-a**	**BC1-b**	**BC2-a**	**BC2-b**
-15	3.86E-06	1.61E-06	7.01E-06	1.06E-06
-6	3.71E-05	2.54E-05	3.24E-05	3.34E-05
-3	1.42E-04	2.42E-04	1.32E-04	8.04E-05
0	2.55E-03	2.36E-03	1.21E-03	2.41E-03

The saturated hydraulic conductivities of BC1 and BC2 are the conductivities at zero water pressure and were similar and comparable to that of peat and sands. The sudden increase in saturated hydraulic conductivity, when compared to unsaturated hydraulic conductivity at -3 cm H_2O, is usually considered a feature of macroporous soils (Baird 1997; Lin, et al. 1998). Thus, the infiltration data like the air permeability data and hanging column test data indicate that very large connected pores existed in both fresh and aged green material.

VG model parameters obtained with RETC were used in Van Genucthen-Mualem (VGM) model to describe unsaturated hydraulic conductivity function. Wooding analysis results were plotted against VGM model perditions in the following graphs.

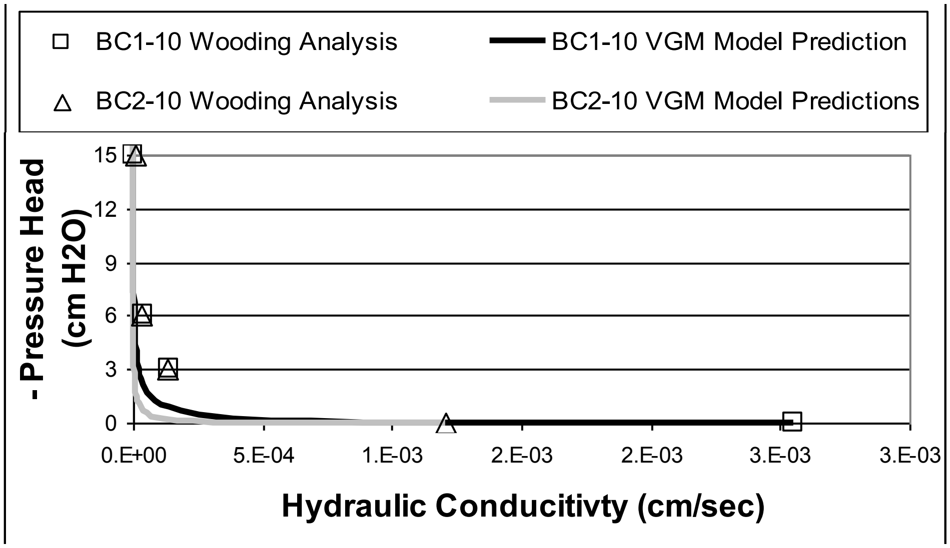

Figure 35. Wooding analysis results and VGM model predictions of pressure head vs. hydraulic conductivity.

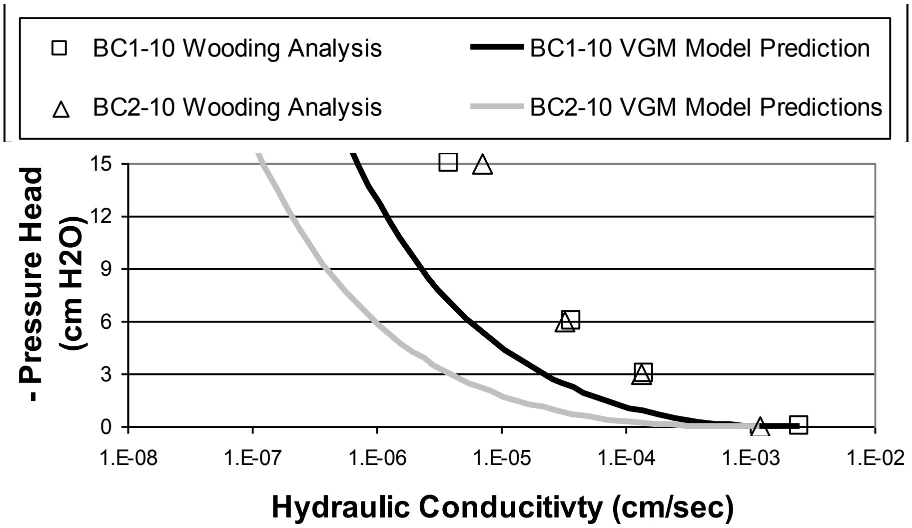

Figure 36 Wooding analysis results and VGM model predictions of pressure head vs. log hydraulic conductivity.

VGM model underestimated Wooding analysis results for the range of 0 to -15 cm H_2O. Wooding analysis results were underestimated by factor of 10 and 100 for BC1 and BC2 respectively. This result is consistent with the inability of the VGM model to describe air flow in fresh and aged green material. The materials behave like a macroporous material with mixtures of very large pores and much smaller pores. It will likely be necessary to employ a dual porosity or dual permeability model to describe water flow.

In the predictive modeling of CH_4 oxidation reported below, we did not model water flow. Instead, measured volumetric water contents from the field were used as model inputs. The constitutive models reported in this section for gas flow and gas diffusion were used. In field situations where detailed information on the water content of biocovers is not available, it will be necessary to model the impact of rainfall and evapotranspiration on material moisture levels. The laboratory and field measurements of water flow and retention reported here can be used to develop such models.

Biocover Temperature

Temperature measurements at each layer and in the atmosphere are shown for BC1 and BC2 in Figures 37 and 38 below. Temperatures in the biocovers were almost always higher than atmospheric temperature, which reflects the heat generated by biological activity. However, the difference between atmospheric and biocover temperatures diminished significantly during the late fall, winter, and early spring months, October through April. Biological activity was significantly diminished during these periods, and biocover temperatures were much closer to atmospheric values. The late fall/winter/early spring periods correspond to periods of poor CH_4 oxidation, as will be shown below.

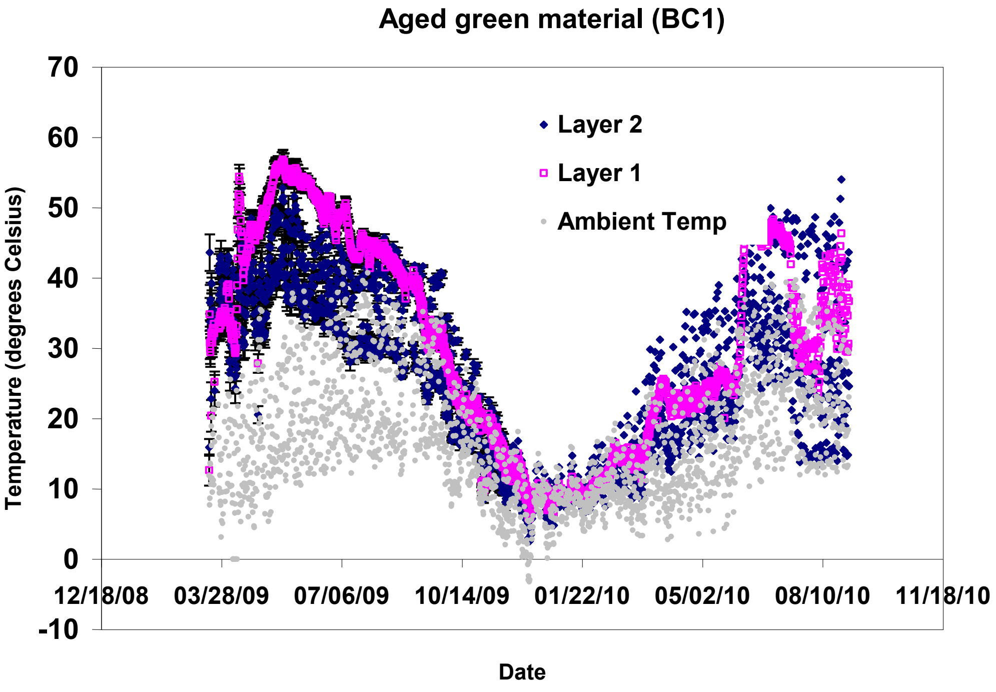

Figure 37. Temperature in BC1.

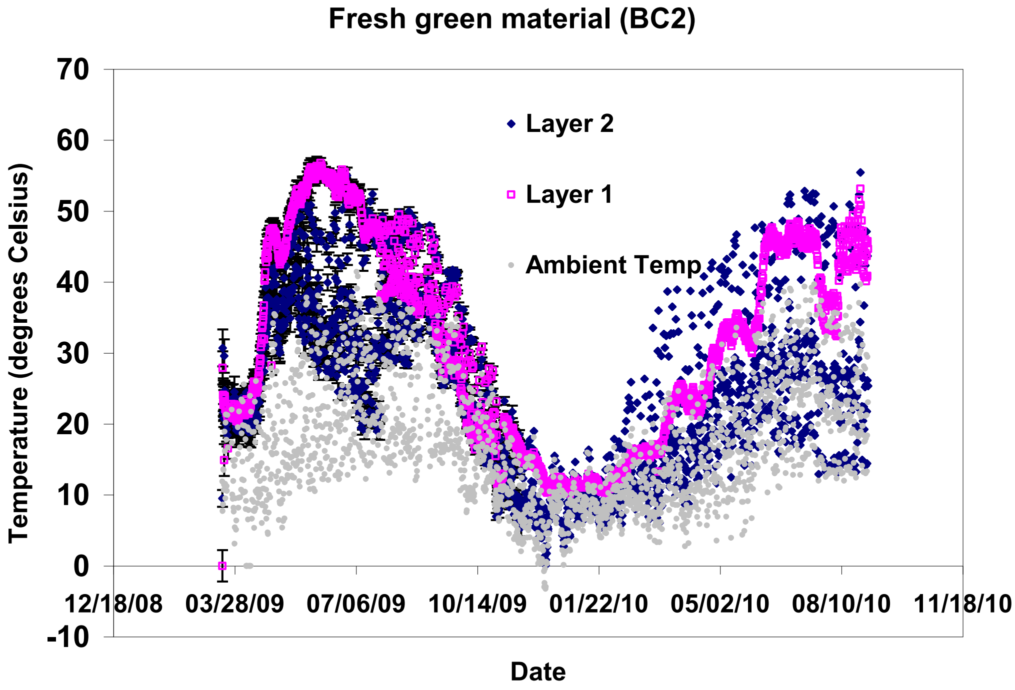

Figure 38. Temperature in BC2.

Biocover Moisture Content

The moisture content of each biocover was determined from core samples collected during seven measurement periods. Moisture content data were converted to volumetric water content using Eq. 3. An example plot for measurements on Feb. 8, 2010, is shown in Figure 39 below. The vertical error bars indicate the vertical depth over which the samples were collected. The horizontal error bars represent the 95 percent confidence interval for the mean measurements at a particular depth, where each data point represents the mean. These data illustrate two observations that were made for measurements on other dates as well. First, the volumetric water content at a given elevation was quite variable. The horizontal error bars are quite large, particularly for samples close to the surface. Second, BC2, the fresh green material, was in general wetter than BC1, the aged green material. Fresh green material held water better. The temporal change of moisture contents through time was important, and these data are discussed below in the modeling section.

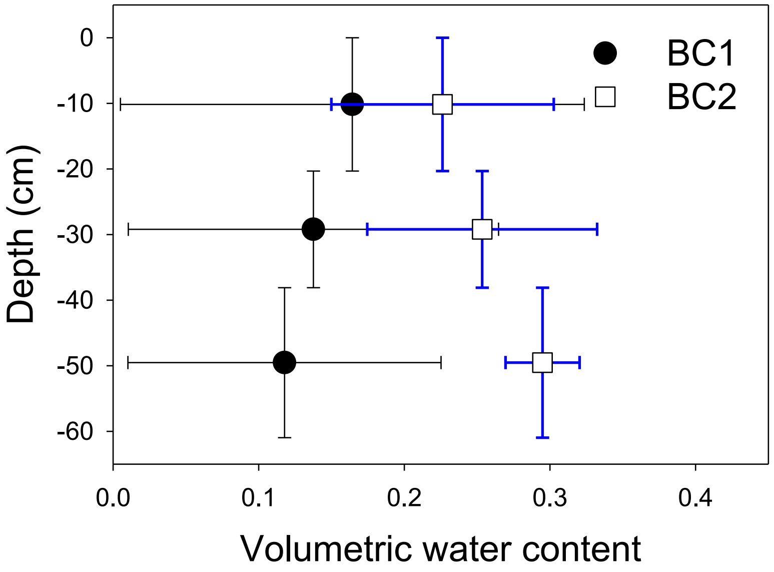

Figure 39. Volumetric water contents determined from core samples on Feb. 8, 2010.

Biocover Settlement

The settlement of the biocovers is shown in Figure 40. The first settlement measurement was performed 163 days after initial installation. Aged and fresh green material settled 13.2 and 23.7 centimeters, respectively, over this time period. Field observations suggest that most of this settlement occurred during the first few months following installation. No substantial further settlement was observed until the last measurement date, which occurred at 263 days after construction of the biocover cells. Fresh green material (BC2) settled more than aged green material (BC1), which likely occurred because of the greater stability of the aged green material.

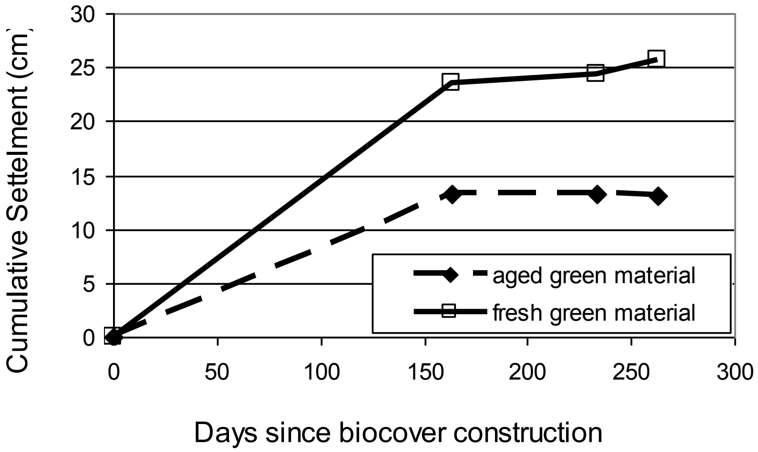

Figure 40. Cumulative settlement for the biocovers.

Biocover Rate of Methane Oxidation

The results from flux tests conducted in June 2009 are shown in Figures 41 and 42 below. Data points with error bars represent field flux box measurements, while single data points represent the results from stable isotope analyses. Rates of methane oxidation for both biocovers are quite large, between 100 to 200 g CH_4/m^2/day, depending on the influent rate and the biocover. These oxidation rates are quite high for field conditions, and indicate significant populations of methanotrophs in both biocover test cells. For example, recent field tests reported for compost biocovers by Abichou, et al. (2009) indicated that CH_4 oxidation rates were only as high as 60 g/m^2/day, while the oxidation rates in BC1 and BC2 were two to three times larger (see Figure 42). Thus, despite the fact that the pH, P, and NO_2-N were outside of recommended ranges for BC1 and BC2, these materials were capable of supporting significant methanotrophic activity.

It is also important to note the similarity of the independent isotope measurements with the flux chamber measurements, and the fact that estimates of CH_4 oxidation rates using isotopes were always smaller than flux measurements. Estimating CH_4 oxidation from isotopes is known to result in underestimation of CH_4 oxidation, and the results presented below are consistent with this. However, the isotope and flux measurements are similar enough to suggest that the field procedures employed in this work to quantify CH_4 flux from the top of the biocovers, particularly the use of a conservative tracer to quantify leakage from the sides of the test cells, were robust.

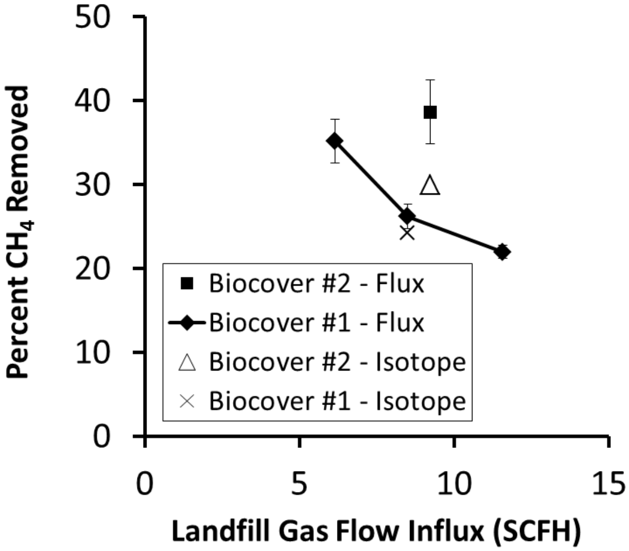

Figure 41. Results from flux tests conducted in June 2009.

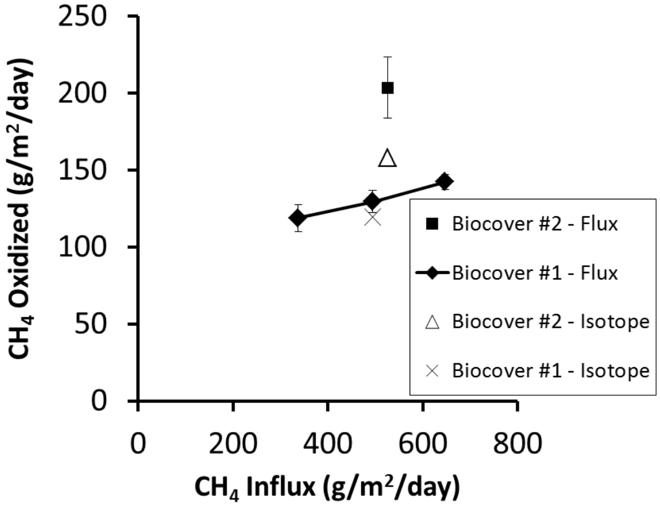

Figure 42. Results from flux tests conducted in June 2009.

While the results for tests in June 2009 indicated excellent performance of the biocovers, similar performance was not achieved in Winter/Spring 2010. In tests conducted in February 2010, CH_4

oxidation was negligible in both biocovers and could not be quantified when the CH_4 influx was 500-700 g/m^2/day. Instead, both biocovers were predominantly anaerobic at the high loading rates used from May 2009-February 2010 (9-10 SCFH) and actually generating CH_4.

The results for the flux tests in BC1 in February 2010 are summarized in Figure 43, where the CH_4 influx and CH_4 oxidized in BC1 are plotted versus test number, where 16 flux tests were conducted over a six-day period from Feb. 11, 2010 through Feb. 17, 2010. The generation rate of CH_4 for BC1 was 150-250 g/m^2/day when the loading rate was 500-700 g/m^2/day. When the loading rate was reduced to 200-250 g/m^2/day, though, the biocover slowly responded and after six days oxidized CH_4 at a rate of 50-70 g/m^2/day. The significant generation of CH_4 within BC1 could be depressed if the loading rate was small enough to allow oxygen to diffuse into the biocover. The maximum CH_4 oxidation rates achieved in February 2010 were roughly half those achieved in summer 2009 for BC1.

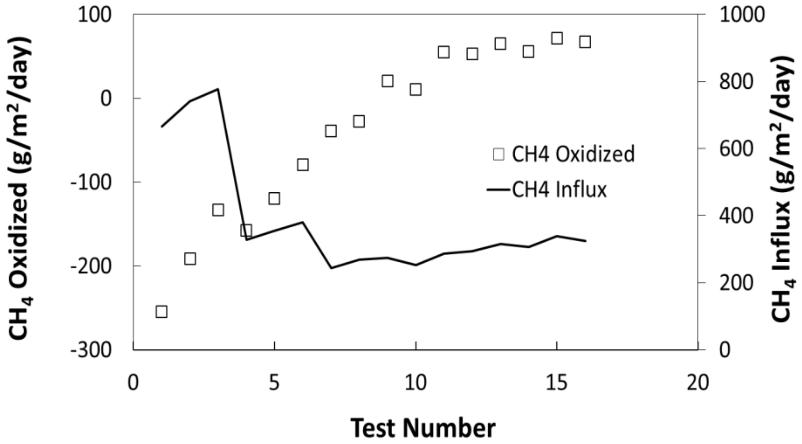

Figure 43. CH_4 oxidized in biocover BC1 during February 2010 testing.

The results shown in Figure 43 are consistent with oxygen profiles collected through BC1: almost no oxygen was detected at Layer 2 in February 2010 when CH_4 influx was 500-700 g/m^2/day, but significant oxygen levels were observed when the CH_4 influx was reduced to 200-250 g/m^2/day. Similar results were found for the fresh green material in BC2.

The results from these field measurements were somewhat surprising and clearly demonstrate that for even “stable” green material biocovers may perform poorly: if too much LFG diffuses and/or advects through the biocover, oxygen penetration will be reduced and anaerobic conditions can occur. In this field test, the green material in both biocovers worked very well in the summer 2009 but for the same CH_4 loading poorly in winter 2010. The capacity of the green material to degrade CH_4 clearly diminished in the winter.

Similar results would be expected for other biocovers even if CH_4 loadings were not as high as the 500-700 g/m^2/day initially tested here. Anaerobic conditions might occur if fresh and aged green materials are not completely stable and if they become water-logged, in which case oxygen diffusion will be limited. For these field tests this was not the cause of the CH_4 generation. However, for landfills where green material is placed on top of a low permeability soil layer, such conditions might be expected under certain climatic conditions. CH_4 generation from decomposing green material biocovers has been observed for other landfill applications (Barlaz et al., 2004). One way to mitigate the generation of CH_4 in green material biocovers is to reduce the thickness of the green material such that the volume of green material in any anaerobic zones is reduced.

To evaluate the impact of a thinner biocover, both BC1 and BC2 were excavated in late July 2010. The top layer of each biocover was removed, the remaining materials were mixed in place, and flux tests were completed to measure CH_4 oxidation and compared with flux tests conducted before thinning. The thickness of BC1 was reduced from 61 cm to 51 cm, while BC2 thickness was reduced from 61 cm to 48 cm. Results from flux tests are shown below in Table 8.

Table 8. Flux tests conducted before and after reduction of biocover thickness. Conditions after reduction of thickness are shaded.

Biocover Cell	**Date - Test**	**CH_4 influx (g/m^2/day)**	**% CH_4 Removal (%)**	**CH_4 Oxidized (g/m^2/day)**
BC1	7/12/2010 - 1	228	-7.8	-19
	7/12/2010 – 2	218	-5.4	-13
	7/13/2010 – 1	225	-0.49	-1.2
	7/13/2010 - 2	202	-8.7	-19
	8/11/2010 - 1	233	12.	31
	8/11/2010 - 2	229	11	27
BC2	7/12/2010 - 1	122	3.8	4.9
	7/12/2010 – 2	129	9.4	13
	7/13/2010 – 1	218	6.2	14
	7/13/2010 - 2	191	1.4	2.9
	8/12/2010 - 1	297	17	56
	8/12/2010 - 2	305	18	59

The oxidation of CH_4 was significantly improved after thinning both biocovers. For BC1, before thinning CH_4 was generated within the cover, while after thinning CH_4 was oxidized. For BC2, before thinning between 1-9 percent of the CH_4 was removed while after thinning approximately 17 percent was removed. Clearly, a thinner biocover made of these green material materials would reduce or eliminate anaerobic zones, reduce CH_4 generation, and thus promote overall removal of CH_4 within each green material.

To gain a clearer understanding of the performance of the green material, the CH_4 oxidation rates determined in this study are compared with other measurements in compost in Table 9. The studies reported in Table 9 employed composts, were conducted in laboratory columns, and were conducted for less than one year. Both the study by Scheutz et al. (2009) and Wilshusen et al. (2004) found that CH_4 oxidation rates peaked in the first few months of column operation and then decreased significantly through time. Scheutz et al. (2009) found that CH_4 oxidation rates gradually decreased to steady-state rates, while Wilshusen et al. (2004) found CH_4 oxidation rates were decreasing even at the end of their 220-day experiments. Data from our field experiments are consistent with this: high CH_4 oxidation rates were achieved in the summer of 2009 three to four months after the start of operations, while rates measured in the summer of 2010 after thinning the biocovers were considerably smaller. Scheutz et al (2009) found that CH_4 was generated in a garden compost/sand mixture, which also occurred in our green material in February 2010.

Finally, the CH_4 oxidation rates observed in our field study are consistent with rates observed for composts in laboratory experiments with similar CH_4 loading rates. The one exception is the leaf compost tested by Wilshusen et al. (2004), where peak CH_4 oxidation rates were 400 $g/m^2/day$, which are approximately twice the peak oxidation rates observed in our field tests. The results presented in Table 9 suggest that the green materials tested in our work oxidize CH_4 at similar rates as many composts.

Table 9. Comparison of CH_4 oxidation rates in this study with other measurements in compost materials.

Study	**Material**	**Loading Rate ($g\ m^{-2}\ day^{-1}$)**	**CH_4 Oxidation Rate ($g\ m^{-2}\ day^{-1}$)**
Scheutz, et al. (2009)	Garden Compost/Woodchips 1:1	229-254	247[b], 161 ± 38[c]
	Garden Compost/Sand 1:1	229-254	116[b], -31 ± 33[c]
	Garden Compost/Sand 1:5	229-254	144[b], 29 ± 22[c]
	Supermuld[a]	229-254	202[b], 110 ± 34[c]

Wilshusen, et al. (2004)	Leaf Compost	> 400	400^{b}, $\sim 100^{d}$
	Garden Compost	> 400	50^{b}
	Woodchip Compost	> 400	275^{b}, $\sim 100^{d}$
	Municipal Solid Waste Compost	> 400	275^{b}, $\sim 100^{d}$
This Study	Fresh Green Material (BC2)	530	200^{b}
		300	60^{e}
	Aged Green Material (BC1)	340-650	$120\text{-}150^{b}$
		230	30^{e}

[a] Supermuld is a commercial compost product (Solum, Denmark)
[b] Peak oxidation rate.
[c] Steady-state oxidation rates for days 50-255 after start of column experiments.
[d] Oxidation rate after 220 days of column experiments.
[e] Oxidation rate after 500 days of field operation and after thinning green material.

Predictive Modeling

Based on the data measured in the laboratory and the field, which included gas transport and CH_4 oxidation parameters, temperature, and moisture content, CH_4 oxidation in each biocover was simulated and compared with field measurements. In total, nine simulations were performed for BC1 and six simulations for BC2, which were selected to cover the range of climatic conditions between June 2009 and August 2010. Simulations were not conducted for the high CH_4 influxes reported in Figure 43 above, since CH_4 generation was known to be significant in this period and this process is not included in the model.

As detailed in the methods section, a simplified approach was used for predictive modeling to describe the spatially and temporally varying properties in the actual biocovers. Therefore, the simulation results should be compared with the measured data with great caution.

Table B1 in Appendix B lists the predicted and measured CH_4 removals for the corresponding LFG influxes. These results are shown graphically in Figure 44 and 45 for BC1 and BC2, respectively, when the influx was between 2-4 SCFH or 150-300 g/m^2/day of CH_4. These were the influx conditions when CH_4 generation was reduced in the February 2010 flux tests reported above. The model does a reasonable job of matching measured CH_4 removal for BC1, with the exception of data in July 2010 where CH_4 was generated in BC1 while the model predicted CH_4

removal. Once BC1 was “thinned” in late July 2010, the model did a reasonable job of matching the CH_4 removal in August 2010.

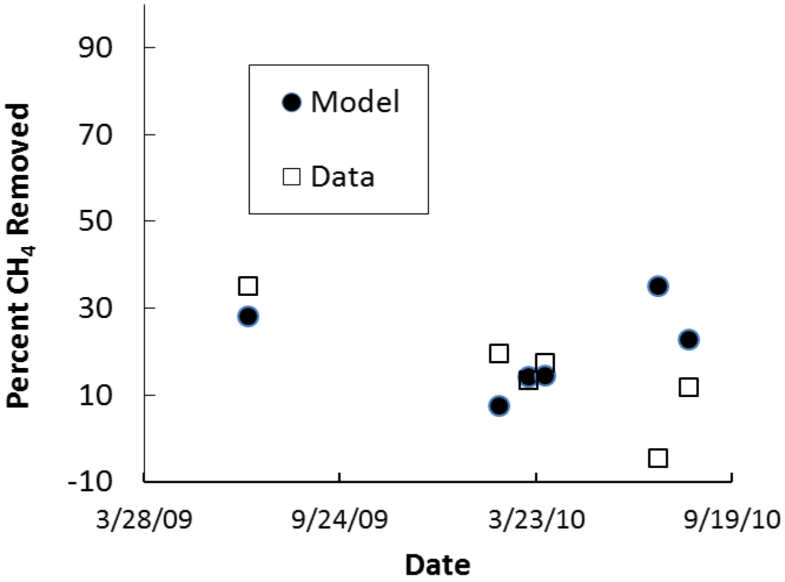

Figure 44. Comparison between model-predicted and measured CH_4 removal for BC1—aged green material.

The match between the model predictions and field data is considerably poorer for BC2. The model matches data in June 2009, but for all subsequent dates the model overpredicts CH_4 removal. We believe this result is associated with the greater instability of this fresh green material, which results in more significant CH_4 generation when anaerobic conditions occur in the bottom of the biocover. This situation is a less significant problem for BC1 composed of aged green material.

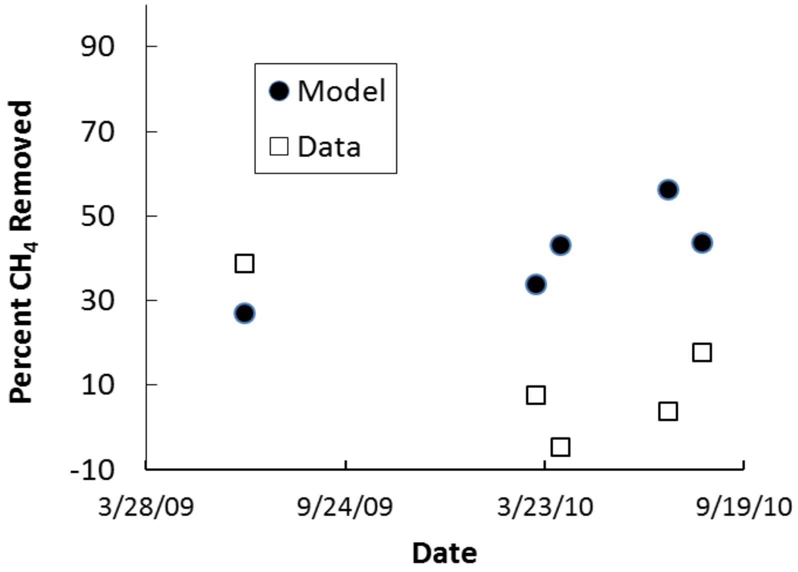

Figure 45. Comparison between model-predicted and measured CH4 removal for BC2—fresh green material.

The simulated and measured gas composition profiles were also compared. As an example, the gas composition profiles for BC1 and BC2 in November 2009 are shown in Figure 46 and Figure 47 respectively. For BC1, the simulated gas composition profile was in good agreement with the measured one. However, for BC2, the model over-predicted CH_4 oxidation. For instance, at Layer 2 the estimated CH_4 concentration was 50 percent smaller than the measured concentration.

One of the reasons for the discrepancy between the predicted and the measured values for BC2 might be the spatial heterogeneity of moisture content. As the biocovers dried out and rewetted in response to changes in climatic conditions, local dry/wet regions might develop, allowing preferential LFG flow through drier regions. Since the average moisture content of core samples was used in the simulations, the effect of the spatially varying properties on CH_4 oxidation could not be accounted for. The inability of the model to simulate CH_4 generation in response anaerobic conditions within the green material is also a significant factor and perhaps the most important. In November 2009, the measured CH_4 concentration at Layer 1 was 56 percent for BC2, which was actually *higher* than the CH_4 concentration of 53 percent in the injected LFG. Thus, differences in gas concentration profiles in Figure 47 for BC2 are likely due to CH_4 generation.

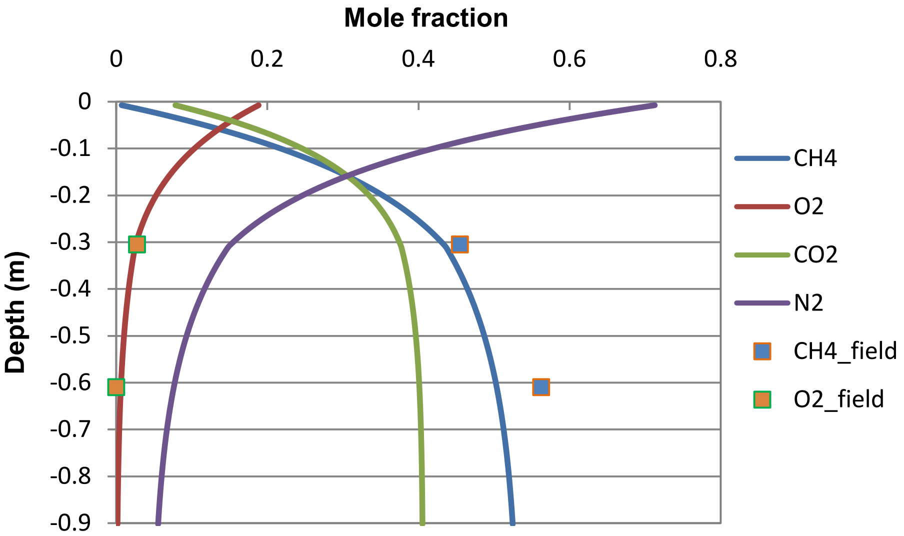

Figure 46. Comparison of the simulated and measured gas composition profiles for BC1 in November 2009.

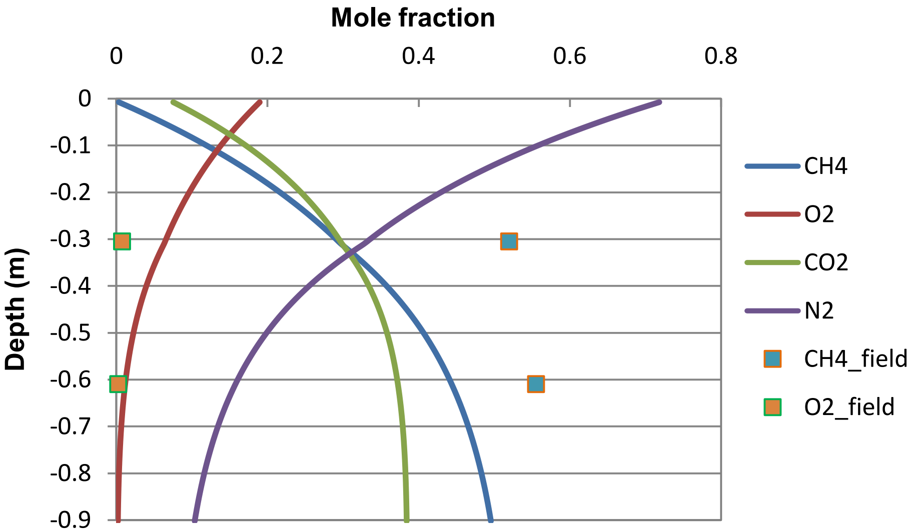

Figure 47. Comparison of the simulated and measured gas composition profiles for BC2 in November 2009.

Effect of seasonal changes on CH4 oxidation: constant LFG injection rate

The comparison between model predictions and field data were generally acceptable for BC1, if data from February 2010 were neglected where CH_4 influx was high. On the other hand, model predictions were almost always poor for BC2 even for low CH_4 influxes. Here, it appears CH_4 generation may have been significant for much of the testing period in BC2. In order to better examine the impact of climatic conditions alone on CH_4 removal, simulations were conducted with a constant LFG injection rate of 5 SCFH for the 2009-2010 testing period and compared with environmental factors of temperature and biocover volumetric water content. The same approach was used as for earlier simulations, assigning volumetric water contents, temperatures, and boundary conditions based on field data.

Figure 48 shows the model-predicted variation of CH_4 removal from June 2009 to August 2010. BC1 and BC2 had a similar trend of the change in the CH_4 oxidation rate: higher CH_4 oxidation rates in summer and lower rates in winter. For instance, from June 2009 to November 2009, the CH_4 removal percentage dropped from 35 percent to 5 percent for BC1, and from 47 percent to 9 percent for BC2. This seasonal change was due to the change in temperature within the upper layers of the biocovers. As shown in Figure 49, the variation of temperature at Layer 2 was very similar with the variation of CH_4 removal over the same period. When the temperature was lowest, which was in November 2009, the CH_4 removal percentage was lowest. Here, note that the temperature data at Layer 2 was used for comparison since most CH_4 would be oxidized above Layer 2.

The volumetric water content in the top 30 cm of BC1 and BC2 are plotted versus time in Figure 50. The relationship between the seasonal change in volumetric water content and CH_4 removal was not as obvious as the relationship with temperature. However, the change in volumetric water content might explain the increase of the difference in CH_4 removal percentages between BC1 and BC2 in 2010. The volumetric water content of BC2 was 50 percent higher than that of BC1 in March 2010 and April 2010. That is, although temperature was a more dominant factor controlling CH_4 oxidation, moisture did have an impact on CH_4 oxidation.

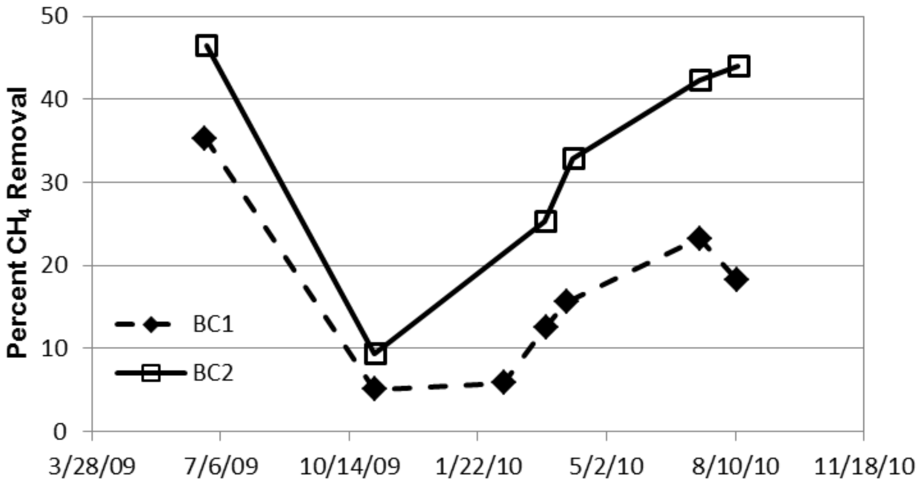

Figure 48. Variation of CH_4 removal percentage.

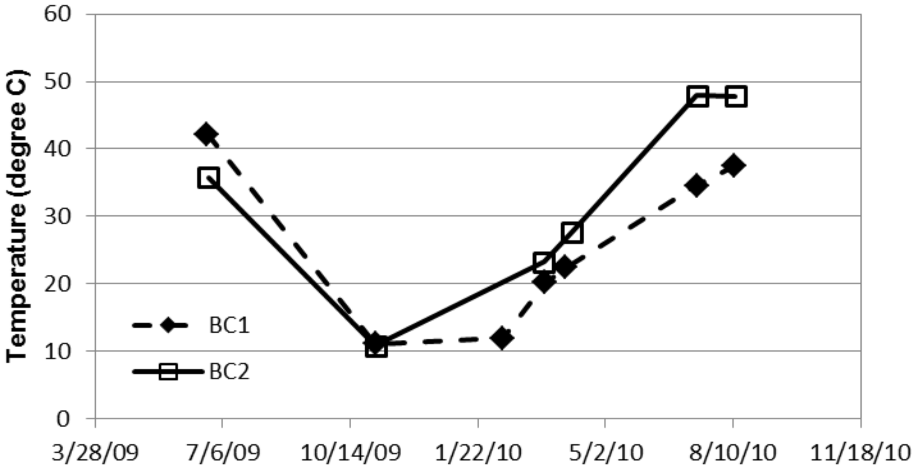

Figure 49. Variation of temperature at Layer 2.

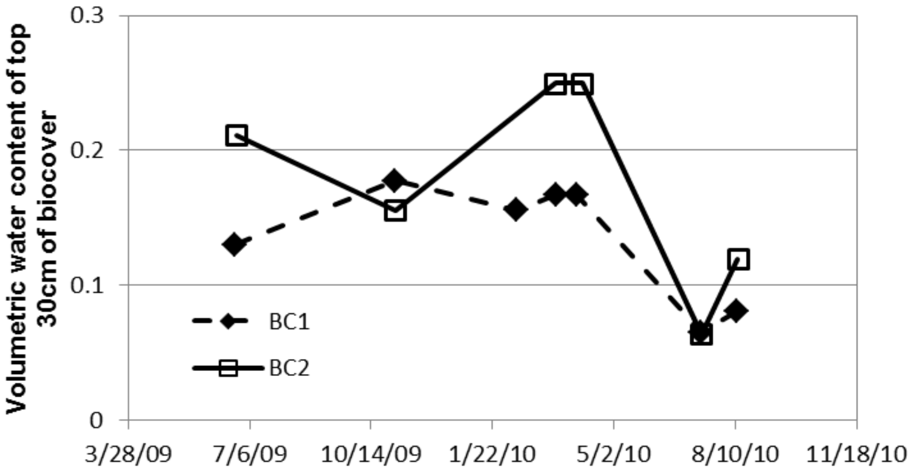

Figure 50. Variation of the volumetric water content of the top 30 cm of the biocover.

Figure 51 shows more clearly the dependence of CH_4 oxidation on temperature. For both BC1 and BC2, the removal rate linearly increased with temperature, supporting the results in Figure 48 and Figure 49. On the other hand, as shown in Figure 52, no trend was observed between CH_4 removal and the volumetric water content of the top 30 cm. CH_4 oxidation is not affected by volumetric water content as long as water contents are sufficiently high (Bender and Conrad, 1995; Boeckx and Van Cleemput, 1996; Park et al., 2002).

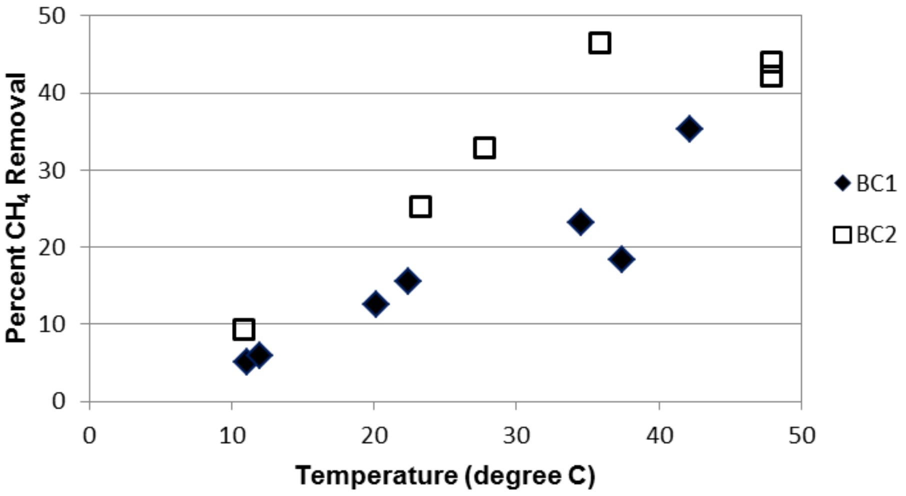

Figure 51. Variation of CH_4 removal percentage as a function of the temperature at Layer 2.

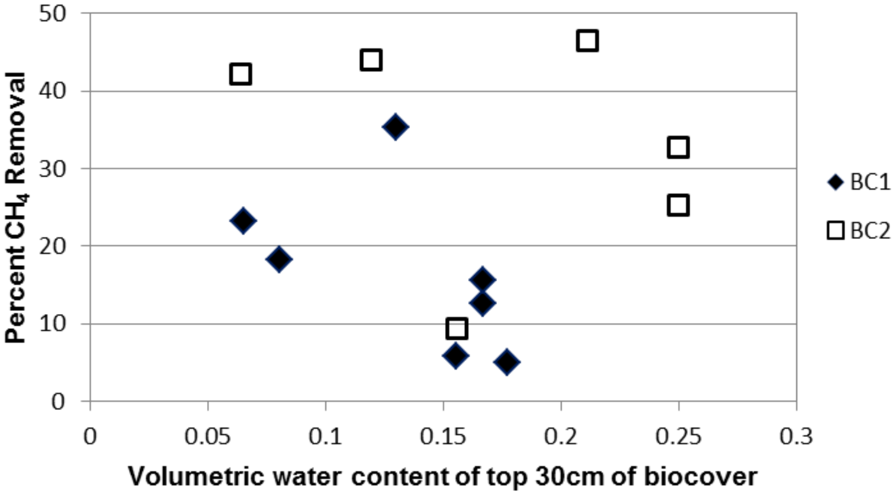

Figure 52. Variation of CH_4 removal percentage as a function of the volumetric water content of the top 30 cm of the biocover.

In summary, the predictive modeling did a reasonable job of matching field CH_4 removal data for BC2, as long as data with high CH_4 influxes in February 2010 were not considered. On the other hand, model predictions of CH_4 removal almost always over-predicted field measurements for BC1. These results suggest that CH_4 generation within the biocover was a more severe problem for the fresh green material in BC1 than the aged green material in BC2. The model did not include the generation of CH_4.

After comparing model predictions with field data, the model was used to help clarify the impact of temperature and volumetric water content on CH_4 removal in BC1 and BC2. Using a time-invariant CH_4 loading, CH_4 removal was tracked during the 2009-2010 testing period. Results indicate that for these biocovers and for the climatic conditions during this period in Yolo County, CA, temperature had the most dramatic impact on CH_4 removal. CH_4 decreased from greater than 40 percent during the summer to less than 10 percent in November 2009. Clearly, it is important to anticipate poorer CH_4 removal in these biocovers in cold weather periods.

Modeling the field data allowed us to develop a better understanding of CH_4 oxidation in the biocovers and the role of CH_4 generation, particularly for the fresh green material. The modeling approach developed here might be useful for evaluating the importance of the simplifying assumptions used in the CALMIM model developed by Bogner, Spokas, and Chanton. Because CALMIM employs a greater number of simplifying assumptions than TMOVC-Bio, for some field situations it may result in poor predictions of CH_4 emissions. For example, when pressure gradients are significant, advective gas flow might be important, but the CALMIM model does not account for this effect. In addition, the impact of wind and barometric pressure changes on CH_4 emissions cannot be described by the CALMIM model, but they can be included in the modeling approach employed here. We postulate that changes in barometric pressure may be an important factor affection whole landfill emissions of CH_4. Future work looking at the impact of the simplifying assumptions in the CALMIM model on predictions of CH_4 emissions by comparing CALMIM results with those using the modeling approach in this work may be a useful exercise.

Conclusions and Recommendations

Two biocovers were employed in this study—fresh and aged green material as defined in Title 14, California Code of Regulations, Section 17852(21). The fresh green material was yard waste green material that was received at the Yolo County Central Landfill, screened, and then installed in the biocover test cell. Aged green material was yard waste placed on the outside landfill slopes for over a year before it was removed and then installed in a second test cell. Characterization of both materials after installation indicated that they could be classified as very stable composts, according to the California Compost Quality Council (2001). However, both materials had lower pH and P, but elevated NO_2-N when compared to recommended compost properties proposed by Huber-Humer, et al., (2009) for landfill biocovers. More importantly, respiration tests indicated both materials were less stable than recommended composts for biocovers: the fresh and aged green material consumed 11.8 and 44.7 mg O_2/mg organic matter for 7-day tests, while Huber-Humer, et al., (2009) recommended less than 8 mg O_2/mg organic matter. Thus, there was some concern these materials would not oxidize CH_4 efficiently (pH, P, and NO_2-N conditions) and might consume excessive O_2 or generate CH_4 (stability conditions).

Results from laboratory and field tests indicated both fresh and aged green material could oxidize CH_4 at high rates, up to 100-200 g CH_4/m^2/day in field tests. These rates are on the high end of oxidation rates reported for composts in the literature. Thus, at least for the duration of the field tests pH, P, and NO_2-N conditions did not significantly affect biocover performance. However, the biocovers were installed in relatively thick layers (~ 90 cm), and after seven months of operation with a high loading of LFG (500-700 g CH_4/m^2/day) thick anaerobic zones developed. The formation of these zones was undoubtedly linked to the high LFG loading and the cooler winter temperatures. In this state both materials generated significant CH_4 (> 100 g CH_4/m^2/day, aged green material) and were ineffective in oxidizing CH_4. However, for the aged green material the performance was improved considerably when the loading rate was decreased to 200-250 g CH_4/m^2/day. In this case the green material oxidized 50-70 g CH_4/m^2/day. When both biocovers were operated at this smaller loading rate for several months, the aged green material performed reasonably well with measured CH_4 removal rates matching independent model predictions. The same was not true for the fresh green material, though, where it appeared that CH_4 continued to be generated and the biocover performance was always significantly less efficient at removing CH_4 than model predictions.

The CH_4 oxidation rates measured for the fresh and aged green materials are similar to rates measured in the laboratory for composts exposed to similar CH_4 loading (see Table 9). In addition, the decrease in CH_4 oxidation rate observed in our field tests was also observed in laboratory studies using compost. Thus, the performance of the green materials appears similar to that for composts.

From these tests we conclude that it is best if green material be aged at least one year before placement on a landfill. It is further recommended that respiration tests be used to quantify the stability of the green material, and that if possible the green material be allowed to age until the stability characteristics proposed by Huber-Humer, et al., (2009) are satisfied.

In order to predict CH_4 emissions through green material covers across seasons and years, constitutive models are needed to describe gas diffusion and gas advection through these porous media. Laboratory experiments demonstrated that the Troeh model is best for describing gas diffusion, with estimated effective diffusion coefficients as much as two times smaller than those predicted from the Millington-Quirk model. We recommend that the Troeh model be employed in CALMIM and other similar codes for describing gas diffusion in green material and compost. Because we were unable to use any existing constitutive models to describe the measured relationship between gas permeability and volumetric water content in green material, we recommend our data be combined with recent measurements of gas permeability in biocovers reported in the peer-reviewed literature to develop an appropriate constitutive model.

The gas flow data and water flow measurements in both materials point to the existence of significant macropores in green material. In order to predict water transport in these materials, it is likely that a dual domain modeling approach (e.g., dual porosity or dual permeability) may be needed.

The predictive modeling employed the TMVOCBio computer code to describe CH_4 oxidation in the fresh and aged green material over the period of this study. This modeling confirmed the impact of CH_4 generation on CH_4 emissions from the biocover test cells. If the impact of CH_4 generation was excluded, modeling indicated that the most predominant factor affecting CH_4 oxidation is temperature. The modeling and field data of gas profiles within the biocovers also suggested that the biocovers would perform better (less CH_4 generation) if they were thinner (less than the ~90 cm thickness in the initial test cells). These thicknesses were reduced to 48 cm (fresh green material) and 51 cm (aged green material) in the biocovers, and in both cases resulted in improved CH_4 oxidation. The thinner biocovers resulted in smaller anaerobic zones and less CH_4 oxidation. Unless it is determined that a green material is sufficiently stable so that CH_4 will not be generated if anaerobic zones form, we recommend green material biocovers be maintained with thicknesses less than 90 cm, although further field data and computer simulations should be conducted to refine this recommendation, which we expect will vary with climate.

Because of the success of the predictive computer model in describing CH_4 oxidation in the aged green material, we recommend that this model be used in future research to evaluate the impact of simplifying assumptions in the CALMIM model on estimates of whole landfill CH_4 emissions. TMVOC-Bio can be used to assess the impact of advective gas flow and, most importantly, barometric pressure changes on CH_4 oxidation and emissions. We postulate that barometric effects could be quite important in controlling CH_4 emissions and might be an important process to add to the CALMIM model.

The biocover test cells that were designed and constructed for this study are useful tools for evaluating landfill cover materials for oxidizing CH_4. The unique use of a gas tracer to quantify and then correct for gas leakage from the cells was an innovative feature that we recommend for similar field tests in the future. Because the field experiments reported here were conducted for only 18 months, longer-term tests are recommended to determine the useful life of green material covers. Computer modeling will be an important component for analyzing these data and extended the results to other field conditions.

The results from this study demonstrate that fresh and aged green material derived from yard wastes can serve as effective landfill biocovers over an 18-month testing period if they are sufficiently stable. Unfortunately, compost and green material are less stable than soils and will likely exhibit greater changes in physical structure, e.g., porosity and bulk density, than soils as they age. These physical changes will alter each medium's ability to retain moisture and support methanotrophic bacteria. While studies similar to ours have been employed to evaluate compost biocovers over a few years, we are unaware of studies for longer time period, e.g., in the range of 3-15 years. Such studies are needed to assess the long-term performance of compost and green material biocovers, and, if necessary, the need to refresh these materials to maintain their capacity to oxidize methane. Such studies should include a variety of climatic conditions.

Another unknown is how effective the green materials will be when placed on all or part of a landfill. Will emissions occur through cracks and thus bypass biocover treatment zones? Since some CH_4 emissions are correlated with wind or barometric pressure changes and since green material biocovers are very permeable, will CH_4 emissions be significantly worse when biocovers are used rather than less permeable soils on windy days or during periods of rapid changes in barometric pressure? Future field tests are required to address these questions. For such tests, it seems likely that measurements of whole landfill (or whole landfill cell) CH_4 emissions will be needed before and after biocover placement to verify that indeed the material addition has a beneficial effect on reducing CH_4 emissions.

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Appendix A: Aerobic Respirometry Testing Protocol

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Sample Preparation:

Samples are delivered in sealed freezer bags and stored at -20 C until analysis. The evening before initiating respirometry analyses, samples are wetted with sterile distilled water to a moisture content of 60 percent wet basis and placed at 4ºC overnight to allow water and biomass equilibration.

Respirometry Analyses:

Approximately 10 dry grams (dry weight) of samples are placed into 250-ml reactors for microbial activity studies (May and VanderGheynst, 2001). Reactors are aerated continuously with humidified air at approximately 20 ml min-1 to avoid oxygen limitations. Aeration rate is monitored continuously using a mass flow meter. Samples are then incubated for eight days at 35ºC.

Oxygen concentration is measured on the influent and effluent air of the reactors using Zirconia oxide oxygen sensors (Neuwghent Technologies, LaGrangeville, N.Y.) and carbon dioxide concentration is measured using an infrared CO2 sensor (Vaisala, Suffolk, United Kingdom). Oxygen and carbon dioxide data and air flow rate is recorded every five hours using a data acquisition system (VanderGheynst et al., 2002). Carbon dioxide evolution (CER) and oxygen uptake rates (OUR) are calculated from mass balances on each reactor according to the following equations:

$$CER = F(CO_{2out} - CO_{2\,in}) \tag{1}$$

$$OUR = F(O_{2out} - O_{2in}) \tag{2}$$

where F is the air flow rate (mg air day^{-1} gdw^{-1}), $CO_{2,OUT}$ and $CO_{2,IN}$ are the concentrations of carbon dioxide in the effluent and influent air, respectively (mg CO2 mg air^{-1}), and $O_{2,IN}$ and $O_{2,OUT}$ are the concentrations of oxygen in the influent and effluent air, respectively (mg O_2 mg air^{-1}).

Data Analysis:

Logged data are imported into Excel and CER and OUR are calculated using equations (1) and (2), respectively. Numerical integration of CER and OUR results are performed using KaleidaGraph v. 4.0 (Synergy Software, Reading, Penn.). All results are plotted using KaleidaGraph.

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Appendix B: Model Results

Table B1 shows the results from model predictions of the percent CH_4 removed from each biocover along with corresponding field measurements. While additional field measurements were made that are not shown here, these results illustrate the utility of the computer model for predicting CH_4 oxidation in each biocover. Clearly, model predictions poorly matched field data during periods when significant CH_4 was generated in the fresh and aged green material.

Table B1. Comparison of the simulated and measured percent CH_4 removal at selected dates during field experiments.

Biocover Cell	**Date**	**LFG inflow ($kg/m^2/s$)**	**Model prediction (%)**	**Field measurement (%)**
BC1	June 24, 2009	6.59E-06	15.0	22.0
	June 26, 2009	4.92E-06	18.6	26.2
	July 2, 2009	3.40E-06	28.2	35.2
	Feb 11, 2010	8.19E-06	1.6	-25.2
	Feb 17, 2010	3.67E-06	7.5	19.5
	March 16, 2010	3.04E-06	14.1	13.3
	April 1, 2010	3.43E-06	14.5	17.3
	July 13, 2010	2.15E-06	35.0	-4.6
	Aug 11, 2010	2.42E-06	22.9	11.7
BC2	June 25, 2009	4.98E-06	27.0	38.7

	March 15, 2010	2.55E-06	33.9	7.5
	April 6, 2010	2.50E-06	43.0	-4.7
	July 13, 2010	2.06E-06	56.1	3.8
	Aug 12, 2010	3.01E-06	43.8	17.8