

MODELING LANDFILL METHANE EMISSIONS FROM BIOCOVERS: A COMBINED THEORETICAL-EMPIRICAL APPROACH

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SUMMARY: The use of methane-oxidizing biocovers to minimize methane emissions to the atmosphere is being examined in an ongoing field study at the Leon County Landfill (Florida, USA). This older site has interim cover in place and does not have active gas extraction; in addition, large quantities of ground and composted garden waste are available on site for biocover construction. The major goal of the current study is to determine the *minimum* biocover placed *above* the interim cover that would be capable of mitigating methane emissions in this subtropical environment. A second goal of this study is to test the use of multiple recycled materials for biocover construction; these include crushed glass and crushed glass fluorescent light tubes for the basal gas distribution layer, as well as ground and composted garden waste for the overlying biocover layer. Two test areas have been established: S1 with a 45-50 cm biocover of composted garden waste overlying a 10 cm gas distribution layer (crushed glass) overlying a 65-75 cm existing cover; and S4 with either a 30 cm or 60 cm biocover of ground garden waste (to compost in place) overlying a 15 cm gas distribution layer (crushed fluorescent tubes) overlying a 15 cm existing clay cover. The median positive fluxes for the S1 biocover subsites are an order of magnitude less than for the control sites; currently, almost half of the S1 biocover fluxes are negative, indicating uptake of atmospheric methane. For the S4 deep biocover area (60 cm biocover), it has been observed during temporal monitoring that the median positive fluxes are two orders of magnitude less than the maximum median fluxes for the controls. The latest S4 data indicate that half of the fluxes from the deep biocover area are now negative. Work is also in progress to expand the Landfill Methane Emissions Model (LMEM) to biocovers using empirical relationships; preliminary data from the S4 area indicate that the modeled oxidation rates overlap with minimum field rates.

1. BACKGROUND, SITE DESCRIPTION, AND METHODS

Landfills produce large quantities of methane; however, the oxidation of methane in landfill cover soils by methanotrophic microorganisms can effectively reduce emissions to the atmosphere (Czepiel et al., 1996; Bogner et al., 1997a, b; Christophersen et al., 2001). Methane oxidation can be optimized in field settings through the implementation of "biocovers" which are designed for maximum methane oxidation rates. Previous biocover studies in Austria have demonstrated that rates of $>200 \text{ g CH}_4 \text{ m}^{-2} \text{ day}^{-1}$, the highest in the literature, are possible within landfill biocovers constructed of 1 m sewage sludge compost overlying a 30 cm gas distribution layer (Huber-Humer, 2004). Typically, a biocover consists of a highly porous gas distribution layer above the waste, which is overlain, in turn, by a compost-amended layer and an upper vegetative layer. Because methane fluxes typically exhibit high spatial variability (orders of magnitude) across a site, the gas distribution layer results in more uniform fluxes to the biocover layer above.

The current field study in progress at the closed Leon County Landfill (Florida, USA) is examining the use of methane-oxidizing biocovers. This older site does not have an active landfill gas collection system. In addition, large quantities of composted garden waste are available on site. In preliminary work using a stable carbon isotopic technique, Chanton and Liptay (2000) observed that the presence of only six inches of yard waste compost (yard waste and woodchips) above an existing 1 m clay cover could significantly enhance methane oxidation relative to the clay cover alone (Fig. 1). The major goal of the current study is to determine the *minimum* biocover placed *above* the existing interim cover that would be capable of mitigating methane emissions in this subtropical environment. The current interim cover varies between 15 cm and 1 m in thickness—it would be prohibitively expensive to remove these soils prior to biocover placement and would result in high interim emissions. A second goal of this study is to test the use of multiple recycled materials for biocover construction; these materials include glass cullet, crushed fluorescent glass tubes, and garden waste. Future studies will be quantifying the emissions of trace hydrocarbons (including aromatic, chlorinated, and fluorinated compounds) using the same techniques as two previous field campaigns at French landfills (Bogner et al., 2003; Scheutz et al., 2003).

Two test areas have been established at the Leon County Landfill: S1 and S4. For S1, there are six 7.5m X 7.5 m subsites on waste older than 8 years: three biocover sites (2D, 4D, 6D) and three controls (2B, 4B, 8B). In all S1 areas, the existing cover thickness is split about evenly between a lower sandy clay and an upper fine sandy loam. For the control areas, the total thickness of the existing cover varies from approximately 40 cm (4B) to 80 cm (8B) to 110 (2B) cm. The S1 biocover was placed over an existing 65-75 cm cover and consists of a basal 10 cm gas dispersion layer (consisting of gravel-sized recycled glass) overlain by 45-50 cm of yard waste compost.

For S4, there are three 18m X 32 m subsites on waste about 2 years old: these include the deep biocover (D) subsite, the shallow biocover (S) subsite, and the control site (N) with no added biocover. The S and D biocovers were placed over a thin interim cover consisting of 15 cm of compacted sandy clay. The biocovers consist of 15 cm crushed fluorescent glass tubes as a gas dispersion layer overlain by either 30 cm (S biocover) or 60 cm (D biocover) of freshly ground garden waste. It is expected that the garden waste will compost *in situ* under local climatic conditions, as opposed to being pre-composted before placement.

Methane flux was determined by the static chamber technique (Rolston, 1986). Major gases and stable carbon isotopes ($\delta^{13}\text{C}$) were analyzed at Florida State University. Methane and CO_2 concentrations below 1% were quantified using a Shimadzu 14A gas chromatograph with a flame ionization detector and a methanizer, a 1 mL sampling loop, and a 2-m 0.32 cm diameter stainless steel column packed with Carbosphere. Methane and CO_2 concentrations above 1%,

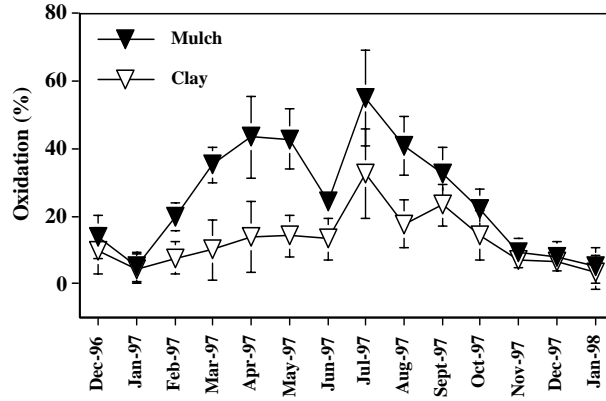


Figure 1. Increased methane oxidation after addition of composted garden waste layer ["mulch"] above existing 1 m clay cover at the Leon County landfill. From Chanton and Liptay (2000).

N_2 , and $[O_2 + Ar]$ were quantified using a Shimadzu 8A gas chromatograph with a thermal conductivity detector. Scott Specialty gases were used as standards. Stable carbon isotopic ratios ($\delta^{13}C$) were determined using a Finnigan Mat Delta S Gas Chromatograph Combustion-Isotope Ratio Mass Spectrometer (GCC-IRMS) following methods adapted from Merritt et al. (1995). For samples with <2000 ppmv methane, a cryogenic focusing device was used on the front end of the gas chromatograph. The standard deviation of replicate analyses was approximately 0.15 %. The high CH_4 source gas samples were diluted to 1% CH_4 with nitrogen, and 0.1 to 0.5 mL were directly injected into the GCC-IRMS inlet system.

The fraction of methane oxidized (f_{ox}) was determined from the proportion of ^{13}C and ^{12}C in the anoxic CH_4 (δ_A) vs. the emitted CH_4 (δ_E) and fractionation factors (α) which are a measure of the temperature-dependent microbial preference for $^{12}CH_4$ (Chanton and Liptay, 2000). The fraction of methane (f_o) oxidized during upward transit through the cover soil is:

$$f_o = \frac{(\delta_R - \delta_A)}{1000 \times (\alpha_{ox} - \alpha_{trans})} \quad (1)$$

where δ_R is the $\delta^{13}C$ (carbon isotopic content) of the emitted methane and δ_A is the carbon isotopic content of the anoxic methane. The terms α_{ox} and α_{trans} are the isotopic fractionation by bacteria during oxidation and transport, respectively. The α_{ox} is determined from batch cultures of landfill soil at a specific site (Chanton and Liptay, 2000; Liptay et al., 1998). The α_{trans} is assumed to be 1 when gas transport is dominated by advection. However when diffusion is important, α_{trans} is > 1 and this approach underestimates methane oxidation (DeVisscher et al., 2004). Thus all oxidation results by this method are conservative estimates. Methane lost by oxidation (L , $g\ m^{-2}\ day^{-1}$) is calculated from f_o and the methane flux from the surface (F in $g\ m^{-2}\ day^{-1}$):

$$L = F \left[\frac{1}{1 - f_o} - 1 \right] \quad (2)$$

Previously, the Landfill Methane Emissions Model (LMEM) was developed to model landfill methane emissions inclusive of methane oxidation (Spokas, 1996, Bogner et al., 1997b). This model is theoretically based and relies on a chemical potential gradient as the driving force for mass transfer of gases through landfill cover soils. Given that small area ($<1\ m^2$) measurements of methane emissions can vary over 7 orders of magnitude (<0.0004 to $>4000\ g\ m^{-2}\ day^{-1}$), with typical variability of 3-4 orders of magnitude across a single site, this model was

developed as a first step to model “net” methane emissions (inclusive of methanotrophic methane oxidation) to within an order of magnitude. The model relies on a limited number of inputs including gas concentration profiles (methane, carbon dioxide, oxygen) and the physical properties of the cover layers (thickness, porosity, moisture content). The rate of methane oxidation is user-selectable (slow, moderate, or fast) relative to the available methane at a given node at a given time step; methane oxidation can also be turned off to model emissions without oxidation. LMEM was validated using field data from Illinois and California (USA) and has been used as a teaching and research tool over the last several years. Additional details regarding this model are given in Spokas (1996), Appendix A of Bogner et al. (1997b), and Bogner et al. (2000). This paper discusses work in progress to modify and extend this model to net methane emissions through methane-oxidizing biocovers using empirical relationships.

2. PRELIMINARY RESULTS FOR S1 AREA

Baseline flux measurements using static chambers were taken from June-Sept. 2003 in randomized locations over the entire Leon County site. Then flux measurements were taken at grid 1 locations (near S1) and on the S1 area ("pre" biocover) during the period Oct.03 - early Mar.04. The S1 biocovers (on 2D, 4D, and 6D subsites) were applied on March 17, 2004. The "post" biocover data discussed below were obtained during the period Mar.04 – Apr.05.

Table 1 compares random and gridded methane fluxes from the "pre" biocover period to "post" biocover fluxes; Table 1a summarizes the positive fluxes and Table 1b the negative fluxes (uptake of atmospheric methane). For the "post" biocover period, data were composited for the biocover areas (2D,4D,6D) and the control areas (2B,4B,8B); the latter had variable cover depths ranging from 40 cm (4B) to 80 cm (8B) to 110 cm (2B). Arithmetic means and standard deviations, medians, and geometric means and standard deviations are reported. The arithmetic means were greatly influenced by a few large fluxes and skewed toward higher values. Medians or geometric means are often favored as a better indicator of the central tendency where data vary over orders of magnitude; in general, the log transformation for the geometric mean typically results in a normalized data distribution. Note that the median values were similar to the geometric means.

For the positive fluxes (Table 1a), the median value for the "random" fluxes was generally an order of magnitude higher than the grid 1, the S1 pre cover, and the S1 controls after biocover placement. In turn, the median value for the positive S1 biocover fluxes was an order of magnitude less than the S1 controls. Recalling that the biocover was placed over a relatively thick 65-75 cm existing cover, this indicates a net benefit for the biocover.

Table 1b summarizes the negative fluxes from the same areas as Table 1a. Negative fluxes indicate uptake of atmospheric methane (no net emission of landfill methane). For the S1 negative fluxes through early April 2004, there were similar numbers of negative fluxes for the S1 controls (2B,4B,8B) and the S1 biocover area (2D,4D,6D). However, in terms of temporal variations, the number of negative fluxes for the D areas has significantly increased, with the latest three datasets having 5 negative fluxes out of 12 replicates (Figure 2). In general, after biocover application in March 04, methane flux increased from the biocover until July 04 due to the low efficiency of oxidation in the very moist and compacted compost (low oxygen diffusion). After July 04, the methane flux decreased dramatically, corresponding with lower precipitation and the growth of vegetation which promoted evapotranspiration. In parallel, methane flux from the non-biocover area increased during the early summer 04, declined in August 04, and increased thereafter. Since September 04, the biocover treatment has consistently had a lower median flux than the no-cover area.

Table 1a. S1 positive methane fluxes in $\text{g m}^{-2} \text{ day}^{-1}$. Includes "pre" biocover random fluxes June-Sept. 03; "pre" biocover grid 1 (1A-8H) fluxes Oct.03-Feb.04; "pre" biocover S1 area fluxes; "post" biocover control fluxes (S1 areas 2B,4B,8B); and biocover fluxes (S1 areas 2D,4D,6D).

Positive Methane Fluxes	pre biocover			post biocover	
	random fluxes whole site	grid 1 (near S1) 7yrs old	S1 7 yrs old	S1 controls (2B,4B,8B) 40-110 cm cover	S1 biocover (2D,4D,6D) biocover over 65-76 cm cover
Count	78	87	69	165	129
Mean	149	32	78	29	22
St Dev	303	70	289	82	64
Median	32	4	2	4	0.4
Geom Mean	29	3	2	2	0.7
Geom St Dev	8	17	32	15	19

Table 1b. S1 negative methane fluxes (uptake of atmospheric methane). Same areas as above.

Negative Methane Fluxes	pre biocover			post biocover	
	random	grid 1 (near S1) 7yrs old	S1 7 yrs old	S1 controls (2B,4B,8B) 40-110 cm cover	S1 biocover (2D,4D,6D) biocover over 65-76 cm cover
Count	14	21	4	53	47
Mean	-3.1	-0.9	-0.06	-0.05	-0.04
St Dev	4.0	1.6	-	0.06	0.06
Median	-1.7	-0.1	-0.04	-0.03	-0.03
Geom Mean	-1.1	-2.2	-	-0.05	-0.04
Geom St Dev	5.8	6.2	-	2.8	2.6

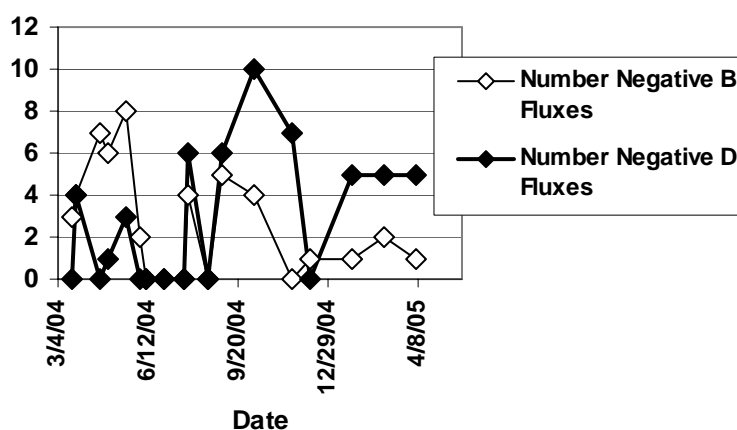


Figure 2. Number of negative fluxes (uptake of atmospheric methane) for S1 sites: all controls (B Fluxes including 2B, 4B, 8B) vs. all biocover locations (D Fluxes including 2D, 4D, 6D). Total number = 12 for each dataset for each day.

3. PRELIMINARY RESULTS AND MODELING FOR S4 AREA

Flux and isotope samples were taken for 6 months before applying the biocover on July 22, 2004. Figure 3 summarizes the temporal variability in positive methane fluxes; the figure compares median values for the controls (N=no cover), shallow biocover (S), and deep biocover (D) subsites. Note that the deep biocover consistently maintained positive methane fluxes that were below $10 \text{ g m}^{-2} \text{ day}^{-1}$ in contrast to the controls, which were at least an order of magnitude higher. The shallow biocovers performed similarly to the deep biocovers in the initial months and then exhibited high values in the same range as the controls in the most recent monitoring data. Thus the advantages of the deeper biocover were consistently lower and more uniform fluxes as compared to the S and N subsites. Figure 4 indicates the temporal variability in the percent of negative fluxes for the N, S, and D subsites since the placement of the biocover (≥ 8 replicates for each subsite for each date). Note that there were no negative fluxes for the controls (N) vs. 50% negative fluxes for the deep biocover (D) in February 2005. Thus there were significant advantages to the D biocover, both in terms of decreased positive fluxes and a higher percentage of negative fluxes.

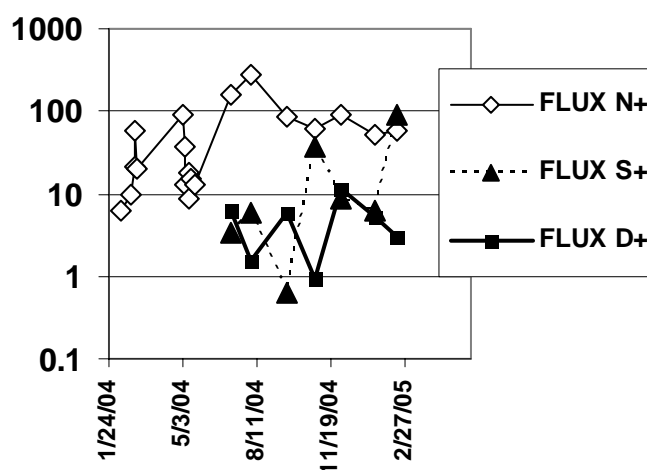


Figure 3 . Temporal variations in S4 area methane fluxes (positive fluxes, median values, $\text{g m}^{-2} \text{ day}^{-1}$). N=controls, no biocover; S=shallow biocover; D=deep biocover.

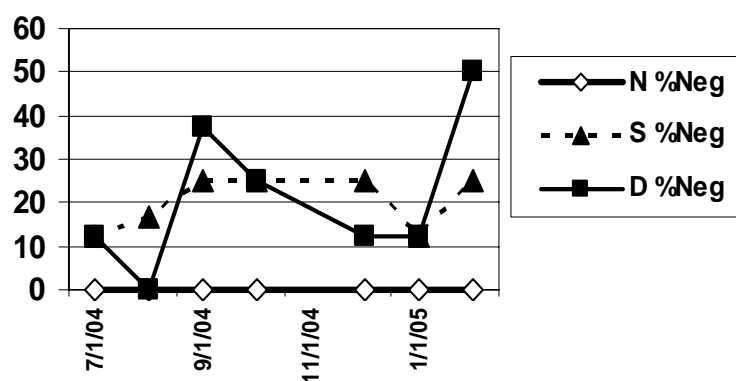


Figure 4. Percentage of negative fluxes after placement of S4 biocover. N=controls;S=shallow biocover;D=deep biocover (≥ 8 replicates for each subsite for each date).

Work is in progress to modify and extend the LMEM model to net methane emissions through methane-oxidizing biocovers using empirical relationships. Based on comparisons to field data over the last several years, LMEM tends to underestimate methane oxidation where oxidation rates are high. Therefore, primarily using data from the S4 biocover area at the Leon County landfill, as well as other data from the literature, we are developing a series of empirical relationships to extend this modeling to seasonal emissions from engineered biocovers. Examining major physical properties and the % oxidation determined by the stable carbon isotopic technique for each of the S4 subsites, relationships to both moisture and temperature were observed. In order to develop more generalized relationships inclusive of all the S4 data, Figure 5 is a plot of temperature vs. fractional oxidation for all of the S4 data to date (subsites N, S, and D combined). In general, there appears to be an upper limit for fractional oxidation which increases at higher temperatures; in addition, the lowest values (with some exceptions) are associated with drier soils where methane oxidation may be moisture-limited or wetter soils where gaseous diffusion is limited by high moisture contents. Also note that there are some values above the line at approximately 25-30 C; we will be obtaining more high temperature data during the summer 2005. One apparent contradiction in the oxidation data to date is that the high fractional oxidation monitored for the deep biocover (D subsite) was typically associated with high surface moisture contents (>60% wt/dry wt); however, it should be kept in mind that the ground garden waste has a high water-holding capacity combined with high porosity.

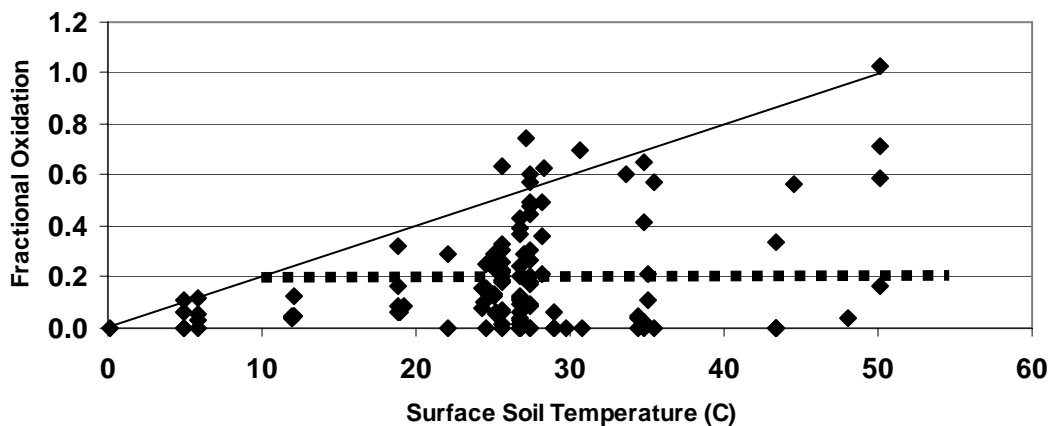


Figure 5. Suggested limiting temperature values for fractional methane oxidation. All S4 field data (N, S, and D subsites). The area under the bold dashed line (oxidation <0.2) has surface 20%>soil moisture>60% which may be limiting oxidation, especially in the N sites.

In Figure 6, plots for each of the three subsites (N, S, and D) compare the gross methane flux (measured methane flux + calculated oxidation using the isotopic method) to the oxidation. Data were limited to positive fluxes with $0 < \text{oxidation} < 100\%$. For each subsite, the oxidation can be reasonably described by a linear relationship which suggests that, to date, limiting values for oxidation have not yet been reached at this Florida site. For the D subsite, the slope and the high r^2 suggest that almost 50% oxidation is routinely being achieved. However, these figures are preliminary and represent only part of the first annual cycle. Note that the same scale was used for the y-axis for each plot to facilitate comparisons among the three subsites. If the gross fluxes were the same among the three subsites, the data should be similarly distributed along the x-axis for each plot; however, the N data to date are clustered in the 0-400 range, the S data in the <100 range, and the D data in the 0-200 range. This suggests a bias for either the oxidation data or the site selection which requires further study.

For modeling using LMEM, a limited number of inputs are required, including the thickness, porosity, and moisture content of up to 3 cover layers and an associated soil gas concentration profile (methane, carbon dioxide, oxygen). The N, S, and D subsites were modeled individually using limited data for surface porosity and moisture content as a starting point. An examination of the measured soil gas concentration profiles suggested that it was feasible to use a feature of LMEM which establishes a non-linear soil gas concentration profile using the atmospheric and source landfill gas concentrations. Then, a series of model runs were completed where the moisture content and porosity were individually modified for increments of 5% (moisture) or 0.05 (porosity), up to 50% deviation from the original. Figure 7 plots the results of these model runs with the composited field data from Figure 6 on a log-log scale.

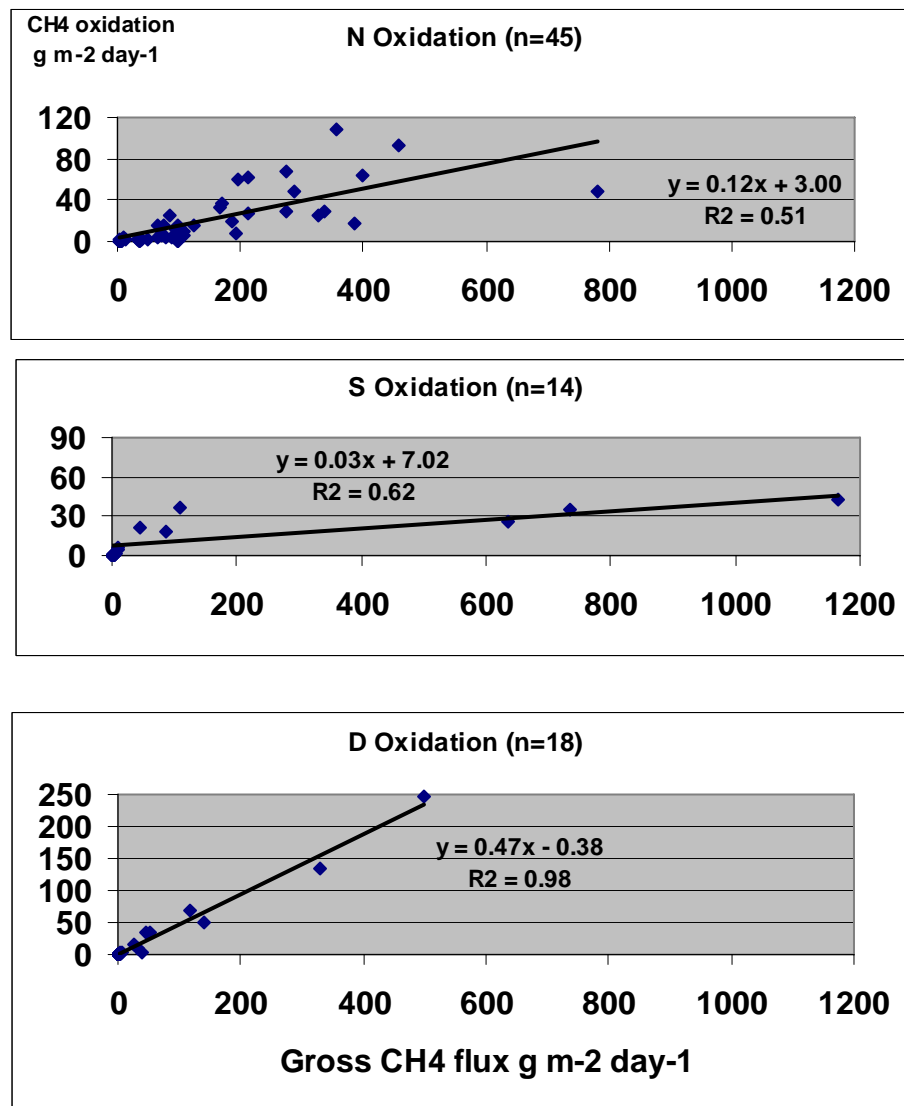


Figure 6. Plots of gross methane flux vs. methane oxidation for S4 subsites (N, S, and D). Gross methane flux = [measured methane emissions + oxidation using the isotopic method].

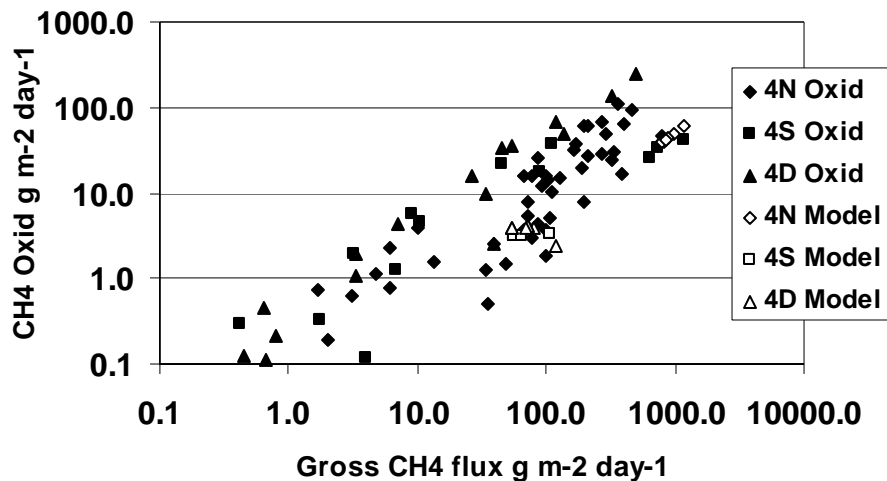


Figure 7. Comparison of modeled (LMEM) to measured methane fluxes and oxidation for all S4 subsites (N, S, and D) with positive CH₄ fluxes. See Fig. 6 for explanation of "gross" flux. Oxid = Measured oxidation using isotopic method; Model = Modeled oxidation using LMEM.

Note the tight clustering of the modeled data in comparison to the wide ranges for the measured data spanning several orders of magnitude. Also note that the modeled data plot generally within the same distribution but at the minimum oxidation for the field data, typically a full order of magnitude less than the maximum. These results suggest that LMEM is underestimating methane oxidation. It should also be noted that the isotopic technique employed yields conservative values of methane oxidation (DeVisscher et al., 2004). One empirical strategy for adapting LMEM to methane-oxidizing biocovers may be to increase the modeled oxidation using temperature data since LMEM currently assumes isothermal conditions. However, a full annual cycle of data, including data for summer 2005, will be needed to determine if this is feasible.

In summary, this paper has discussed preliminary data and data analysis from an ongoing field study at a Florida landfill examining engineered biocovers using recycled materials. To date, significant decreases of an order of magnitude or more in median positive fluxes have been observed at both S1 and S4 biocover sites. In addition, a significant percentage of negative fluxes have been recently monitored—approximately 50% for both the S1 biocover areas and the S4 deep biocover (D) area. Preliminary empirical relationships have been examined and discussed between methane flux, soil temperature, moisture, and oxidation. Work is in progress to expand LMEM modeling using these empirical relationships when additional seasonal data are available.

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