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Technical paper

Use of a biologically active cover to reduce landfill methane emissions and enhance methane oxidation

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Abstract

Biologically-active landfill cover soils (biocovers) that serve to minimize CH_4 emissions by optimizing CH_4 oxidation were investigated at a landfill in Florida, USA. The biocover consisted of 50 cm pre-composted yard or garden waste placed over a 10–15 cm gas distribution layer (crushed glass) over a 40–100 cm interim cover. The biocover cells reduced CH_4 emissions by a factor of 10 and doubled the percentage of CH_4 oxidation relative to control cells. The thickness and moisture-holding capacity of the biocover resulted in increased retention times for transported CH_4. This increased retention of CH_4 in the biocover resulted in a higher fraction oxidized. Overall rates between the two covers were similar, about 2 g CH_4 m^{-2} d^{-1}, but because CH_4 entered the biocover from below at a slower rate relative to the soil cover, a higher percentage was oxidized. In part, methane oxidation controlled the net flux of CH_4 to the atmosphere. The biocover cells became more effective than the control sites in oxidizing CH_4 3 months after their initial placement: the mean percent oxidation for the biocover cells was 41% compared to 14% for the control cells ($p < 0.001$). Following the initial 3 months, we also observed 29 (27%) negative CH_4 fluxes and 27 (25%) zero fluxes in the biocover cells but only 6 (6%) negative fluxes and 22 (21%) zero fluxes for the control cells. Negative fluxes indicate uptake of atmospheric CH_4. If the zero and negative fluxes are assumed to represent 100% oxidation, then the mean percent oxidation for the biocover and control cells, respectively, for the same period would increase to 64% and 30%.

1. Introduction

Atmospheric CH_4 has more than doubled in concentration over the last 150 years (Schlesinger, 1997; Dlugokencky et al., 2003). Methane is the third most important greenhouse gas after water vapor and carbon dioxide, accounting for approximately 20% of positive forcing relative to CO_2 (Hansen et al., 1998). Over a period of 100 years, the global warming potential, or GWP, of CH_4 is 23 times that of an equal mass of CO_2 (IPCC, 2001).

Landfills are estimated to account for about 35% of anthropogenic CH_4 emissions in the United States and 5–10% of global CH_4 emissions to the atmosphere (Stern and Kaufmann, 1996; EIA, 2000; USEPA, 2000; IPCC, 2001; Czepiel et al., 2003). Landfills represent a large CH_4 source with a potential for mitigation through management practices. The difference between global atmospheric sources and sinks of CH_4 is less than 6% of the total CH_4 production. Therefore, even a small reduction in anthropogenic CH_4 emissions would be significant (Dlugokencky et al., 1994, 1998; Etheridge et al., 1998; Dlugokencky et al., 2003). In addition, the relatively short atmospheric lifetime for CH_4 (7–10 yr) means that the beneficial effects of management schemes to reduce

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emissions could be observed in a relatively short period of time.

Over the last half century, solid waste disposal in developed countries has been largely transformed from open dumping and burning practices to sanitary landfilling, consisting of engineered burial of waste with use of cover materials and management of leachate and gas. As a result, decomposition of solid waste proceeds anaerobically with the microbial generation of large quantities of CH_4 by methanogenic microorganisms. Methane emissions from landfills are in part controlled by the rate of oxidation as CH_4 is transported through the aerobic soil cover materials on top of the landfill. Oxidation of CH_4 is achieved by aerobic methanotrophic microorganisms that consume CH_4 and oxidize it to CO_2. As CH_4 migrates through aerobic soil layers, the residual CH_4 become increasingly enriched in $^{13}CH_4$ due to the preferential consumption of $^{12}CH_4$ (Barker and Fritz, 1981; Coleman et al., 1981; Happell et al., 1994; Tyler et al., 1994; Happell et al., 1995; Liptay et al., 1998). In this study, we exploited this fractionation to calculate the % oxidation (Chanton et al., 1999).

Methane oxidation is controlled by several factors, including soil temperature, moisture, and texture, as well as pH and nutrient content (Kightley et al., 1995; Boeckx et al., 1996; Chanton and Liptay, 2000; Borjesson et al., 2001). Previous studies have shown seasonal variation in CH_4 oxidation, which is greater during warmer months (Chanton and Liptay, 2000; Borjesson et al., 2001). Oxidation is also higher in organic-rich soils than in clay (Chanton and Liptay, 2000). In addition, there appears to be an optimum soil moisture for CH_4 oxidation, 10–20% (w/w) at temperatures from 25 ° C to 30 °C (Whalen et al., 1990; Boeckx et al., 1996). One incubation study of composted municipal solid waste used as landfill cover showed a high percentage oxidation at a soil moisture content of 45% (w/w) (Hilger and Humer, 2003).

Soil composition is also an important parameter, as soil texture and grain size affect oxygen diffusion into landfill cover soils. Coarser grained soils and porous mulch have been found to be superior to finer grained soils and clays. Methane oxidation in landfills can be enhanced by the emplacement of a biologically active compost or mulch cover (Humer and Lechner, 1999; Hilger and Humer, 2003; Barlaz et al., 2004).

This study examines CH_4 emission and oxidation in landfill soils with and without a "biocover," a biologically active layer of mulch placed over a gas dispersion layer on top of an existing interim cover soil. The purpose of this biocover is to optimize the environment for methanotrophic bacteria. The biocover must be sufficiently permeable for oxygen transport but also have good moisture-holding capacity. The depth of oxygen penetration controls the depth and thickness of the zone of CH_4 oxidation. Moreover, at greater depth, oxidation can typically proceed under more stable moisture and temperature regimes (Hilger and Humer, 2003). In an Austrian landfill, the pioneering work of Humer and Lechner (1999) and Huber-Humer (2004) showed that a 1 m layer of sewage sludge composted with woodchips overlying a 0.3 m gas dispersion layer can mitigate CH_4 emissions of several hundred g m^{-2} d^{-1}. Positive results were also seen from a biocover consisting of 1 m yard waste mulch underlain by 0.15 m tire chips and 0.15 m clay placed at the Outer Loop landfill in Louisville, Kentucky, USA (Barlaz et al., 2004).

At the Leon County landfill (Florida, USA), the site of this study, it was previously shown that just 15 cm of mulch (composted yard waste and woodchips) overlaying a clay cover significantly increased CH_4 oxidation (Chanton and Liptay, 2000). We hypothesized that a relatively thin (~50 cm) biocover consisting of the same material would, likewise, be more effective in oxidizing CH_4 than untreated landfill soils. Here we present the results of flux and oxidation field measurements for biocover and control cells for one annual cycle beginning in March 2004 and ending May 2005.

2. Methods

2.1. Biocover construction

This study was conducted at the Leon County Landfill near Tallahassee, Florida. The experiment was set up over waste that had been covered for 8 yr by 20–60 cm of sandy clay overlain by 20–50 cm of fine sandy loam. The site was thickly vegetated prior to biocover application. We mowed prior to placement. Thick vegetation grew upon the fresh compost by the end of summer. Prior to this study and placement of the biocover on March 17, 2004, CH_4 emission rates were measured for an area called S1-grid, a 61 by 61 m plot divided into sixty-four 7.6 by 7.6 m cells (Fig. 1). The purpose was to establish baseline CH_4 flux from this typical older landfill with a vegetated cover (Abichou et al., 2006). For the present experiment, three biocover cells and three control cells, all 7.6 m × 7.6 m, were selected. Three biocover test cells were constructed by placing a 10-cm-thick layer of glass cullet over the entire 7.6 × 7.6 m surface of the cell. The glass layer was overlain by a 50 cm-thick mulch layer placed in one lift. The mulch extended 3.8 m beyond the edges of the glass layer. Mulch was provided by the landfill, and consisted of chipped yard waste that had been composted (windrowed and turned) for 3 yr. The experiment contrasted three untreated control cells (2B, 4B, and 8B) and three biocover cells (2D, 4D, and 6D). Four collars were installed on each cell for measurement of fluxes using static chambers (Fig. 1).

2.2. Methane emission rates and gas analysis

Methane emission rates from the landfill surface were determined using a static chamber technique. The chambers used in this study were constructed of polished aluminum sheeting and have dimensions of 0.63 × 0.63 × 0.2 m (covering an area of 0.4 m^2). They contained a small fan to circulate air inside the chamber. Chambers were sealed to the

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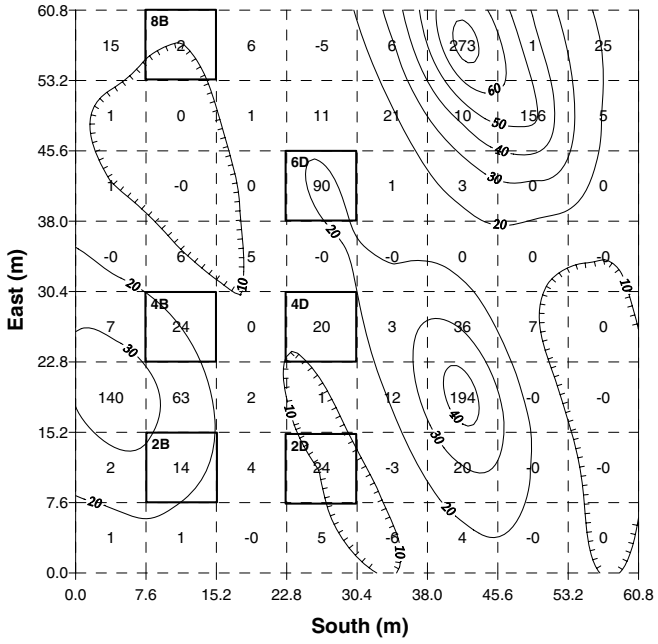

Fig. 1. Contour map of flux over grid S1 prior to biocover placement (summer and fall, 2003) with locations of biocover and control cells. Contours represent flux measurements in g $CH_4\,m^{-2}\,d^{-1}$. Cells are identified by the numbers and letters in the upper left corner of each square.

ground by clamping them to pre-installed collars. The chamber technique was more suitable for this research than large-scale tracer dilution methods because we were directly comparing emissions and oxidation in the six 7.6×7.6 m biocover and control cells. Methane samples were collected from each chamber sequentially over a 20-min period using 60 mL disposable syringes (Becton, Dickinson, and Co.) fitted with plastic stopcocks (Cole Parmer Instrument Co.). Samples were analyzed on a gas chromatograph equipped with a flame ionization detector within 5 h of collection. Methane flux was determined from concentration data (C in ppmv) plotted versus elapsed time (t in minutes). The CH_4 concentration within the chambers generally increased linearly, in which case dC/dt_0 is the slope of the fit to the data. This change in volumetric concentration was converted to a mass flux by using the ideal gas law. The CH_4 flux, F (g $CH_4\,m^{-2}\,d^{-1}$), was calculated as follows:

$$F = PVMU(dC/dt)/(ATR) \quad (1)$$

where P is pressure (1 atm), V is chamber volume (80+ l), M is the molar mass of CH_4 (16 g/mol), U is the units conversion factor (0.00144 l min/(μl d)), A is the surface area covered by the chamber (0.4 m^2), T is chamber temperature (K), and R is the gas constant (0.08205 l atm/(K mol)). The slope of the line, dC/dt, was determined by linear regression between CH_4 concentration and elapsed time. The median r^2 value for the flux data was 0.95.

Following the general approach of Barlaz et al. (2004), a non-zero flux was reported only if the there was 90% confidence ($p < 0.1$) in the correlation between CH_4 concentration and time, otherwise a zero-flux is reported. The zero value flux rates resulted from measurements which showed little increase or decrease in CH_4 concentration over time and thus no correlation of CH_4 with time.

To determine means, the CH_4 flux values from the 4 collars within each cell were averaged, and then the three cells were averaged to yield an overall mean. The number of replicates within each cell was 4, and the number of replicate cells within each treatment was 3. We then used Mann–Whitney Rank Sum Test and ANOVA (Tukey test, Sigmastat statistical software) to analyze for difference between the treatments. Our objective was to determine seasonal differences over the course of the study. We assumed that the plots were unique each time they were sampled due to variations in temperature, moisture, atmospheric pressure and the age of the treatment or biocover age. The Tukey test is conservative and is less likely to determine that a given difference is statistically significant than other tests. The percent oxidation data were treated similarly.

2.3. Stable carbon isotopes

Stable isotopes for initial and final samples from each chamber were collected using 60 mL disposable syringes fitted with plastic stopcocks and immediately transferred to evacuated glass vials. Samples were only analyzed when flux was positive to determine the carbon isotopic composition of residual CH_4 following oxidation as it passed through the soil beneath the chamber. The $\delta^{13}C$ of residual CH_4 was determined from the equation:

$$\delta_R = \frac{(\delta_F \times C_F) - (\delta_I \times C_I)}{C_F - C_I} \quad (2)$$

where δ_R is the $\delta^{13}C$ value of the residual CH_4 emitted from the landfill, δ_I and δ_F are the initial and final $\delta^{13}C$ values of CH_4 measured at the initiation and completion of the flux measurement, and C_I and C_F are the initial and final CH_4 concentrations.

The $\delta^{13}C$ values for δ_R and anoxic zone CH_4 (δ_A), that is unexposed to methanotrophic bacteria can be used to calculate the percentage of CH_4 oxidized, provided we know the carbon isotopic fractionation factor for bacterial oxidation. This parameter, α, is a measure of the bacteria's preference for the light isotope over the heavy isotope, given by:

$$\alpha_{ox} = k_L/k_H \quad (3)$$

where k_L and k_H refer to the rate constants of the light ($^{12}CH_4$) and heavy ($^{13}CH_4$) isotopes.

The fraction of CH_4 (f_{ox}) oxidized in upward transit through the landfill cover soil is then given by (Chanton and Liptay, 2000; De Visscher et al., 2004):

$$f_{ox} = \frac{(\delta_R - \delta_A)}{1000 \times (\alpha_{ox} - \alpha_{trans})} \quad (4)$$

where δ_R is calculated using Eq. (2) and δ_A is the carbon isotopic content of anoxic CH_4 sampled by soil gas probes placed deep into the waste (−55.4‰, (Abichou et al., in press)), and α_{ox} and α_{trans} are the isotope fractionation fac-

tors appropriate for the soil type (clay or mulch) and associated with transport of CH_4, respectively.

The fractionation factor (α_{ox}) was determined from the measured soil temperature (T, °C) using the regression equation for α_{ox} with temperature for soil or mulch at this same landfill reported in Chanton and Liptay (2000):

$$\alpha_{ox}\text{soil} = -0.000433T + 1.0421 \quad (5)$$

$$\alpha_{ox}\text{mulch} = -0.000438T + 1.0411 \quad (6)$$

The parameter α_{trans} is assumed to be 1, which assumes that CH_4 transport is dominated by advection, a process that does not cause isotopic fractionation (Bergamaschi et al., 1998; Liptay et al., 1998). Recent laboratory experiments have shown that this approach can underestimate CH_4 oxidation by not taking into account diffusive flux (De Visscher et al., 2004). Thus the oxidation values reported here are conservative determinations. However, the assumption of convective flux is supported by observations of a negative relationship between CH_4 emission and atmospheric pressure at several landfills (Czepiel et al., 1996a, 2003). In addition, the Leon County landfill has no gas collection system.

The rate of CH_4 oxidation, R_{ox} (g CH_4 m^{-2} d^{-1}) was calculated from flux and percent oxidation using the following equation:

$$R_{ox} = f_{ox}\left(\frac{F}{1 - f_{ox}}\right) \quad (7)$$

where f_{ox} is the fraction oxidized (% oxidized/100), calculated from Eq. (4), and F is flux (g CH_4 m^{-2} d^{-1}), calculated from Eq. (1). Oxidation rate can only be calculated when a positive flux is measured, as the $\delta^{13}C$ value of the residual positive flux is required (Eq. (4)) to obtain f_{ox}. Because areas where zero or negative fluxes were observed may be indicative of high rates of CH_4 oxidation (100% oxidation of CH_4 from below), the rates calculated with Eq. (7) are thus lower limits. As more such zero and negative flux areas were observed in the biocover cells than in the control cells, this underestimation affects biocover oxidation rates to a greater extent.

Stable carbon isotopes values were measured by direct injection into a Hewlett Packard Gas Chromatograph coupled via a combustion interface to a Finnigan Mat Delta S Isotope Ratio Mass Spectrometer (GCC-IRMS) following Merritt et al. (1995). Samples with small concentrations (<4000 ppm) were cryogenically focused using a device coupled to the front end of the GC. Replicates were analyzed for most samples, yielding a standard deviation of approximately 0.15‰. Values are reported in the "δ" scale in ‰ relative to the standard, VPDB (Vienna Pee Dee Belemnite).

3. Results and discussion

3.1. Methane emissions

Studies of CH_4 emissions from the S1 grid prior to the emplacement of the mulch indicate an uneven pattern of flux across the surface of the grid (Fig. 1), with an average flux of 24.6 ± 63.3 g CH_4 m^{-2} d^{-1} and fluxes ranging from −6.07 to 330 g CH_4 m^{-2} d^{-1} (Abichou et al., 2006). This spatial variation can come from differences in CH_4 generation within the landfill, as well as the heterogeneity of the cover material. Surface cracking of clay was observed, as were CH_4 "hotspots" where gas bubbles were observed in standing water after rain. A Mann–Whitney Rank Sum Test indicated no significant difference between the flux from the general vicinities of the biocover and control cells from January 12 to February 18, 2004, prior to mulch placement (Table 1). The Mann–Whitney test is a non-parametric statistical significance test for assessing whether the difference in medians between two observed distributions is statistically significant, or whether the distributions overlap less than would be expected by chance.

Following biocover placement, we monitored CH_4 emissions on a monthly basis. We found that Chamber 2B1 in the control cells and 2D1 in the biocover cells consistently had higher fluxes relative to other locations and dominated the calculation of mean fluxes for the control and the biocover cells. Statistical analysis was performed to determine whether some values could be excluded as outliers. Those flux values that (a) did not fall within two standard deviations of the mean for each treatment on a given date and (b) did not pass a Q-test were excluded from calculations. The Q-test is generally considered to be the most legitimate statistical test available for the rejection of deviant values from a small sample with a Gaussian distribution (Rorabacher, 1991). Values are placed in rank order and the differ-

Table 1
Results of a Mann–Whitney rank sum test for flux data (g CH_4 m^{-2} d^{-1}) prior to placement of biocover (January 12 to February 18, 2004)

	N	Mean	Std error	Median
Control	34	18.1	8.1	1.3
Biocover	39	117.5	60.8	0.46

There was no statistically significant difference between the general areas where the two treatments were placed prior to the experiment. N represents the number of individual measurements.

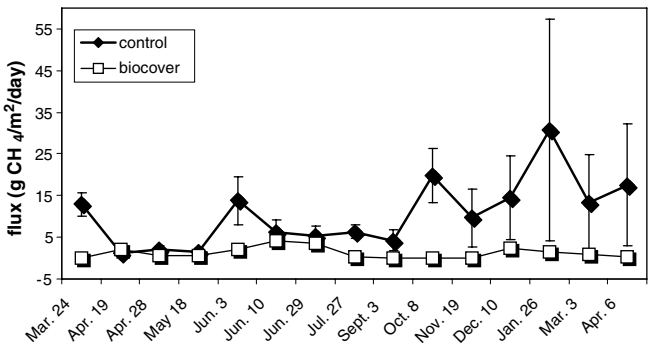

Fig. 2. Mean CH_4 emission rates or flux (g CH_4 m^{-2} d^{-1}) from control and biocover cells. Error bars represent standard error of the mean of three cells; each cell contained 4 flux locations.

ence between the outlier and the next closest value is divided by the range of values, i.e., the gap divided by the range. This quotient is compared to a table of critical Q values, and if larger than the critical Q value at a specified confidence level, the outlier can be rejected. Average flux data corrected for these outliers are presented in Fig. 2. Measured flux from the control cells ranged from −0.280 to 218 g CH_4 $m^{-2}d^{-1}$ and measured flux from the biocover cells ranged from −0.389 to 22.2 g CH_4 m^{-2} d^{-1}.

Table 2
Results of ANOVA for CH_4 emission data (g CH_4 m^{-2} d^{-1}) following biocover construction

	N	Mean	Std error	P
March 2004 through April 2005				
Control	45	10.61	2.30	<0.001
Biocover	44	1.20	0.26	
March 2004 through June 10, 2004				
Control	18	6.29	0.90	0.001
Biocover	17	1.57	0.41	
June 29, 2004 through April 2000				
Control	27	13.50	3.22	0.003
Biocover	27	1.01	0.32	

N represents number of cell measurements.

These values are on the order of those reported by Chanton and Liptay (2000) for the same landfill.

ANOVA tests were performed on landfill flux data over the time period of the experiment. Over the entire study period, the mean flux from the control cells was significantly more than the flux from the biocover cells (10.6 compared to 1.2 g CH_4 m^{-2} yr^{-1}, Table 2). The flux from the control cells was similar to pre-treatment values while the flux from the biocover cells was reduced (Tables 1 and 2). Fig. 2 indicates that during the first part of the study, flux was more similar for both treatments (Table 2). Carbon isotope and oxidation data reveal that the biocover cells became more efficient in oxidizing CH_4 around the June 29, 2004, sampling date (Figs. 3 and 4). After this point, the mean control flux increased from 6.29 to 13.50 g CH_4 m^{-2} d^{-1}, while the mean biocover flux decreased from 1.57 to 1.01 g CH_4 m^{-2} d^{-1}. Increases in flux similar to those observed in the control cells from September to January were also observed at this same landfill in a previous year (Chanton and Liptay, 2000).

3.2. $\delta^{13}C$ of Emitted CH_4 as an Indicator of Cover Oxidation

Stable isotope data indicated that the emitted CH_4 from the biocover cells had more positive $\delta^{13}C$ values than the

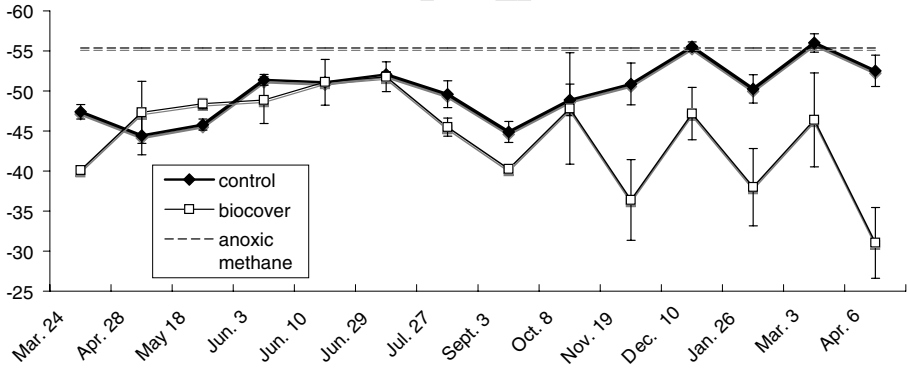

Fig. 3. Mean $\delta^{13}C$ values (‰) of CH_4 in the control and biocover cells compared to anoxic CH_4 dashed line represents the value of anoxic CH_4 (Abichou et al., 2006, in press). Error bars represent standard error of the mean of three cells.

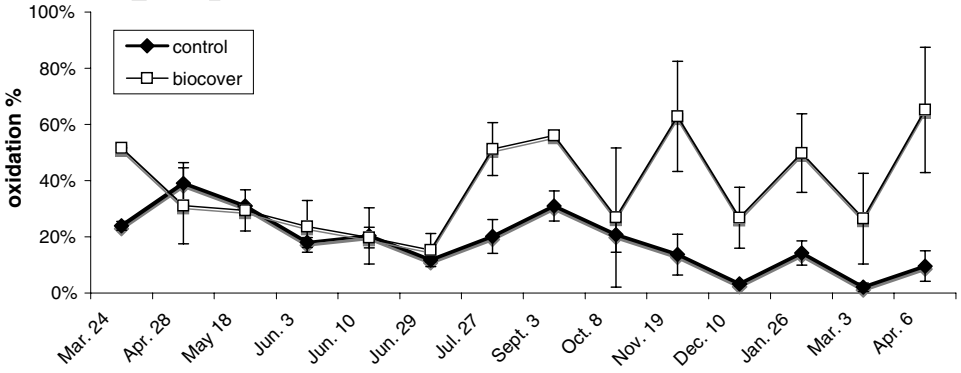

Fig. 4. Percent oxidation of CH_4 in the control and the biocover cells, calculated from isotope data only. If there was no flux, or if there was CH_4 uptake, both of which might be due to 100% oxidation of the flux from the underlying waste, no value is entered into these means. Error bars represent standard error of the mean of three cells.

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control cells from June 29, 2004, through April 2005. This indicates that more oxidation was occurring in the biocover cells relative to the control cells several months after its initial emplacement (Fig. 3). Average values were calculated for each cell and then the 3 cell means were averaged for each treatment. The annual mean carbon isotopic composition of CH_4 emitted at the landfill surface for the control cells (−50.1‰) and the biocover cells (−44.3‰) indicated enrichment in ^{13}C relative to the anoxic zone CH_4 (−55.4‰). Oxidation in both layers is occurring except perhaps in the control cells on December 10, 2004, and March 3, 2005, when $\delta^{13}C$ of residual CH_4 was very close to that of anoxic CH_4 (−55.4‰).

Previously at the Leon County Landfill, Chanton and Liptay (2000) found that $\delta^{13}C$ of anoxic CH_4 did not vary seasonally, presumably because the temperature at which CH_4 is produced within the landfill is relatively constant. This lack of seasonal variability was confirmed for 2004–2005 by Fleiger (2006). Both the increasing rate of CH_4 emissions in fall and winter and the decreasing $\delta^{13}C$ of emitted CH_4 in control cells observed in this study replicated behavior observed at this landfill previously (Chanton and Liptay, 2000). As will be discussed below, we also found a similar inverse relationship between flux and $\delta^{13}C$, indicating that emission rates, particularly for the biocover, are controlled by bacterial oxidation of CH_4.

3.3. Methane oxidation

Percent oxidation of CH_4 in the control and biocover cells calculated from stable isotope data (Fig. 3) is plotted in Fig. 4. Prior to June 29, there was no significant difference between CH_4 oxidation in the control and the biocover cells (Table 3). After June 29, the biocover became significantly more effective in oxidizing CH_4. Analyses of variance (Table 3) using the data after and including June 29 indicate a significant difference ($p < 0.001$) between oxidation in the control and the biocover cells, with mean oxidation of 14% for the control cells and 41% for the biocover cells. Over the entire course of the experiment, the percent of CH_4 oxidation in the control and biocover cells were significantly different ($p < 0.001$), with a mean oxidation of 18% for the control cells and 38% for the biocover cells (Table 3).

A negative flux indicates oxidation of atmospheric CH_4, so it is likely that high oxidation rates in cover soils are oxidizing landfill CH_4 transported from below as well as atmospheric methane from above. It is reasonable to assume that these fluxes represent 100% oxidation of CH_4 from below. Alternatively, negative fluxes could indicate blockage or failure of CH_4 to be transmitted through a less permeable zone below the surface. Possibly both explanations serve to describe different areas.

Following the 3-months curing period, we observed 29 negative CH_4 fluxes and 27 zero fluxes in the biocover cells, while only 6 negative fluxes and 22 zero fluxes were observed in the control cells. Thus the biocover was frequently a sink for atmospheric CH_4 especially after the 3-months curing period.

The inclusion of negative and zero fluxes to represent 100% oxidation primarily affects only the amplitude of the trends (compare Figs. 4 and 5). Both Figs. 4 and 5 and Table 3 show that before late June 2004 there was no significant difference in percent CH_4 oxidation by the control and biocover cells, but after that time, the biocover cells were more effective in oxidizing CH_4 than the control cells. When 100% values are included, the mean oxidation values were significantly different ($p = 0.001$) with the mean oxidation for the biocover cells at 56% and the mean oxidation for the control cells at 39% over the entire period from March 2004 to April 2005. From late June 2004 to April 2005, the mean oxidation for the biocover cells was 64%, and the mean oxidation for the control cells was 30%, with $p < 0.001$.

Table 3
ANOVA results for percent CH4 oxidation data

		N	Mean %	Std error %	P
March 2004 through April 2005					
No 100% values	Control	40	18.5	2.67	<0.001
	Biocover	33	38.3	3.12	
Using 100%	Control	42	39.0	3.39	0.001
Values	Biocover	40	55.8	3.51	
March 2004 through June 10, 2004					
No 100% values	Control	13	26.4	3.78	0.431
	Biocover	11	31.1	4.37	No difference
Using 100%	Control	15	54.4	6.49	0.476
Values	Biocover	13	40.6	7.10	No difference
June 29, 2004 through April 2005					
No 100% values	Control	27	14.0	3.47	<0.001
	Biocover	22	41.3	4.08	
Using 100%	Control	27	30.4	5.20	<0.001
Values	Biocover	27	64.3	5.89	

The "no 100% values" are based solely on isotope data calculated with Eq. (4). The values calculated "using 100% values" include 0 emission measurements and negative emissions as representing 100% oxidation. *N* represents number of cell measurements.

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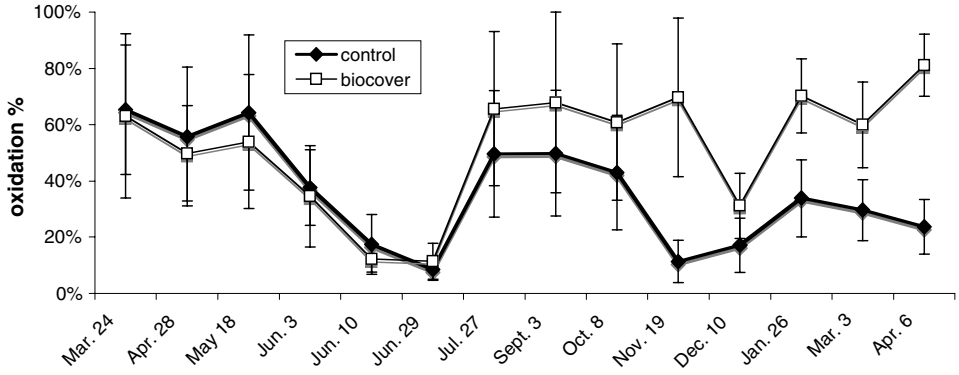

Fig. 5. Percent oxidation of CH_4 in the control and the biocover cells, calculated using values of 100% oxidation of methane flux from the underlying waste for incidences of negative and zero flux at the surface.

Methane oxidation rates for both the biocover and the control cells were calculated from flux and oxidation data using Eq. (7). Only isotopically-determined CH_4 oxidation values were used. If there was not a positive emission, we could not determine the CH_4 oxidation rate by this method, so these rates may be lower limits as discussed earlier. Biocover CH_4 oxidation data were impacted more than control cell data because there were more zero and negative fluxes there. Given these significant caveats, there was no difference in the absolute oxidation rate for the control and the biocover cells over the time period of this study (Table 4), despite the fact that the percent oxidation in the biocover cells was significantly greater than the percent oxidation in the control cells.

Table 4
ANOVA results for methane oxidation rate (g CH_4 m^{-2} d^{-1})

	N	Mean	Std error	*P*
March 2004 through April 2005				
Control	39	2.25	0.45	0.446
Biocover	30	1.72	0.54	No difference
March 2004 through June 10, 2004				
Control	13	2.09	0.51	0.139
Biocover	11	0.87	0.59	No difference
June 29, 2004 through April 2005				
Control	26	2.37	0.64	0.898
Biocover	19	2.24	0.79	No difference

These rates were calculated using only isotope determined % oxidation. If zero and negative flux measurements represent 100% oxidation, then these rates may be underestimates. This would affect the biocover cell rates more than the control cell rates since biocover rates contained more observations of zero and negative emission. *N* represents the number of cell measurements.

The biocover cells were thus apparently more successful in reducing the flux of CH_4 from the surface of the landfill via more complete oxidation assisted by longer retention times and less desiccation in the thicker cover materials. The biocover cells contained significantly more soil moisture than the control (Fig. 6), 0.74 ± 0.2 (w/w) compared to 0.22 ± 0.1 (w/w) for the soil. Similar effects were noted at the Outer Loop landfill (Barlaz et al., 2004), where the soil cover generally performed well, but occasionally released large quantities of methane associated with desiccation cracks. No such cracks were observed in the biocover cells. Barlaz et al. (2004) concluded that biocovers serve both to reduce emissions and as deterrents to soil cracking. Our results support these conclusions.

An inverse relationship between CH_4 flux and oxidation indicates that CH_4 oxidation in part controls the emission

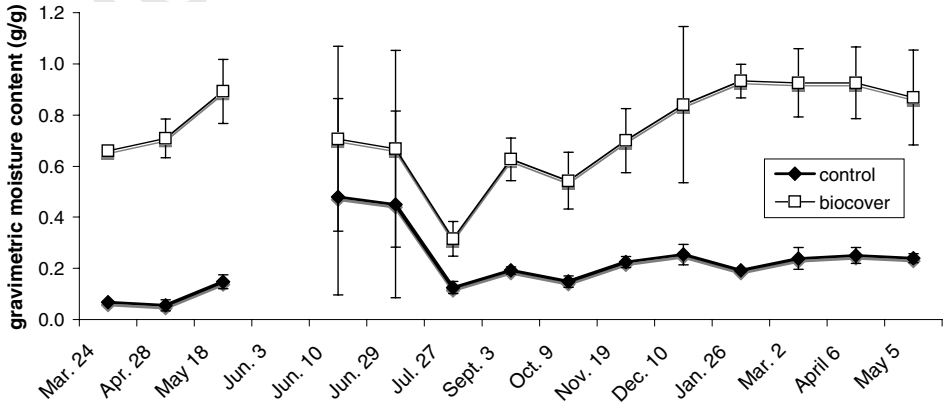

Fig. 6. Gravimetric water content (w/w) of control and biocover soils. Error bars represent standard deviation of three cells.

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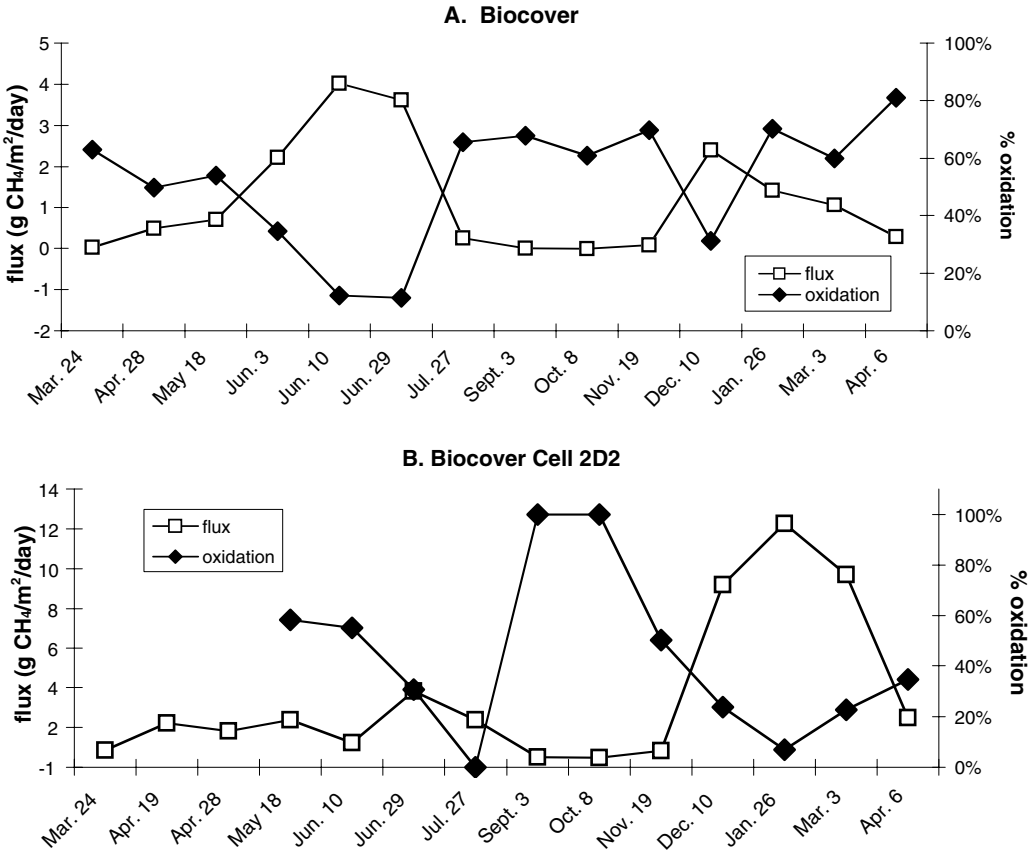

Fig. 7. (a) Percent CH_4 oxidation and flux in the biocover, mean of three cells. (b) Percent CH_4 oxidation and flux in chamber 2D2 from the biocover cells. Negative and zero flux values were entered as 100% oxidation in these figures.

of CH_4 from the landfill. The biocover cells were consistently more effective at this than the controls. For the biocover cells, plots of monthly mean data (including 100% oxidation data) show an inverse correlation between flux and oxidation (Fig. 7a). This result was also found for individual chamber sites (Fig. 7b). There was no overall relationship between CH_4 flux and oxidation for the control cells (Fig. 8a); however, some individual chambers showed an inverse relationship between flux and oxidation (Fig. 8b).

When all chamber data were plotted together (not shown), there was no relationship between soil moisture and CH_4 oxidation or soil temperature and CH_4 oxidation due to the high spatial variability of the flux rates. However, individual chambers in both the biocover and the control cells showed inverse correlation ($p < 0.001$) between soil moisture and CH_4 oxidation and positive correlation ($p < 0.001$) between soil temperature and CH_4 oxidation. In cells where an inverse relationship between soil moisture and CH_4 oxidation appeared, it is likely that high soil moisture limited oxygen influx.

In the present study, soil temperature remained relatively high throughout the year, averaging 25.7 ± 8.8 °C (Fig. 9). This study supports observations of higher percentages of CH_4 oxidation at landfills in warmer climates. Conservative estimates put the average annual percent CH_4 oxidation at the Leon County MSW landfill from 19% for untreated areas of the landfill to 38% for mulch treated areas (Table 3). Upper limit estimates, assuming negative fluxes represent 100% oxidation give mean annual percent CH_4 oxidation values of 39% for the control cells and 56% for the biocover cells. Similarly, a landfill in Kentucky had mean values of 21–55% CH_4 oxidation (Barlaz et al., 2004). This is significantly higher than the average annual percent CH_4 oxidation of 10% for a landfill in New England (Czepiel et al., 1996b), where CH_4 oxidation was enhanced during the warmer months (20–30%) and near zero during winter. Studies conducted at two landfills in Sweden also indicate seasonal dependence of CH_4 oxidation. During summers, CH_4 oxidation was near 100%, while CH_4 oxidation could not be detected during the winter, once the temperatures dropped below 0 °C (Borjesson et al., 2001). However, Bogner et al. (1997) measured negative CH_4 fluxes in winter in thick cover soils at an Illinois landfill. Therefore, temperature is an important factor, but complex relationships exist between temperature, moisture, the CH_4 oxidizing capacity of cover materials, and their physical properties.

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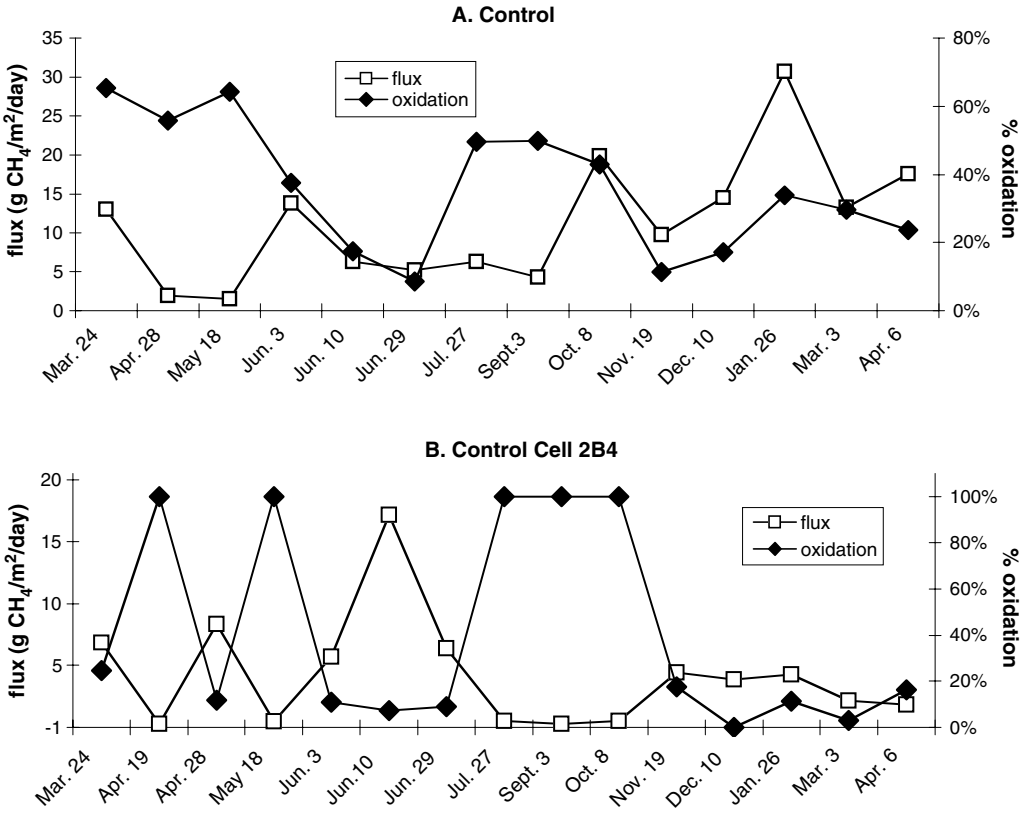

Fig. 8. (a) Percent CH_4 oxidation and flux in the control, mean of three cells. (b) Percent CH_4 oxidation and flux in chamber 2B4 from the control cells. Negative and zero flux values were treated as 100% oxidation in these figures.

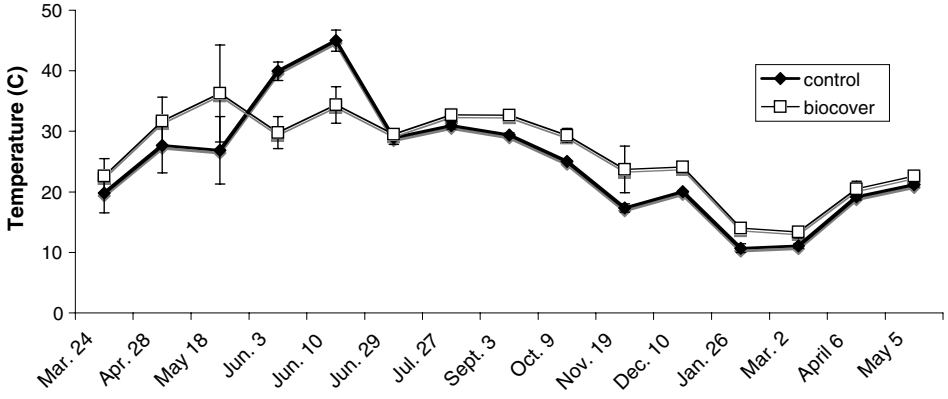

Fig. 9. Soil temperature measurements for control and biocover cells. Error bars represent standard deviation of three cells.

4. Summary and conclusions

Three biocover cells were constructed at the Leon County landfill over an existing 40–100 cm soil cover area with high CH_4 emissions. The biocovers consisted of a 10-cm-thick glass cullet dispersion layer overlain by a 50-cm-thick mulch layer (composted yard or garden waste) over the existing soil cover. Over the annual study, the percent CH_4 oxidation in the biocover cells was almost twice that of the non-treated control cells while methane emission rates were reduced 10-fold. The biocover both increased the retention time for transported gases through the cover and oxidized a greater portion of the gross flux to the base of the cover. The biocover cells became more efficient than the control cells in oxidizing CH_4 3 months after initial emplacement. Presumably this is the amount of time required for the formation of an appropriate methanotrophic community. There was no significant difference between flux in the control and biocover cells prior to the placement of the mulch. After placement, flux from the control cells (10.6 g CH_4 m^{-2} d^{-1}) was significantly greater ($p < 0.001$) than flux from the biocover cells (1.2 g CH_4

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$m^{-2} d^{-1}$). Over the period of this study, the difference between CH_4 oxidation values of the control and the biocover cells was statistically significant ($p < 0.001$). From June 29, 2004 to April 2005, when values for 0 and negative fluxes are included in the averages as if they represent 100% oxidation, the mean oxidation for the biocover cells was 64%, and the mean oxidation for the control cells was 30%, with $p < 0.001$.

A distinctive inverse relationship existed between percent oxidation and flux for the biocover cells. This is seen both for individual chambers as well as the averages for all twelve chambers on each date. Some individual chambers in both the control and the biocover cells also showed an inverse relationship between oxidation and soil moisture and a positive relationship between soil temperature and oxidation, although this was not reflected in averaged data.

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