Observations on the methane oxidation capacity of landfill soils

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ABSTRACT

The objective of this study was to determine the role of CH_4 loading to a landfill cover in the control of CH_4 oxidation rate (g CH_4 m^{-2} d^{-1}) and CH_4 oxidation efficiency (% CH_4 oxidation) in a field setting. Specifically, we wanted to assess how much CH_4 a cover soil could handle. To achieve this objective we conducted synoptic measurements of landfill CH_4 emission and CH_4 oxidation in a single season at two Southeastern USA landfills. We hypothesized that percent oxidation would be greatest at sites of low CH_4 emission and would decrease as CH_4 emission rates increased. The trends in the experimental results were then compared to the predictions of two differing numerical models designed to simulate gas transport in landfill covers, one by modeling transport by diffusion only and the second allowing both advection and diffusion. In both field measurements and in modeling, we found that percent oxidation is a decreasing exponential function of the total CH_4 flux rate (CH_4 loading) into the cover. When CH_4 is supplied, a cover's rate of CH_4 uptake (g CH_4 m^{-2} d^{-2}) is linear to a point, after which the system becomes saturated. Both field data and modeling results indicate that percent oxidation should not be considered as a constant value. Percent oxidation is a changing quantity and is a function of cover type, climatic conditions and CH_4 loading to the bottom of the cover. The data indicate that an effective way to increase the % oxidation of a landfill cover is to limit the amount of CH_4 delivered to it.

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1. Introduction

The ubiquitous nature of methanotrophic activity in natural bodies of water, wetlands, and human-created rice fields began to be fully appreciated in the 1970's (Rudd and Hamilton, 1975; Reeburgh, 1976; Rudd et al., 1976; Reeburgh and Heggie, 1977; Rudd and Taylor, 1980; Hanson, 1980; Kiene, 1991; King, 1992; Hanson and Hanson, 1996). The importance of methanotrophs in landfill soils was first recognized by Whalen et al. (1990) who observed the highest rates of CH_4 oxidation in any soils examined to date. Whalen et al. (1990) estimated that methanotrophs were able to consume roughly 50% of the CH_4 escaping the landfill surface. Methanotrophs are also able to consume non-methane organic compounds (Kjeldsen et al., 1997; Scheutz and Kjeldsen, 2005, 2004; Scheutz et al., 2008).

Landfills are responsible for 3–7% of global total CH_4 emissions (Lelieveld et al., 1998; Bogner and Matthews, 2003) and are among the largest anthropogenic CH_4 sources in the United States (USEPA, 2007). Landfills may be thought of as point sources of CH_4 to the atmosphere and therefore they make good targets for mitigation. Landfills are a greenhouse gas source that can be reduced without causing undue societal pressure. At older and smaller landfills without gas collection systems some fraction of CH_4 generated in the landfill passes through the soil where it is oxidized by soil methanotrophic bacteria (Chanton and Liptay, 2000; Stern et al., 2007; Abichou et al., 2006a,b). Passive vents at these sites can be treated with biofilters (Powelson et al., 2006, 2007; Gebert and Groengroeft, 2006). At modern landfills, gas capture for power generation or flaring reduces CH_4 emissions considerably. Nonetheless, some fraction of the produced CH_4 also escapes these landfills through the soil and through leaks in the gas collection system (Spokas et al., 2006; Börjesson et al., 2007). Recently, the technique of enhancing the activity of soil methanotrophic bacteria to further reduce fugitive emissions has received considerable attention including recognition from environmental agencies in Finland, Germany and Canada (Humer and Lechner, 1999, 2001; Huber-Humer and Lechner, 2002; Huber-Humer, 2004; Scheutz et al., 2009). Currently, the default value for the IPCC and the USEPA for

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landfill cover CH_4 oxidation is set at a relatively low value, between 0% and 10% of emitted CH_4 (IPCC, 2006; USEPA, 2004). This value was based on seasonal results for a New Hampshire landfill as determined by the studies of Czepiel et al. (1996a,b). Recently Chanton et al. (2009) reviewed the literature and compiled CH_4 oxidation results for 42 determinations of the fraction of CH_4 oxidized following and including Czepiel's landmark study and reported a mean value of 36 ± 6% for this parameter. Fifteen seasonal studies ranging from latitude 30° to 55°N yielded a similar value of 35 ± 6%.

Many factors control rates of CH_4 oxidation, among them, pH, moisture, temperature, and nutrient levels. Several investigators have documented the effect of nitrogen levels on CH_4 oxidation rates (Boeckx and Van Cleemput, 1996; Boeckx et al., 1996; Bender and Conrad, 1995; Hilger et al., 2000b). It has recently been observed that diurnal temperature cycling has a dynamic impact on the rate of oxidation (Spokas and Bogner, 2011). These results suggest that rates may not be adequately predicted from equivalent isothermal incubations (e.g. average daily temperature) and may need to be accounted for by calculating the rate through the actual temperature ramps. Several studies have examined the effect of different levels of moisture on soil oxidation (Bender and Conrad, 1995; Boeckx and Van Cleemput, 1996; Boeckx et al., 1996; Park et al., 2002; Scheutz and Kjeldsen, 2004). Basically, if the soil is too dry, the activity of methanotrophic bacteria is inhibited, and if the soil is too wet, the diffusion of oxygen can limit their activity.

The first objective of this study was to examine the extent to which the rate of CH_4 delivery to the soil methanotrophic zones controls CH_4 oxidation rates (in g CH_4 m^{-2} d^{-1}) and CH_4 oxidation efficiency (% CH_4 oxidation) in a field setting. Specifically, we wanted to assess how much CH_4 a cover soil could handle. To achieve this objective we conducted landfill CH_4 emission and CH_4 oxidation measurements in several synoptic sampling events in a single season. We hypothesized that percent oxidation would be greatest at sites of low CH_4 emission and would decrease as CH_4 emission rates increased. The trends in the experimental results were then compared to predictions by two differing numerical models designed to simulate gas transport in landfill covers, one by modeling transport by diffusion only and the second allowing both advection and diffusion.

Ultimately we hope that our work can result in the design of better landfill covers. For this reason, we evaluated the potential for soils to mitigate CH_4 emissions following landfill closure in two cases, with and without gas collection systems.

Our second objective was to assess the reproducibility of CH_4 emissions as measured with static chambers and to compare rates of emission from sloped areas of the landfill with those from flat top areas. We hypothesized that sloped areas would have higher CH_4 emissions relative to the flat top areas for two reasons. The first reason is that rainfall erodes the slopes to a greater degree than the flat top areas. A second reason that sloped areas might have greater CH_4 emissions has to do with the manner in which waste is placed in landfills. Waste is placed in horizontal layers, with a daily soil cover overlying each layer. This type of placement allows for greater lateral movement of gas, relative to vertical movement.

These measurements were made in summer when CH_4 oxidation in the Southeastern USA has been shown to be at a maximum (Chanton and Liptay, 2000). As our objective was to determine the maximum amount of methane that a landfill could oxidize, a summer measurement program was appropriate to achieve our objectives. We assumed that % moisture, temperature, nutrient levels, and other factors that control CH_4 oxidation would be relatively constant across the synoptic measurements that were made at a single site.

2. Methods

2.1. Methane oxidation rate and percent oxidation

Methane emission rate and stable isotope measurements to determine methane oxidation were conducted at two landfills in the Southeastern USA. Because we wanted to contrast variations in oxidation with variations in emission rate across the surface of a particular cover in several synoptic observations, we used the chamber technique. Landfill X is located in Northwest Florida at 31 degrees North latitude. The climate is humid subtropical. Average annual rainfall is on the order of 150 cm yr^{-1} and the annual mean temperature is 20 °C. Landfill Y is located at 38 degrees North latitude, in a more temperate but still humid climate. Average rainfall is 110 cm yr^{-1} and the annual mean temperature is 14 °C. The areas tested at landfill Y were operated as bioreactors. Soil temperatures at Landfill X varied from 24 to 32 °C during May measurements and 29–36 °C in June measurements. Percent water varied from 8% to 21% by weight over both periods. At landfill Y, soils temperatures varied from 28 to 37 °C and moisture varied from 5% to 21%.

At landfill X, CH_4 emissions from the soil were measured for three different cells. The North area was a closed cell with a final composite cover consisting of 45 cm of compacted clay (low permeability layer) overlain with 1.52 mm (60 mil) LLDPE geomembrane. A 1 m thick sandy loam soil and a dense vegetative layer were over the geomembrane. Both the flat top and the sloped side were examined. A second closed cell was a Beanie cap, consisting of the same composite cover on the top but no geomembrane on the slopes. A Beanie cap has a geomembrane on the flat surface but no geomembrane on the side slopes. The cover was densely vegetated and a 1 m thick sandy loam soil and a vegetated layer covered the flat top and the slopes. The third (South) cell was an intermediate covered area with 30–45 cm of sandy loam soil cover and sparse to no vegetation. The north area and the beanie cap area had completed active gas collection systems. However, the gas collection system in the south area of landfill X was under development at the time of testing, and additional gas wells are planned. The existing wells at the south area were screened only in lower portions of the waste mass. Emission measurements were conducted at all three areas, and CH_4 oxidation measurements were conducted using the stable isotope approach (Chanton and Liptay, 2000) at the south area.

At landfill Y, chamber flux measurements were conducted on the flat tops and side slopes of two bioreactor landfill cells (sandy clay) and in one daily covered area. The bioreactors had 2 m of soil overlying the waste, while the daily cover had only 15 cm of sandy loam overlying the waste. These were intermediate covered areas and no geomembranes had been installed. Isotopic measurements were conducted at two areas, bioreactor 2 and on the daily cover.

The chambers used in this study were constructed of polished aluminum with a size of 0.63 × 0.63 × 0.2 m (covering an area of 0.4 m^2). Within them was a small fan to circulate air. Chambers were sealed to the ground by clamping them to pre-installed collars. Total volume was 80–100 l. Five to six methane samples were collected from each chamber sequentially over a 25 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 20 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 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:

$$F = PVMU(\mathrm{d}C/\mathrm{d}t)/(ATR) \qquad (1)$$

where P is pressure (1 atm), V is chamber volume (80 L), M is the molar mass of CH_4 (16 g CH_4/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 (Kelvin), and R is the gas constant (0.08205 L atm/(K mol)). The slope of the line, $\mathrm{d}C/\mathrm{d}t$, was determined by linear regression between CH_4 concentration and elapsed time. 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.

Chambers were placed on a grid pattern with chambers 10–15 m apart. The geospatial mean CH_4 emission rate for the area was determined by use of inverse distance weighing (IDW) using "Surfer," developed by Golden Software, Inc., Golden, CO (Surfer, 2002; Spokas et al., 2003; Abichou et al., 2006a,b). Abichou et al. (2006b) compared the IDW approach with point kriging and found that the geospatial means in this area obtained by both methods were almost identical. Both results were similar to the arithmetic mean. Spokas et al. (2003) reported similar findings.

Methane oxidation was determined from the stable isotope approach. 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 the 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:

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

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:

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

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 (CH_4 oxidation efficiency) in upward transit through the landfill cover soil is then given by (Chanton and Liptay, 2000; De Visscher et al., 2004):

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

where δ_R is calculated using Eq. (2) and δ_A is the carbon isotopic content of anoxic CH_4 sampled from gas wells, and α_{ox} and α_{trans} are the isotope fractionation factors for methane oxidation and associated with transport of CH_4, respectively.

To achieve greater clarity of presentation, examine the mean trends in the data, and estimate variability, the % oxidation data were binned according to emission rate and then averaged and standard error calculated as (standard deviation/($sqrt(n)$)). At low fluxes we binned all data within the range of 0–1, 1–2, 2–3, 3–4, 4–5 g CH_4 m^{-2} d^{-1} and beyond that, with increasing emission rates, we grouped the data to generally include 3 values. Some

exceptions were made if there were few measurements of similar emission value. In the May data from Landfill X, the point at 1330 on the x-axis only contains two measurements and the point at 2125 g m^{-2} d^{-1} only contains one measurement. For the June landfill X data the two highest points in terms of emission only have two values in each bin. For landfill Y data the two highest points in terms of emission only have two values in each bin.

The fractionation factor (α_{ox}) was determined from the measured soil temperature (T, °C) using the regression equation for α_{ox} with temperature (Chanton et al., 2008a). The parameter α_{trans} was assumed to be 1. This assumption requires 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 and field studies have shown that this approach can underestimate CH_4 oxidation by as much as a factor of 2 by not taking into account diffusive flux (De Visscher et al., 2004; Chanton et al., 2008b). Thus the oxidation values reported here represent lower limits of CH_4 oxidation.

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:

$$R_{ox} = f_{ox} \left(\frac{F}{1 - f_{ox}} \right) \qquad (5)$$

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. (5) are lower limits.

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 Merrit 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).

2.2. Diffusion-based model

A comparison to a one dimensional mathematical diffusion/oxidation model was conducted at Landfill X south intermediate cover area to compare the field and model response of CH_4 oxidation rate to variation in rates of CH_4 emission. The model accounts for climatic influence on soil CH_4 oxidation activity (Bogner et al., 2009). As mentioned above, soil moisture and temperature play critical roles in determining the resulting rate of oxidation. This model utilizes the average annual cycle of air temperature, solar radiation and precipitation patterns coupled to a soil heat and water transport model (STM^2) (Spokas and Forcella, 2009) to arrive at the soil microclimate conditions (soil temperature and moisture) through the landfill cover soil for each minute of the year. By coupling these results with a gas diffusion–oxidation model, the potential climatic influence for any particular landfill can be estimated from these predictions of the soil conditions. In this fashion, the climatic influence of oxidation can be accounted for at the site. Various flux rates of CH_4 through this intermediate cover were simulated by altering the CH_4 concentration at the base of cover from 100 ppm to 50% CH_4. Since this is a diffusion-based model, changing the concentration gradient leads to differing flux rates of CH_4 into the cover soil.

2.3. Advection–diffusion-based model

In a landfill setting, water content, temperature, and barometric pressure are constantly changing depending on climate conditions, soil type, cover thickness, and vegetation. We also applied a numerical model to attempt to re-produce the data from Southeastern USA landfills. This model combines water and heat flow with a gas transport and oxidation model (Abichou et al., 2008, 2009; Yuan et al., 2009). One of the key input terms in this model is the landfill gas pressure and CH_4 concentration in the waste at the base of the cover. Based upon the gas conductivity of the soil, which is determined as a function of volumetric water content, CH_4 advection towards the surface is modeled and attenuated by CH_4 oxidation to predict surface emissions. This model does not (yet) include the effect of macro-pores or duel phase gas permeability.

The volumetric water content and the temperature profile of the landfill cover were resolved with simulations of water and heat flow in variably saturated soils using HYDRUS1D v3.0 (Simunek et al., 2005). Volumetric water content and temperature were generated at each node each day by HYDRUS1D. The gas transport model used these dynamic results to simulate CH_4 emission and oxidation. Continuity and mass balance equations were then used to describe the gas flow and reaction within the porous media. The reaction component of the gas transport equation was assumed to be in accordance with the reaction rate of methanotrophic bacteria calculated by Michaelis–Menton kinetics (De Visscher and Van Cleemput, 2003).

The CH_4 oxidation rate is calculated by dual-substrate Michaelis–Menten kinetics from incubation experiments using the equation,

$$r_{CH_4} = V_{max} \frac{C_{CH_4}}{K_{m[CH_4]} + C_{CH_4}} \frac{C_{O_2}}{K_{m[O_2]} + C_{O_2}} \quad (6)$$

where V_{max} is the maximum methane consumption rate (nmol s^{-1} $g^{-1}_{dry\ soil}$) and K_m is the half saturation constants for oxygen and methane (mol m^{-3}). V_{max} and K_m are estimated from incubation experiments in the laboratory. The Michaelis–Menten parameters, V_{max} and K_m, are corrected for variation in soil temperature and water content (Abichou et al., 2009). In the model, the air filled porosity ε, diffusion coefficient D, and gas permeability k are a function of volumetric water content. A temperature correction was introduced for the biological oxidation parameters similar to De Visscher and Van Cleemput (2003). Biological oxidation was also corrected for moisture content based on Boeckx et al. (1996).

A constant mass flux escaping the gas collection system was set as the lower boundary of the gas transport model. An equal flux of CO_2 (volume based) was also assumed to be transported with CH_4. The gas transport model then used the daily soil water and temperature profiles along with the daily flux into the bottom of the landfill cover to estimate CH_4 oxidation in the landfill cover and therefore estimate surface emissions. Simulations were performed for different values of flux into the bottom of the soil cover (bottom flux).

3. Results

3.1. Results of emission measurements

Representative replicate determinations of CH_4 emissions are shown for landfill X in Figs. 1 and 2. For the South flat top area measurements were conducted on May 23, May 24, and June 14, 2006. The geospatial means were 22.5, 40.4, and 22.7 g CH_4 m^{-2} d^{-1}, respectively (Table 1). For the South side slope area measurements were conducted on May 30 and May 31, 2006. The geospatial means of these measurements were 199 and 236 g CH_4 m^{-2} d^{-1}, respectively. The arithmetic means were similar. As described previously gas collection wells in this portion of the landfill were screened only at depth. Gas migrated laterally which explains the high fluxes measured on the slopes of this area. Repeated flux measurements for the exact same areas were also conducted at the flat tops and slopes of two final covered North and Beanie areas as described above, and at a second site along the slope of the intermediate covered South area.

At landfill Y, repeated measurements were conducted at one site. The mean of the replicate measurements for all 8 sites where measurements were repeated at the two landfills is shown (Table 1) and the coefficient of variation (CV). The average CV for the 8 cover types was 32%.

At landfill Y, the geospatial mean values were 12.8 g CH_4 m^{-2} d^{-1} for the daily cover and 2.45 and 82.6 g m^{-2} d^{-1} for the slopes on bioreactors 1 and 2. On the bioreactor top flat area, emissions were 9.7 and 2.8 g CH_4 m^{-2} d^{-1}, respectively.
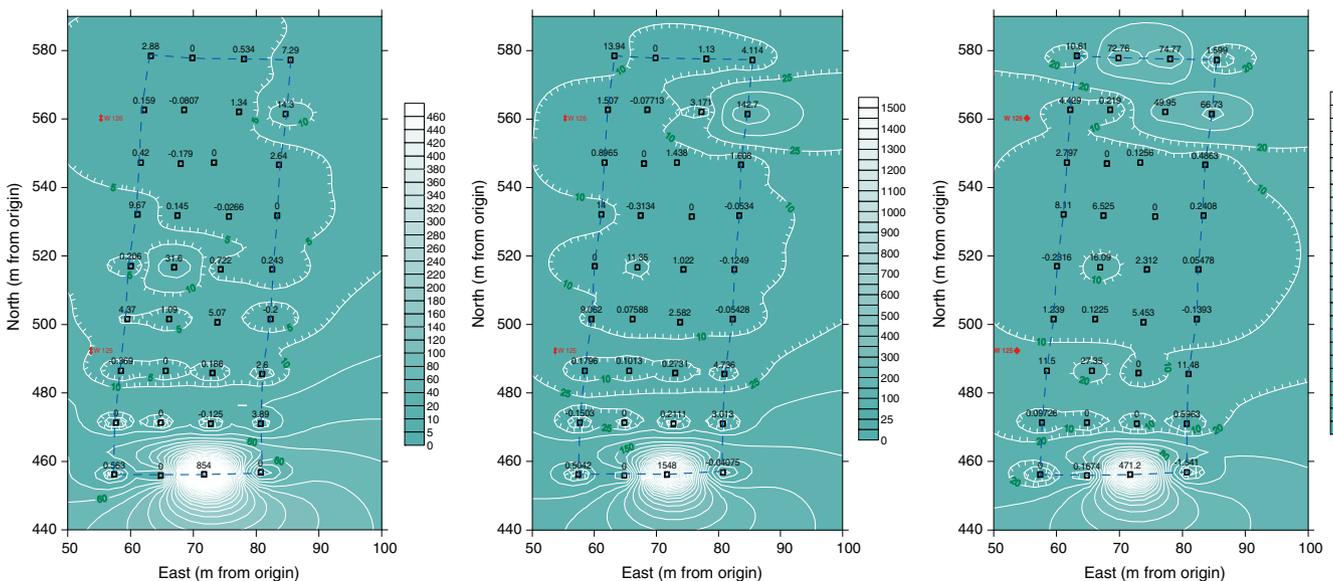

Fig. 1. Replicated fields of chamber measurements made at landfill X, South flat top area May 23, May 24, and June 14, 2006. The geospatial means of these measurements were 22.5, 40.4, and 22.7 g CH_4 m^{-2} d^{-1}, respectively.
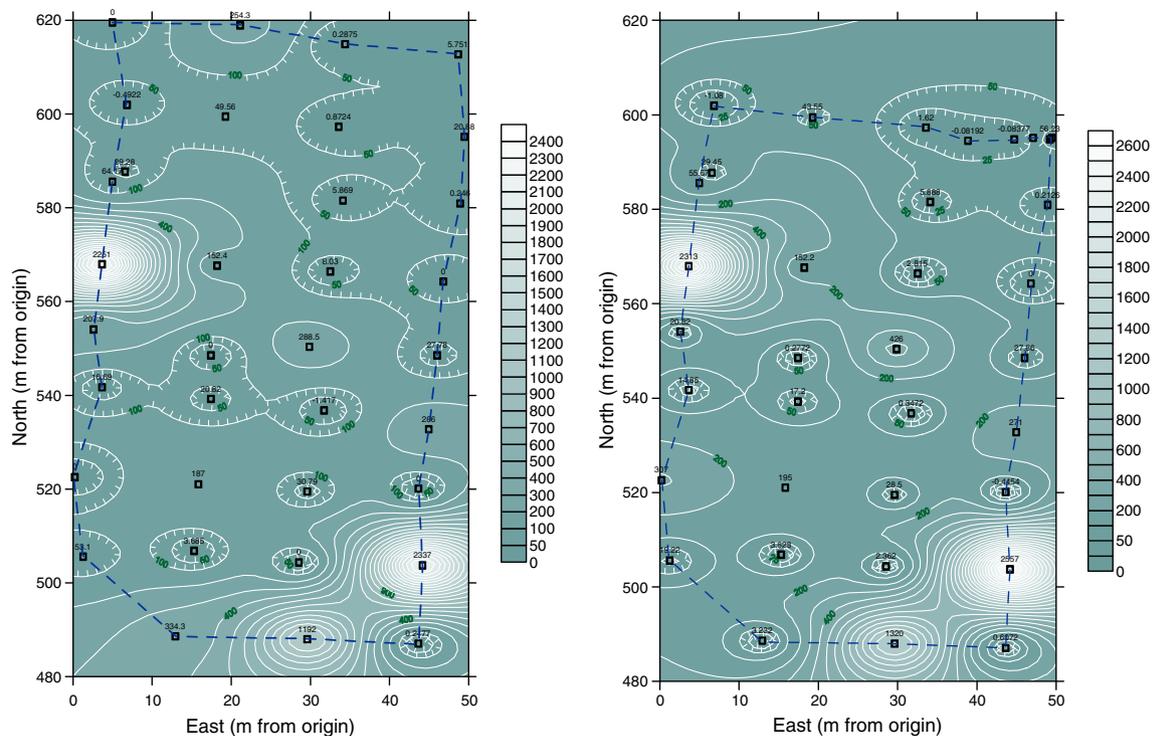
Fig. 2. Replicated fields of chamber measurements made at landfill X, south side slope area May 30 and May 31, 2006. The geospatial means of these measurements were 199 and 236 g CH_4 m^{-2} d^{-1}, respectively. Elevated emissions were due to an incomplete gas collection system.

3.2. Results of oxidation measurements

At the sites where CH_4 oxidation was determined with the isotope technique, the % oxidation was observed to vary from near 100% to near 0% (Figs. 3A, 4A and 5A). Higher % oxidation was generally associated with lower emission rates, while at higher emission rates % oxidation values were lower. At low emission rates, % oxidation values ranged from 0% to 100%, but as CH_4 emissions increased, the range in % oxidation decreased and the higher % oxidation values were not observed. Binned data (see methods) are plotted as the mean of the % oxidation values within each bin (y-axis) and their standard error (Figs. 3B, 4B and 5B). Midpoint and range of each bin are shown on the x-axis. The data were then fit to exponential curves. The exponential relationships between decreasing % oxidation and increasing CH_4 emissions were significant, p values varied from <0.01 to <0.001, confirming our hypothesis that at lower rates of emission, % oxidation would be greater. Overall, the exponential fits were constrained by low % oxidation results at higher fluxes to yield y intercepts ranging from 0.21 to 0.43. However, the average % oxidation values for emission rates below 10 g CH_4 m^{-2} d^{-1} for Figs. 3–5 were 39.4 ± 6.2%, 41.9 ± 6.0% and 54.5 ± 8.3%, consistent with our hypothesis that % oxidation varied inversely with increasing emission rate. It should be stressed that these are absolutely minimum values for % oxidation as no correction was applied to the isotope data for the effects of diffusion.

We also plotted the CH_4 oxidation rate, calculated with Eq. (5) above, and found significant positive correlations between the oxidation rate and the emission rate at lower emission rates, e.g., below 300 g CH_4 m^{-2} d^{-1} (Fig. 3C), 500 g CH_4 m^{-2} d^{-1} (Fig. 4C), and 305 g CH_4 m^{-2} d^{-1} (Fig. 5D). The criteria we used to select these "cut-off" points for the linear regressions was that beyond the "cut-off" x-axis values the methane oxidation rates (y-axis) reached a plateau or decreased. Figs. 3C and 4C resemble a Michaelis–Menten enzyme kinetic plot of a biological reaction's response

to increasing substrate concentrations. The rate increases linearly initially, and the levels off to a relatively "flat" value. In Fig. 5C, the emission rate does not reach sufficient magnitude to allow observation of this plateau in the oxidation rate. The results in Fig. 5D, lower panel, appeared to fall into two populations, emission that passed through the soil and was exposed to oxidation (closed symbols), and that which apparently without exposure to oxidation (opens symbols). The values (open symbols) that fell along the x-axis were excluded from the regressions. The justification for this exclusion was that these data did not appear to exhibit CH_4 oxidation and we wanted to determine the relationship for those samples that did. The cover here was 1.5–2 m thick, so it may be that cracks could allow for bypassing of the main zone of oxidation, as well as allowing rapid transit of CH_4 across the cover. The isotope technique, applied with chambers, is apparently able to capture this phenomenon.

3.3. Model results

Fig. 6 illustrates the results from the diffusion-based mathematical modeling conducted for the intermediate area at landfill X. In Fig. 6A, the exponential trend that was observed in the field measurements (Figs. 3B, 4B, and 5B) is also seen in the model results for varying flux rates of CH_4 (set by varying concentrations of CH_4 at the base of the cover soil). The reason for this behavior in the model is the finite capacity of the soil to oxidize CH_4. For the current model, a maximum CH_4 oxidation rate of 400 ug CH_4 g_{soil}^{-1} d^{-1} was used, based on laboratory incubations (Spokas and Bogner, 2011). Using a bulk density of 1.6 g cm^{-3} for the cover soil and optimum conditions present throughout the cover, this would result in 195 g CH_4 m^{-2} d^{-1} ultimate oxidation capacity for this intermediate landfill cover. This value is close to the field data, which illustrate a plateau value of about 200 g CH_4 m^{-2} d^{-1} (Figs. 3C and 4C), particularly when the field emissions saturated the oxidation capacity. The diffusion model accounting for soil

Table 1
Geospatial mean of chamber-determined CH_4 emission rates for different cover types at landfills X and Y. The mean of the replicate measurements is shown and the coefficient of variation (CV) is calculated as 1/2 the range of the measurements divided by the mean times 100. The average of the CV for the 8 cover types was 32%.

Landfill area	CH_4 emission rate ($g\,m^{-2}\,d^{-1}$)	CH_4 emission rate mean ($g\,m^{-2}\,d^{-1}$)	CV
Landfill X			
North top			
15-May	26.1	20.0	30.8
5-Jun	13.8		
North slope			
22-May	111.3	62.7	77.5
	14.1		
Beanie top			
17-May	1.3	1.2	5.8
8-Jun	1.1		
Beanie slope			
18-May	0.6	0.4	37.1
8-Jun	0.3		
South flat			
23-May	22.5	28.6	21.1
24-May	40.5		
14-Jun	22.7		
South slope 1			
30-May	199.0	217.6	8.5
31-May	236.1		
South slope 3			
1-Jun	123.1	83.4	47.7
12-Jun	43.6		
Landfill Y			
Bioreactor 1, flat top			
29-Jun	6.95	9.7	28.2
1-July	12.4		
Bioreactor 1, side slope			
13 July	2.45		
Daily covered area			
2-July	12.8		
Bioreactor 2, flat top			
3 and 5 July	2.8		
Bioreactor 2, side slope			
10 and 11 July	82.6		
Average CV %			32.1
			n = 8

Fig. 3. Measurements in May 2006, in first round of sampling, landfill X, South area. Panel A, % CH_4 oxidation versus CH_4 emission rate, individual chamber fluxes. Panel B, % oxidation versus CH_4 emission rate, binned data, see text. Bins indicated by *x*-axis error bar. Panel C, CH_4 oxidation rate versus CH_4 emission rate. Solid diamonds, fit to linear regression represent data with emission rates less than 300 g CH_4 m^{-2} d^{-1}. Open symbols were not included in the regression. The criteria we used to select these "cut-off" points for the linear regressions was that beyond the "cut-off" *x*-axis values the methane oxidation rates (*y*-axis) reached a plateau or decreased.

temperature and moisture conditions predicted a seasonal variability in net surface emission of 150–325 g CH_4 m^{-2} d^{-1}.

As shown in Fig. 6B, the overall annual average for the oxidation rate predicted by the model is around 100 g CH_4 m^{-2} d^{-1}. However, there is a discrepancy in the predicted percent oxidation between the model [illustrating 100% oxidation at low CH_4 flux rates (<100 g CH_4 m^{-2} d^{-1})] and field observations not always illustrating complete oxidation at these low flux rates, with the linear increase in CH_4 oxidation rate as a function of net flux rate, as discussed above. The field data (Fig. 3C) has a slow gradual increase to the plateau, and the model results (Fig. 6B) possess a virtual step function behavior (no gradual increase to the plateau). This difference could indicate that despite the fact that conditions are favorable for oxidation at a particular depth; the CH_4 in the field setting is not being oxidized to the extent predicted by the model. As postulated above, these reduced oxidation rates could indicate the presence of macro-pore flow (e.g. cracks, etc.), less than optimal rates of oxidation due to past environmental conditions, the presence of exopolymeric substances (EPS) (Hilger et al., 2000b) that reduces oxygen availability, or even complications due to diffusion differences between the isotopes (De Visscher et al., 2004). These diffusion differences would be further complicated by temporal differences in the fractionation factor as a function of temperature and soil moisture at different depths within the CH_4 oxidation zones. Additionally, this discrepancy could also result from the
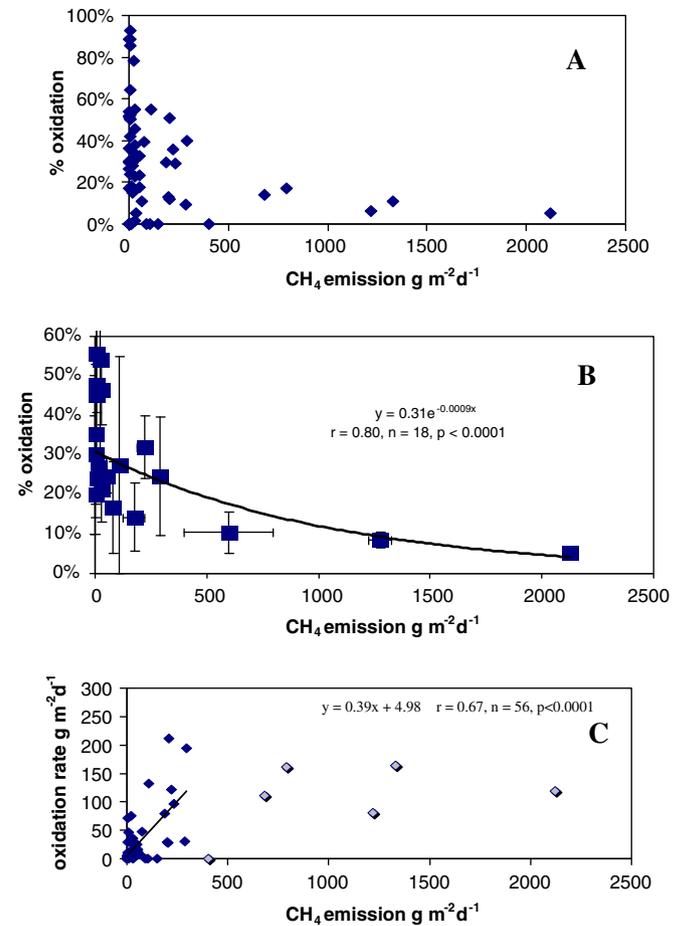
one dimension diffusion transport assumptions and be solely a limitation of the current model not accounting for advective gas transport and preferential flow, which could also impact soil moisture availability.

Fig. 7 shows the results obtained from the simulations performed using the advection-based model. Fig. 7a shows the same trend observed in field measurements and in the diffusion-based model. When a curve fit is added to the simulation results (Fig. 7a), the following equation is obtained ($r^2 = 0.97$):

$$\text{Fraction oxidized} = 0.9823 \times \exp(-0.0044 \times \text{surface emissions})$$

(7)

One can think of this equation as a unique relationship between surface emissions and fraction oxidized for an interim landfill cover located in the same climatic conditions. Abichou et al. (2010) has developed such relationships for several cover types for the different climates of the state of California. The results from the field data and the modeling results indicate that percent oxidation should not be considered as a constant (10% or any other single value). Percent oxidation is a changing quantity and is a function of cover type, climatic conditions and CH_4 loading to the bottom of the cover.
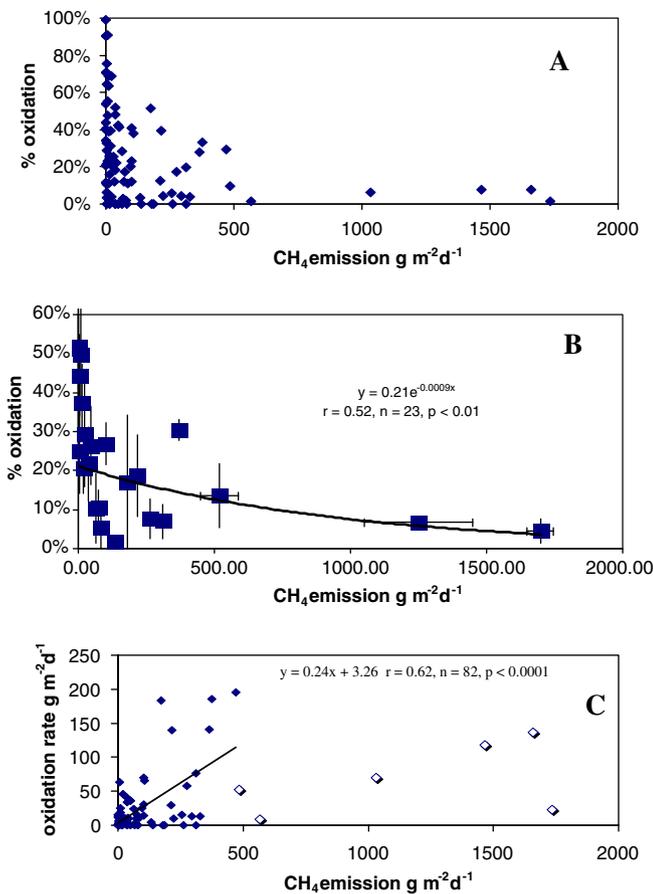
Fig. 4. Measurements in June 2006, in second round of sampling, landfill X, South area. Panel A, % CH_4 oxidation versus CH_4 emission rate, individual chamber fluxes. Panel B, % oxidation versus CH_4 emission rate, binned data. Bin range indicated by x-axis error bar. Panel C, CH_4 oxidation rate versus CH_4 emission rate. Solid diamonds, fit to linear regression represent data with emission rates less than 500 g CH_4 m^{-2} d^{-1}. Open symbols were not fit to the regression. The criteria we used to select these "cut-off" points for the linear regressions was that beyond the "cut-off" x-axis values the methane oxidation rates (y-axis) reached a plateau or decreased.

Fig. 7b shows a similar trend as was observed in the field data. The maximum oxidation rate was approximately 120 g CH_4 m^{-2} d^{-1}. The modeled maximum oxidation rate is lower than that observed in the field because the model results are an average daily rate for an average year of climatic conditions. Measured higher oxidation rates might be due to higher than average temperatures during the field sampling campaign. The oxidation rate declines in Fig. 7b due to the upwards flow of CH_4 from the landfill limiting the diffusion of oxygen into the soil. Such effects were not observed in the diffusive model (Fig. 6).

4. Discussion

4.1. Methane oxidation rate and percent oxidation

Geospatial mean landfill CH_4 emissions ranged from 0.3 to 236 g m^{-2} d^{-1} as a function of cover type (Table 1). At landfill X, CH_4 emissions varied from 0.4 to 63 g CH_4 m^{-2} d^{-1} on the final covered (North area and Beanie) areas, and from 29 to 218 g CH_4 m^{-2} d^{-1} at the intermediate covered area. The North cell of the landfill had a number of cover penetrations for gas wells and leachate recirculation wells and CH_4 emission occurred primarily around these penetrations. These penetrations were subsequently
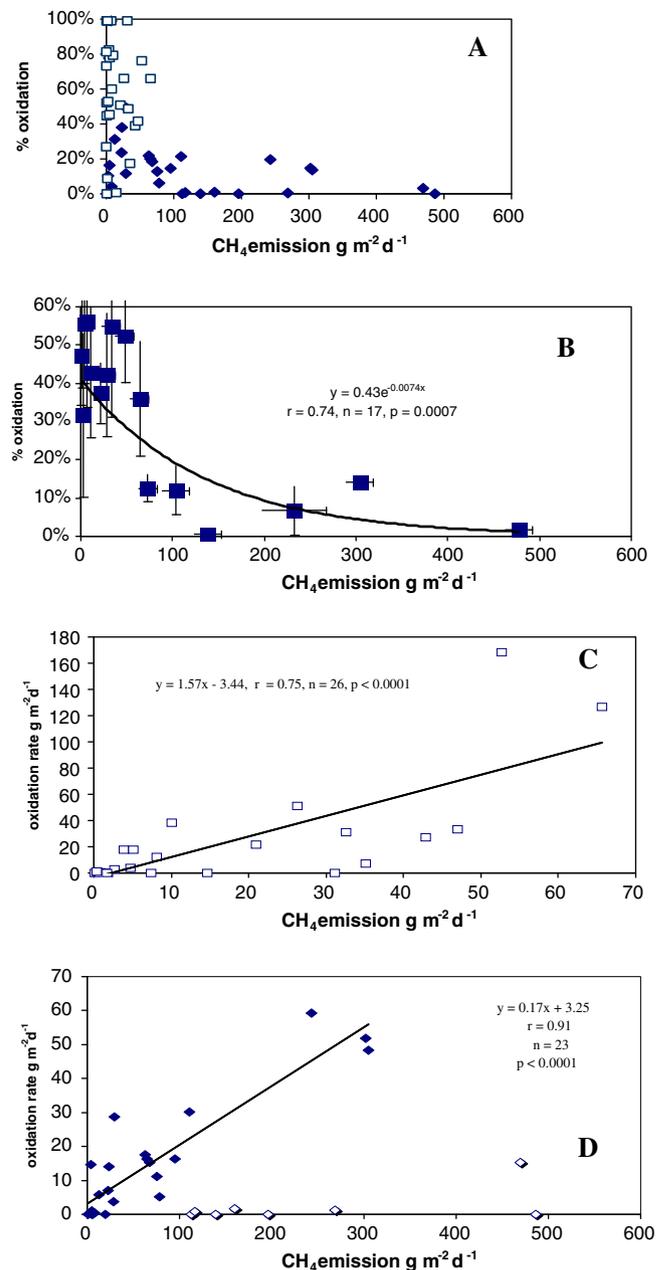

Fig. 5. Measurements in July 2006 at landfill Y. Panel A, % CH_4 oxidation versus CH_4 emission rate, individual chamber fluxes. Open symbols were from the daily covered area, closed symbols were from bioreactor 2. Panel B, binned data, % oxidation versus CH_4 emission rate from both areas. Bins indicated by x-axis error bar. Panel C, CH_4 oxidation rate versus CH_4 emission rate for soil daily cover. Panel D, CH_4 oxidation rate versus CH_4 emission rate for the bioreactor clay cover, solid diamonds, fit to linear regression represent data with emission rates less than 305 g CH_4 m^{-2} d^{-1}. Open symbols were not fit to the linear regression (see text).

repaired and emissions reduced by approximately 60% (Nathan Swan, Cygnus Environmental, personal communication, 2010.)

At landfill "Y" emissions ranged from 2 to 83 g m^{-2} d^{-1}. Four of the areas examined exhibited emissions below 15 g m^{-2} d^{-1}, elevated emissions were observed only at one side slope 83 g m^{-2} d^{-1}. The bioreactor cells at landfill "Y" were not elevated relative to the cells at landfill "X". The best maintained final covers only allowed the emission of small quantities of CH_4 (~1.3 g m^{-2} d^{-1}) while covers in different stages of development or disrepair obviously released more CH_4. Five landfill flat tops were compared with slopes in this study, and in 3 of 5 cases, the slopes had greater
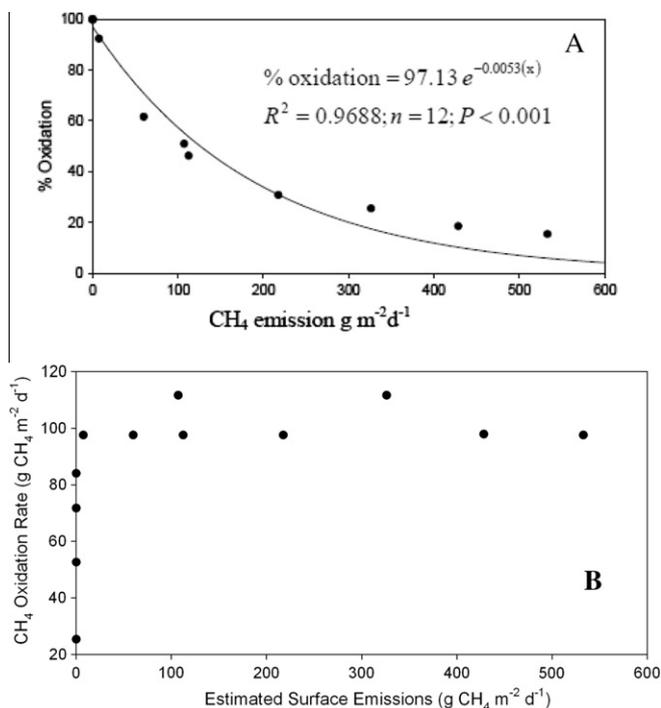
Fig. 6. Diffusion based model output reproduction of field data. Panel A, % oxidation versus surface emitted CH$_4$, Panel B, oxidation rate versus surface emitted CH$_4$.

Fig. 7. Results of simulations performed using pressure based model. Panel A, % oxidation versus surface emitted CH$_4$. Panel B, oxidation rate versus surface emitted CH$_4$.

emissions by a factor of 3, factor of 7, and a factor of 30. In two cases the slopes emitted less CH$_4$ than did the tops. Thus while slopes have the potential to contribute higher emissions relative to flat tops, this is not always the case. Well maintained side slopes where the effects of erosion have been either prevented or repaired are not necessarily greater sources of CH$_4$ than top areas.

As previously reported, (Bogner et al., 1997; Czepiel et al., 1996b) CH$_4$ emissions from the landfill surface were dominated by "hotspots". But this study offers clear evidence that these features persist at the same location, at least on timescales of weeks (Figs. 1 and 2). The persistence of these features indicates that with increased monitoring some hot spots could be identified, repaired and the cover emissions attenuated by coverage with bio-cells (Abichou et al., 2006a, b). Furthermore, the reproducibility of the chamber technique for measuring methane emission patterns averaged 32%, $n = 8$. This reproducibility includes measurement error and short term temporal variability. These observations pertain to this specific period of measurement under these climatic conditions and this cover soil. Diurnal variations in flux measurements from landfills have not been found to be discernable (G. Hater, 2010, unpublished data).

Based on the field measurements of landfill cover soils and confirmed by both models (Figs. 3–7), there is a finite limit to the absolute soil CH$_4$ oxidation capacity. If this is expressed in a percentage, the percent oxidation is a decreasing exponential function of the total CH$_4$ flux rate into the bottom of the cover. Once this oxidation limit is reached, increasing the delivery of CH$_4$ to the soil does not continue to increase the rate of oxidation, which stays constant.

The diffusion model predicted a seasonal variability in net surface emission of 150–325 g CH$_4$ m^{-2} d^{-1}, as a function of the variable soil temperature and moisture. These predicted values are very close to the geospatial means of two landfill X field measurements (199 and 236 g CH$_4$ m^{-2} d^{-1} – Fig. 2). Overall, the diffusion-based mathematical model duplicates the observations in the behavior between % oxidation and observed net emission rate
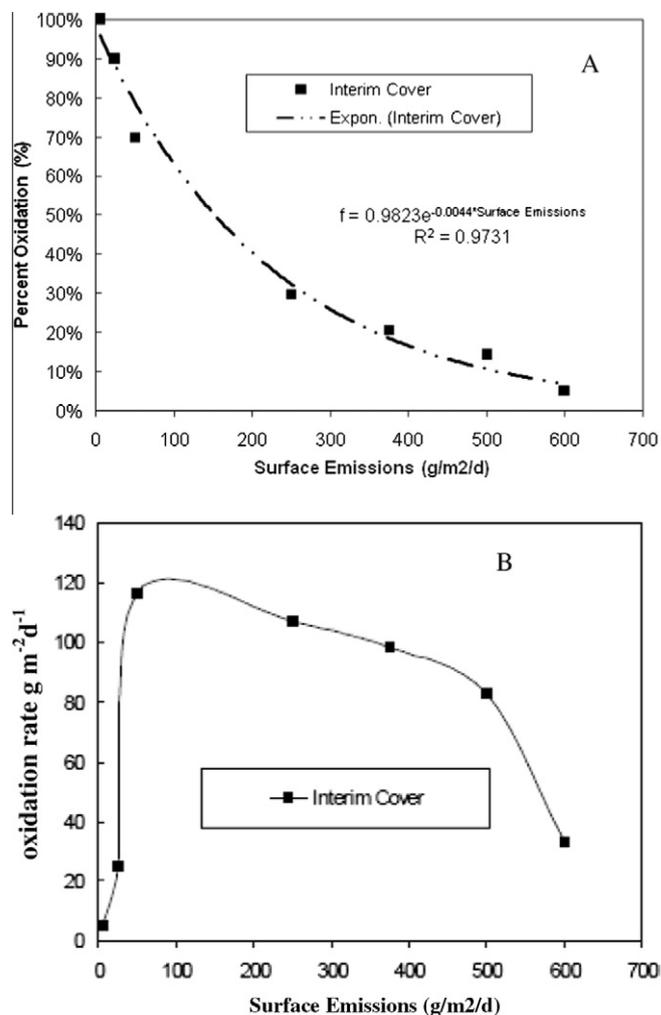
(Figs. 2 and 6). These model results further support the hypothesis that the higher observed surface emissions (>350 g CH$_4$ m^{-2} d^{-1}) result from non-diffusive transport through the entire cover or non-oxidized CH$_4$ (e.g. macro-pore flow).

The advection-based model shows similar behavior for % oxidation versus emission (Fig. 7a). However in this model, oxidation rate decreases as emissions continue to increase (Fig. 7b). In this model, the gas pressure below the landfill cover controls the flux of CH$_4$ into the cover soil. As pressures increase the upward flow of CH$_4$ reduces the diffusion of oxygen from the upper boundary and thus reduces the amount of CH$_4$ that can be oxidized. The diffusive model described above does not account for these advective transport mechanisms. However, both models have similar predictions for the percent CH$_4$ oxidation occurring in the cover soil as a function of CH$_4$ emission (Figs. 6A and 7A).

Landfill cover soil oxidation is conducted by a biological system and it behaves as such. When substrate (CH$_4$) is supplied, the cover's rate of CH$_4$ uptake is linear to a point, and then the system apparently becomes saturated. This is a classic enzyme response. The reaction rate increases linearly with substrate concentration. Methanotrophs in the oxic zone of the soil are limited by CH$_4$. When the oxidation rate levels off, at higher emission rates, the methanotrophic community is apparently limited by some other factor, presumably either oxygen or microbial population.

Additionally, the response could be due to hysteresis in microbial response to the presence of CH_4 (whether concentrations are increasing or decreasing; Spokas and Bogner, 2011). These driving factors vary from one landfill climate type to another. However, as seen in the modeling results, the value of 400 ug CH_4 g_{soil}^{-1} d^{-1} appears to be near a value for ultimate capacity of landfill soils at least from the Southeast US sites used in this study. Incidentally, this oxidation rate also is the ultimate rate observed in soils from Western US (California) sites (Spokas and Bogner, 2011).

The two trends in the data may seem contradictory. If CH_4 oxidation rate is a constant function of emission rate, how can the % oxidation decrease with emission rate? The behavior is due to a non-zero intercept in the oxidation rate versus emission rate data, and also possibly due to the considerable scatter in the data.

An additional complicating factor is the degree to which the CH_4 is able to short circuit exposure to the soil microbial community by bypass flow through cracks, and other conduits. As observed in Fig. 5D, at this particular soil cover, at emission rates above 100 g CH_4 m^{-2} d^{-1} a subset of the emissions experience no CH_4 oxidation. We hypothesize that this CH_4 is bypassing the methanotrophic bacteria. Since these emissions were captured in chambers, these chambers must have covered cracks or fissures of sufficient size to allow the CH_4 to pass through the cover with minimal interaction with methanotrophic bacteria. In addition, it could be hypothesized that just as CH_4 is able to migrate through cracks, there could be occurrences of CH_4 being trapped within the soil and then being oxidized to a higher extent than the CH_4 that is free to move through the soil. Gas can be trapped or its rate of transport slowed due to variation in soil conductivity and tortuosity. This leads to a scatter on both sides of the average flux value. However, overall the geospatial means of the flux rates were within the same order of magnitude as the flux predicted from the diffusion-based model. This leads us to suggest that these phenomenons (crack transport and trapped CH_4) are not the dominant processes in landfill CH_4 transport, at least at these sites. The exact contributions of advection and crack transport to overall site emissions are unknown and requires further research.

Our results indicate that one effective way to increase the % oxidation of a landfill cover is to limit the amount of CH_4 delivered to it. Obviously when CH_4 production rates are high, in the early life of a landfill, limiting the amount of CH_4 delivered to the cover is accomplished by an efficient gas collection system. Early installation of these systems is warranted (Barlaz et al., 2010). The presence of a gas collection system reduces the concentration and pressure of CH_4 at the base of the cover and thereby reduces the source strength of CH_4 entering the cover system. However, the cover may be relied upon to consume a portion of the CH_4 so that the extraction strength of gas collections systems can be adjusted downward to obtain landfill gas with an elevated CH_4 composition to better supply energy generating systems. Obviously % oxidation will be greater in landfills with gas collection than in those without gas collection if other factors such as the age and thickness of the waste are equal. A cover with an efficient well-functioning gas collection system will achieve a higher % oxidation than a cover with a gas collection which is inefficient and poorly maintained.

Over time, as the waste within a landfill matures and the CH_4 production rate decreases, it will at some point become possible to turn off gas collection systems and rely upon the landfill cover for the consumption of the remaining gas produced. The soils that we examined consumed minimum estimates of 39–54% of the CH_4 delivered to them at emission rates below 10 g CH_4 m^{-2} d^{-1}. At 50% oxidation, this means that the delivery rate of CH_4 to the base of the oxidation zone (e.g. the bottom flux) was 20 g CH_4 m^{-2} d^{-1}. These soils were low organic and non-vegetated. Amendment of landfill cover soils with organic materials can enhance the soil's capacity to hold water which may enhance oxidation (Stern

et al., 2007; Huber-Humer, 2004; Huber-Humer et al., 2008; Huber et al., 1999). There is also evidence that a healthy vegetated cover can enhance biotic CH_4 uptake by providing an optimum environment for bacteria and by facilitating oxygen transport into the soil via an increased surface/atmosphere contact (Hilger et al., 2000a; Maurice, 2001; Wang et al., 2008). Organic matter amended and vegetated soils have the added benefit of reducing cracks and fissures in clay soils, thus reducing the input of gas to the bottom of covers and allowing for more efficient gas collection by extraction systems (Stern et al., 2007).

For example, Scheutz et al. (2009) compiled and tabulated results from laboratory column studies that determined CH_4 oxidation % and rate from the difference between the CH_4 input and output at the column top. Mineral soils and organic rich soils (compost) which are often used for bio-covers were compared. These results are presented graphically in this paper in Fig. 8. For both soil types there was no relationship between the column inflow rate and % oxidation. The lack of a relationship for mineral soils is possibly due to a dearth of studies conducted at low flow rates, below 150 g CH_4 m^{-2} d^{-1}. For organic materials a range of values was obtained but under the best of conditions it is apparently possible to attain quantitative oxidation at flow rates as high as 600 g CH_4 m^{-2} d^{-1}. Similar results have been obtained in biocover simulations at a larger scale (Cabral et al., 2010). A plot of oxidation rate as a function of column input rate (Fig. 8B) shows the typical falling off of oxidation rate at higher CH_4 flux values in some cases, however. Nonetheless, it appears that landfill cover soils can be improved to increase CH_4 oxidation percentage by amending them with organic matter and vegetation. As noted above, this will also serve to reduce desiccation cracks
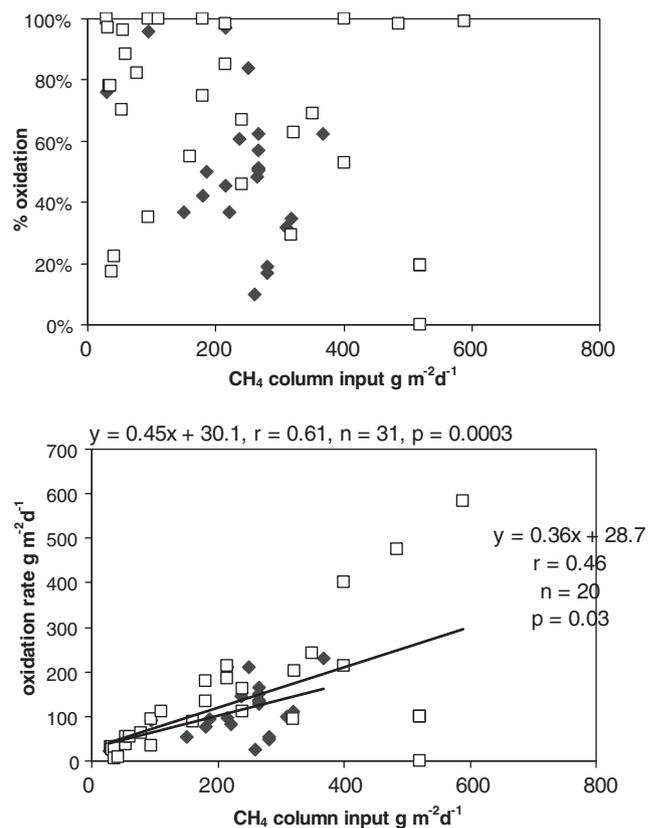

$$y = 0.45x + 30.1, \ r = 0.61, \ n = 31, \ p = 0.0003$$

$$y = 0.36x + 28.7$$
$$r = 0.46$$
$$n = 20$$
$$p = 0.03$$

Fig. 8. Laboratory column studies of CH_4 oxidation percent (upper panel) and CH_4 oxidation rate (lower panel) at differing rates of CH_4 loading to the bottom of the column. These literature results were compiled by Scheutz et al. (2009) and are presented graphically here. Open symbols represent organic rich materials while filled diamonds are column studies that utilized landfill mineral soil. The regression of the organic soils had an r of 0.61, while the mineral soil regression r was 0.46.

reducing bypassing of the soil and thus further increasing % oxidation. But organic matter amendments are not without problems themselves, including degradation of the organic matter, settlement, loss of permeability, CH_4 formation and so on. Healthy vegetation can maintain an organic treatment, however.

4.2. Hypothetical case study

An illustrative case study was developed to evaluate when fugitive inputs to the cover are within the soil's capacity to attenuate CH_4 emissions by biological oxidation. The CH_4 production rate was calculated for a landfill that received 10^6 Mg of waste per year for 10 years by using EPA's LandGem model (USEPA, 2005). Methane production and emissions are presented at the AP-42 default decay rate of 0.04 yr^{-1} as well as at 0.1 yr^{-1} to simulate accelerated decomposition (USEPA, 1998a,b). The ultimate CH_4 yield (L_0), 63.9 m^3 Mg^{-1}, was calculated from waste component specific CH_4 yield data and statewide waste composition data as presented in Staley and Barlaz (2009). To convert CH_4 production and collection rates (m^3 yr^{-1}) to a flux (g^{-2} yr^{-1}), the waste was assumed to have an in place density of 833 kg m^{-3} in a landfill that included 5% cover soil and airspace utilization of 248,656 m^3 ha^{-1}. These values were adopted from a survey of landfill practice (Camobreco et al., 1999) and represent a landfill with an average height of 25.8 m including the top area and the slide slopes. The resulting CH_4 production and uncollected CH_4 are presented in Fig. 9a and b, respectively. The uncollected CH_4 (Fig. 9b) represents CH_4 input to the bottom of the soil cover (bottom flux) in response to an assumed landfill gas collection efficiency. This efficiency was adopted from Barlaz et al. (2010) and is linked to the age of the waste cell. The collection efficiency regime developed by Barlaz et al. (2010) is as follows: 0% in years 1 and 2, 50% in year 3, 70% in year 4, 75% in years 5–10 and 95% thereafter. For this illustration, it was assumed that a final cover was placed after 10 years of waste disposal, at which time the gas collection efficiency was 95%. Data in Fig. 9 are only presented after year 10 (the year of closure) at which time the landfill footprint was constant. The CH_4 flux is independent of the mass of waste buried since the flux is calculated from a mass of waste buried in a given area.

The scenarios presented in Fig. 9 are illustrative and there are many factors that would shift the production curves up or down. A lower L_0 would shift these curves down. The effect of decay rate is illustrated by the shift between 0.04 and 0.1 yr^{-1} and higher decay rates are possible at bioreactor landfills.

As illustrated in Fig. 9b, with a gas collection efficiency of 95% after landfill closure, the input of uncollected CH_4 to the soil cover is well within the range where the soil cover CH_4 oxidizing bacteria are under-saturated with respect to CH_4. Even if gas collection was only 85% and the input to the cover was three times the values shown in Fig. 9B, the CH_4 flux would be well within the capacity of the soil for oxidation. With proper management and soil organic enhancement including vegetation, oxidation should be nearly quantitative and emissions should approach zero as was found on the beanie landfill "X" (Table 1). This analysis assumes even distribution of CH_4 over the landfill cover which is not completely accurate. Nonetheless, a more even distribution would be expected over time as the CH_4 production rate decreases and a final cover is in place. Examination of Fig. 9A shows that at the higher decay rate, the landfill CH_4 production will be at or below 40 g CH_4 m^{-2} d^{-1} after 25–30 year which represents 15–20 year post closure, since closure occurred in year 10. If the gas collection system was turned off at this time, CH_4 would migrate at this rate towards the bottom of the landfill cover. Based on column studies, oxidation could be above 80% effective in this range, resulting in emissions on the order of 8 g CH_4 m^{-2} d^{-1}. Based on the field studies, which were organic poor mineral soils, % oxidation at this rate
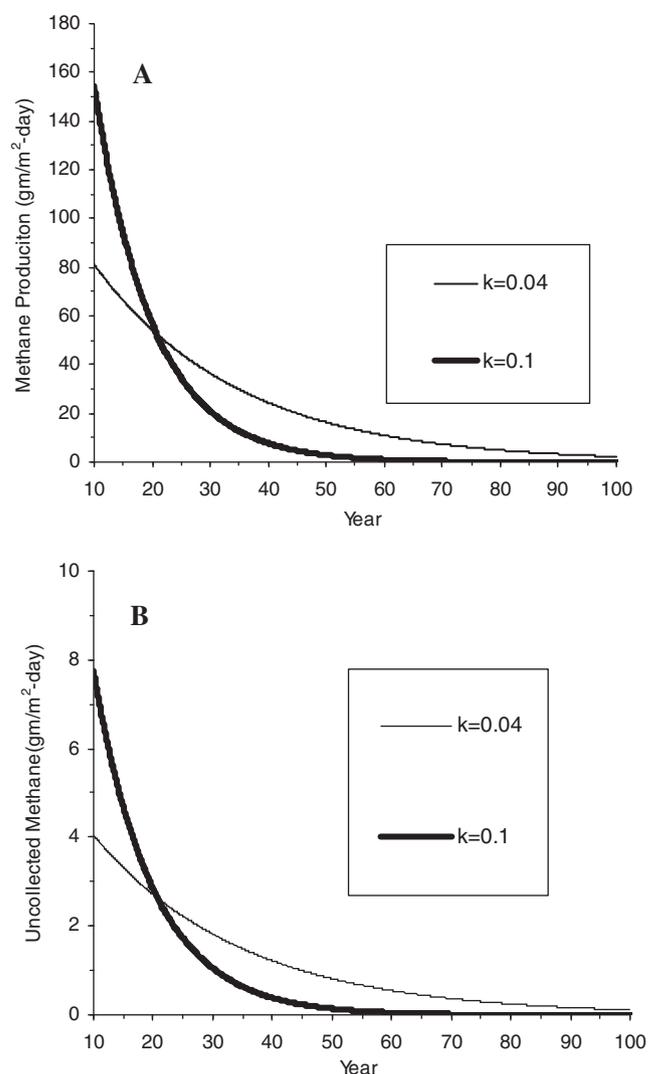

Fig. 9. Panel A, Methane Production in a hypothetical landfill that received 10^6 Mg of waste annually for ten years. Factors required to convert the production volume to a mass per area, and factors to convert production to emissions after collection are given in the text. Panel B assumes 95% gas collection efficiency to calculate the CH_4 flux to the bottom of the soil cover. Note that the x-axis starts at year 10 which is the year of closure.

varied from 21% to 43% effective, which would result in emissions ranging from 23 to 31 g CH_4 m^{-2} d^{-1}. Thus, emissions of 8 to 31 g CH_4 m^{-2} d^{-1} represent upper and lower limits to CH_4 emission rates once the gas collection system was turned off in this scenario.

5. Conclusions

The results from the field data and the modeling results indicate that percent oxidation should not be considered as a constant 10% or any other single value. Percent oxidation is a changing quantity and is a function of cover type, climatic conditions and CH_4 loading to the bottom of the cover.

Increasing methane loading to a landfill soil cover reduces the efficiency of methane oxidation. Methane oxidation rate behaves in a fashion similar to enzyme kinetics, increasing in a linear manner with increasing substrate at relatively low substrate levels and then flattening out with continued substrate addition. The methanotrophic community is CH_4 limited at low CH_4 loading rates, and then as loading increases, some other factor, either oxygen or

microbial populating becomes limiting. The data indicate that the best way to increase the % oxidation of a landfill cover is to limit the amount of CH_4 delivered to it.

As previously reported, CH_4 emissions from the landfill surface were dominated by "hotspots." Persistence of these features was observed indicating that with increased monitoring such hot spots could be identified, repaired and the cover emissions attenuated by with bio-covers and bio-cells (Abichou et al., 2006a,b).

Acknowledgements

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