

Kinetics of Methane Oxidation in a Landfill Cover Soil: Temporal Variations, a Whole-Landfill Oxidation Experiment, and Modeling of Net CH₄ Emissions

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Rates and controlling variables for methanotrophic oxidation of methane at a northeastern Illinois landfill with pumped gas recovery were examined in a field study from June to December 1995. Cover materials consisted of a simple clay-topsoil sequence without geomembranes. Through use of a static enclosure (closed chamber) technique supplemented by soil gas concentration profiles and field incubations, the study concentrated on proximal (near gas recovery well) and distal (between well) sites established in 1994. A personal computer-based three-dimensional finite-difference model was also developed which includes both gaseous mass transfer (CH₄, CO₂, O₂) and microbial CH₄ oxidation. Mass transfer is modeled through a modified chemical potential gradient within a cubic network of nodes; a strict mass balance for each gas is maintained through successive timesteps. Methane-oxidizing conditions with no net CH₄ emissions to the atmosphere persisted into full winter conditions in December, 1995. Rates of CH₄ oxidation (negative fluxes) from closed chamber experiments were similar to rates obtained from *in vitro* field incubations with initial headspace CH₄ at ambient atmospheric concentrations (1–2 ppmv). Composited data from the chamber tests and field incubations demonstrated that oxidation rates were able to rapidly increase over 4 orders of magnitude as a direct kinetic response to broad ranges of initial CH₄ concentrations (from ambient to 8.4 vol %). The maximum observed rate was 48 g m⁻² day⁻¹. Kinetic plots indicated at least two major trophic groups of methanotrophs: a CH₄-limited group (low CH₄; ambient O₂) and an O₂-limited group (high CH₄; subambient O₂). The whole-landfill CH₄ oxidation experiment was conducted over a 2 day period when the pumped gas recovery system was shut down and restarted; oxidation rates increased and then decreased more than 2 orders of magnitude in response to changing CH₄ concentrations. Although the modeling relies on theoretical considerations for both gaseous flux and development of microbial populations, the Landfill CH₄ Emissions Model requires a limited number of input variables and provides a practical tool for order-of-magnitude prediction of net CH₄ fluxes at field sites.

Background

Landfills have been implicated as the largest anthropogenic source of atmospheric CH₄ in the United States (1) and as a significant contributor to global warming in greenhouse gas scenarios. Recent landfill studies have shown that methanotrophic CH₄ oxidation in aerated cover soils can be a major natural control on net CH₄ emissions (2–7), with rates as high as 166 g m⁻² day⁻¹ (8, 9), indicating high capacities for CH₄ oxidation in landfill soils. Previous studies in nonlandfill soils suggest that high capacities may be observed in soils with historically elevated CH₄ fluxes (10–12). At landfill sites, “negative” CH₄ emissions (inward fluxes) have also been measured by several investigators using static enclosure (closed chamber) methods (4, 5, 7, 13, 14). In such cases, methanotrophs in the cover soil are oxidizing all of the CH₄ transported upward from landfill sources and additionally are oxidizing CH₄ from the atmosphere, resulting in the cover soil functioning as a sink for atmospheric CH₄, as originally documented in tundra soils (15). Numerous research issues remain, however, regarding the major controls on CH₄ oxidation at field sites, the spatial and temporal dynamics of oxidation, and the coupled processes of CH₄ transport, oxidation, and emissions.

The bulk of previous studies demonstrating high capacities for CH₄ oxidation in landfill soils have been laboratory-based; thus, studies are needed that consider the temporal dynamics of CH₄ oxidation and net emissions in field settings where anaerobic zones of CH₄ production may occur at a shallow depth. Limitations on physical transport become major controls in the field, where relative rates of CH₄ and O₂ transport to a given depth are restricted by rates of methanogenesis below and by O₂ transport from atmospheric sources above. Other factors that directly control methanotrophic microbial activity in the field include temperature, moisture, organic carbon content, available nutrients, and predation by or competition with other soil microorganisms (5, 6, 16–18). Bender and Conrad (19) demonstrated direct relationships between the CH₄-oxidizing activity determined from soil incubations and the numbers of methanotrophs. Previous laboratory studies of landfill and nonlandfill soils have found that CH₄ oxidation may reasonably fit Michaelis–Menten kinetics, where kinetics were first order at low CH₄ concentrations and zero order at higher CH₄ concentrations (6, 9, 16, 20). It has also been suggested that different trophic groups of methanotrophs may function over different dynamic ranges of CH₄ concentrations (19, 21). Methanotrophic bacteria in soil environments were recently reviewed by Mancinelli (17). In all cases, the first step is the oxidation of CH₄ to methanol by methane monooxygenase (MMO), a complex enzyme system, typically using NAD(P)H as the reductant. The generalized sequence (using several potential pathways) is from methanol to formaldehyde to formate to CO₂. Methanotrophs appear to be an important regulator of atmospheric CH₄ concentrations with rates of CH₄ oxidation dependent on the numerous physicochemical factors mentioned above. Furthermore, methanotrophs are able to encyst themselves for protection from heat and desiccation, enabling them to survive for extended periods of time in natural soils under virtually all conditions (17).

The development of realistic models to better predict net emissions in field settings becomes especially important in light of existing measurements of landfill CH₄ emissions and oxidation which may both vary by several orders of magnitude, the former from 0.0004 to 4000 g m⁻² day⁻¹ and the latter

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from 0.0002 to 166 g m⁻² day⁻¹ (Bogner et al. [22] and references cited therein). At a larger scale, national and worldwide models for landfill CH₄ emissions, as well as U.S. Environmental Protection Agency regulatory models, which rely on estimates of CH₄ generation from a given mass of solid waste as a surrogate for CH₄ emissions, have historically disregarded oxidation and may thus be overpredicting emissions. Therefore, improved models are needed at several scales that consider field measurements at sites with various types of engineering design, physical and chemical soil properties, and management strategies.

In this paper, we report on a time-series of measurements and model development that follow on from previous work at the Mallard Lake Landfill, DuPage County, Illinois (4, 13). This site has the highest level of engineered gas control: an optimized system of vertical wells recovering gas for commercial use (on-site electrical generation). Our techniques included static enclosure (closed chamber) measurements of net CH₄ flux, field incubations (ambient and elevated CH₄), and determination of soil gas profiles for CH₄, CO₂, and O₂. This paper specifically addresses (1) oxidation rates and kinetics during field monitoring and parallel field incubation studies, (2) dynamic CH₄ oxidation rates during a fortuitous whole-landfill CH₄ oxidation experiment when the entire gas recovery system was shut down for maintenance and restarted (mid-October, 1995), and (3) an evolving 3D finite-difference model for net CH₄ emissions, which is inclusive of gaseous mass transfer (CH₄, CO₂, and O₂) and microbial CH₄ oxidation. Algorithms for both processes were developed from basic mass transfer and biochemical theory and were tested with site-specific data. Although extensive literature exists on various aspects of gas movement through porous media (including modeling the porous medium for diffusional transport [23–27], development of an effective soil gas diffusion coefficient from gas-filled porosity [28–31], and modeling gas transport [11, 32–37]), a majority of the previous work in soil settings has focused on bulk diffusion rather than on the mass transfer of gases. Such models are often hampered by the need for large computer resources or are based on empirical site-specific relationships for soil gas diffusion. Moreover, the model described herein is based on an alternative geometric representation of the porous medium. The 3D space is modeled as a series of stacked cubes with possible mass transfer of gases through any side. At each cubic node, the surface of an inscribed sphere of variable size (representing soil solids) is available for partitioning of soil moisture, development of microbial populations, and gaseous collisions: the gas-filled porosity is proportionally represented as the volume difference between the cube and the sphere. To facilitate use in field settings, the primary goals for initial model development were to limit the number of required input parameters and achieve only order-of-magnitude predictive capability for net CH₄ fluxes. Further model development is planned, concurrent with field programs for model validation. Although the modeling specifically addressed landfill CH₄ emissions, the generic approach has applicability to gaseous fluxes in natural ecosystems, agricultural soils, and contaminated sites.

Methods

Previous field investigations, field and laboratory techniques, and an overview of the Mallard Lake Landfill (DuPage County, Illinois) were discussed in prior publications (4, 13, 38, 39). A transect study conducted during 1992 and 1993 examined proximal (near-well) and distal (between-well) differences, confirming that the newly installed pumped gas recovery system was a major control on net emissions. In 1994, following optimization of the gas extraction system by wellhead adjustments, two semipermanent monitoring locations were established at a proximal location immediately adjacent to well EW-37 and at a distal location approximately

midway between wells EW-37 and EW-40. These locations were chosen to examine temporal changes at sites that would maximize proximal–distal differences as determined from the previous transect study. At both sites, duplicate static closed chambers were supplemented by duplicate clusters of soil gas probes for observation of vertical soil gas concentrations. Results from limited 1994 monitoring (April and May) indicated a continuous series of negative fluxes for CH₄ at the proximal and distal locations (no net landfill emissions, plus additional oxidation of atmospheric CH₄). The negative fluxes ranged from –0.003 to –0.005 g m⁻² day⁻¹, with the higher absolute numbers associated with drier and warmer cover soils (4). Supporting data included a reversal in the soil gas CH₄ concentration gradient at the depth of optimum CH₄ oxidation (about 25 cm) and similar rates of CH₄ oxidation obtained from parallel incubation studies conducted *in vitro* at the field site. For the current study, the proximal and distal locations from the 1994 study were maintained for the purpose of obtaining temporal data spanning several seasons. Both sites are located about 40 m above grade on the south-southwest face of the south hill, where final cover placement occurred in the late 1980s. Annual average precipitation is 0.89 m. The locally derived cover materials consist of compacted silty clay (recycled Wadsworth Formation diamicton, mainly glacial till, approximately 100 cm thick) overlain by topsoil (replaced mollisol approximately 25 cm thick) with abundant surface vegetation. Soil studies conducted previously suggest a functional microbial ecology in the landfill cover (40) with organic carbon contents in the replaced topsoil exceeding 3% (wt/dry wt). Each site included duplicate soil gas probes at depths ranging from 10 to 175 cm and semipermanent iron collars for flux measurements via closed chamber techniques. Specific methods used during 1995 will be summarized below.

For measurement of fluxes by static enclosure methods, the combined volume of the chamber and the semipermanent collar was approximately 19 L. The iron collars were custom constructed with an upper trough that exactly fit the base of the chamber; they remained in the same proximal and distal locations (pushed 5–10 cm into the soil) from spring 1994 to spring 1996. During monitoring periods of 30 min, a stainless steel chamber was placed on top of each collar and secured with hand clamps; the trough was filled with distilled water to provide a gas-tight seal with the chamber. Four samples were taken at 0, 10, 20, and 30 min in parallel from duplicate chambers at each site. Fluxes were calculated from the product of the change in concentration over time (dC/dt) and the volume:area ratio of the chamber (41). Fluxes where the *r*² for the linear regression was less than 0.8 were disregarded; all reported daily fluxes are the average of two to four replicates. Fluxes were routinely measured between 8 and 10 a.m. to minimize diurnal variations.

All samples were taken by using 50 mL gas-tight glass syringes with a Teflon plunger (Hamilton). The last sample sets in December 1995 were taken by using a similar syringe with a double-flanged plunger (Hamilton) which had been custom fabricated for cold-weather sampling to mitigate problems of Teflon shrinkage (inability to tightly retain gas samples). Samples were immediately transferred to pre-evacuated stainless steel containers with a nominal internal volume of 11 mL. These containers were custom made at Argonne National Laboratory (ANL) (38, 42). Before the containers were taken out to the field, each was thermally treated, tested with standard gases, and preevacuated to less than 10⁻² Torr by using a laboratory vacuum system (Fischer). Approximately 40–45 mL of gas was injected into each container (overpressurized). Gas samples were analyzed at ANL on a customized gas chromatography (GC) system that consisted of three Hewlett-Packard (HP) 5890 Series II GCs and one Varian 3700 GC interplumbed into a single automated analytical unit. This evolving system (four GCs with six

columns and six detectors for this study) has been customized primarily for landfill gas work and allows the simultaneous analysis of major gaseous components (CH₄, CO₂, N₂, O₂, and Ar) as well as selected trace components (*n*-paraffins, aromatics, and chlorinated compounds) from a single direct injection (38). For gases of interest to this study, redundant analyses for CH₄ were obtained from a flame ionization detector (FID; Varian) and a thermal conductivity detector (TCD; HP). The former used a 6 ft × 1/8 in. Carbosieve 80/100 column, a flow rate of 44 mL/min with a He carrier, and an oven temperature of 220 °C; the latter used a 6 ft × 1/8 in. CTR-III column, a flow rate of 45 mL/min with He carrier, and an oven temperature of 90 °C. Nitrogen, oxygen, and argon were also quantified by using the CTR-III column to the TCD detector. Carbon dioxide was analyzed on a TCD (HP) by using a 10 ft × 1/8 in. Hayesep Q 80/100 column, a flow rate of 25 mL/min with a He carrier, and an oven temperature of 90 °C. The signals from the various detectors were stored via either HP-INET linked to HP-Chemstation software or through an HP-3396 integrator to PEAK-96 software. The system was fully calibrated via an external standard method in which detector response was fitted against the concentration for each component separately. The system had a repeatability of ±1% and an absolute accuracy of ±5%.

The static chamber method assumes diffusive flux only. Discussions in the soils literature tend to limit convective diurnal barometric pressure influences to the upper few centimeters (29); however, the Mallard Lake Landfill situation, with both a large source of continuously generated CH₄ and a pumped gas recovery system, suggests that convective fluxes may also be important. Nevertheless, extensive continuous measurements of differential soil gas pressures on probes and chambers by the authors at the Mallard Lake site (4, 13) (unpublished data, 1995) indicated that barometric pressure variations were minimal and the direct convective influence of the pumped gas recovery system did not extend into the cover materials. Previous landfill monitoring (43) has indicated that, at the landscape scale, elevated soil gas pressures in shallow landfill cover materials across a site develop primarily in response to surface saturation, where the net result is to drive increased lateral migration of gases under the saturated surface. Modeling work in the literature (44) has suggested that the passage of major storm events (large delta pressure) may drive larger-scale convective fluxes in landfills. Overpumping of a gas recovery system is also possible, inducing convective air intrusion, but pressure monitoring in the study areas and concentration monitoring at the wellheads documented that this did not occur during the course of this study in the wells adjacent to the study area.

Rates of CH₄ oxidation were examined via an *in vitro* field incubation technique implemented four times during the Mallard Lake study: June 1994 (prior to the start of the 1995 monitoring), September 1995 (2 sets), and November 1995. The technique was adapted from Ryden et al. (45). For each incubation, 24 cores (triplicates of eight trials), each with a volume of approximately 200 mL, were taken in a closely spaced gridded design at proximal and distal sites. Trials included ambient atmospheric air at 1–2 ppmv CH₄, plus trials with added gas standards to yield initial headspace concentrations over several orders of magnitude, up to 8.4 vol % CH₄. To maintain static pressure conditions, equivalent headspace volumes were removed using a syringe before injection of gas standards at the start of 2 h incubations. Rates of CH₄ oxidation were quantified by loss of headspace CH₄.

A whole-landfill CH₄ oxidation experiment was conducted on October 17 and 18, 1995, when the pumped gas recovery system was temporarily shut down. This shutdown permitted direct observation of changing CH₄ oxidation rates relative to CH₄ concentrations at the proximal and distal subsites.

Measured chamber fluxes were completed in duplicate five times during the 2 day period; soil gas profiles were completed in duplicate three times.

A 3D finite-difference model was developed for net CH₄ emissions from landfill surfaces. The current Landfill Methane Emissions Model (LMEM) simulates the movement of gases through the cover soils via a 3D mass transfer algorithm. The gas flux is modeled using a modified chemical potential gradient (the sum of kinetic and potential energies) (see Appendix).

Results and Discussion

Negative CH₄ Fluxes and Soil Gas CH₄ Profiles. The measured fluxes for CH₄, from static closed chamber measurements for both the proximal and distal locations were consistently negative, even into full winter conditions of soil freezing in December 1995. This was attributed to high capacities for CH₄ oxidation in soils which now had significantly reduced CH₄ concentrations in comparison with previous years, largely because of optimization of the pumped gas recovery system (4, 13). The mean negative (–) flux for the proximal location was $6.81 \times 10^{-3} \text{ g m}^{-2} \text{ day}^{-1}$ (range, 4.07×10^{-4} – 4.33×10^{-2} ; SD, 1.15×10^{-2} ; *n* = 22 daily measurements). The mean negative (–) flux for the distal location was $1.05 \times 10^{-2} \text{ g m}^{-2} \text{ day}^{-1}$ (range, 6.67×10^{-4} – 9.19×10^{-2} ; SD, 2.00×10^{-2} ; *n* = 25 daily measurements). The minimum absolute values were attained in December 1995, when air temperatures in the chamber reached a minimum of –25 °C. The wide ranges and high standard deviations of the negative CH₄ fluxes at both locations reflect the inclusion of data from the October 17 and 18, 1995, shutdown; then, the negative fluxes reached their maximum absolute values. If the shutdown data are excluded, the proximal negative (–) CH₄ flux averages $2.89 \times 10^{-3} \text{ g m}^{-2} \text{ day}^{-1}$ (SD, 1.09×10^{-3}) while the distal negative (–) flux averages $3.85 \times 10^{-3} \text{ g m}^{-2} \text{ day}^{-1}$ (SD, 2.27×10^{-3}).

For comparison to the proximal and distal fluxes, both a nonlandfill control and a “worst case” landfill flux were also completed. The nonlandfill control fluxes on November 1, 1995, used identical methods on a grassy lawn area at the Argonne National Laboratory site. These measurements were completed at a time of surface soil saturation following approximately 5 cm of rain over the past 48 h. Because methanogenesis can occur following saturation of normally aerated surface soils (29), a positive CH₄ flux might also be expected and, indeed, was measurable but low, averaging $5.61 \times 10^{-3} \text{ g m}^{-2} \text{ day}^{-1}$. In terms of actual numbers, this CH₄ flux is similar to the lowest positive values in landfill or wetland settings of 10^{-3} – $10^{-4} \text{ g m}^{-2} \text{ day}^{-1}$ (22, 46). Such values appear to approach the dynamic minimum values for CH₄ emissions in terrestrial settings where CH₄ production and oxidation coexist (e.g., a dynamic equilibrium at the microbial level, where low CH₄ production and transport rates are easily matched by similar rates of CH₄ uptake). As a second control, a limited series of fluxes (*n* = 9 daily measurements) were also completed at a settlement depression located between the proximal and distal areas. This area was undergoing active subsidence, with assumed higher local rates of CH₄ generation and possibly positive CH₄ fluxes to the atmosphere; however, except for two occasions, all of the CH₄ fluxes were negative, averaging $-8.53 \times 10^{-4} \text{ g m}^{-2} \text{ day}^{-1}$ with a high standard deviation (2.90×10^{-4}). The two exceptions were both times of high soil moisture contents (26–30%, expressed as wt/dry wt). The maximum positive flux was $1.84 \times 10^{-2} \text{ g m}^{-2} \text{ day}^{-1}$. At that time, limitations of O₂ mass transfer into surface soils limited CH₄ oxidation rates.

Temperature, moisture, and (initial) CH₄ concentration were investigated as controlling variables for the negative fluxes. The period of July and August 1995 was characterized by high soil temperatures and variable soil moisture content [temperatures of 24–30 °C with moisture contents ranging

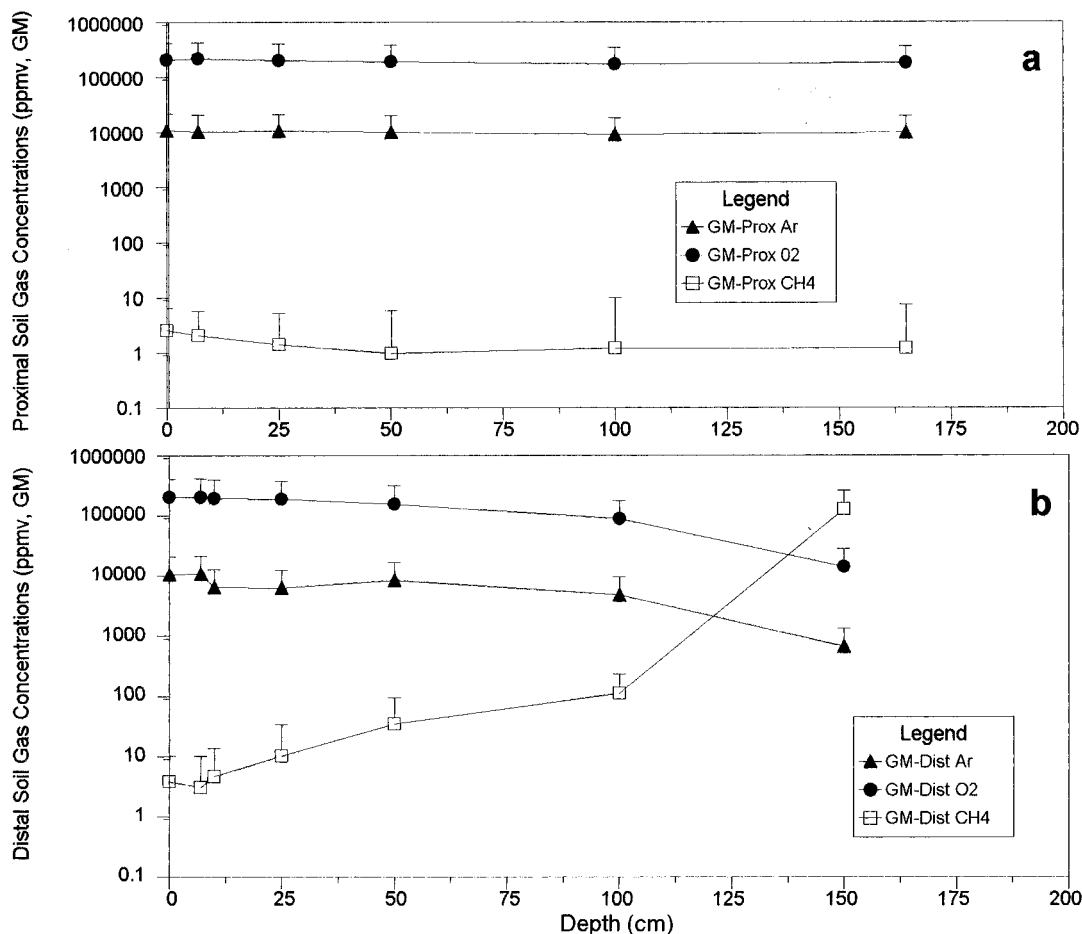


FIGURE 1. Geometric mean soil gas profiles for selected gases (CH_4 , O_2 , and Ar) for proximal and distal locations during July–December 1995. Probe data are composited for duplicate probe clusters at each location. Error bars indicate 1 geometric SD.

from 10 to 25% (wt/dry wt)] while the period of September–November 1995 was characterized by steadily decreasing temperatures and increasing moisture until the time of ground freezing in November 1995 (temperatures of 5–15 °C and moisture contents of 15–35%). However, simple Pearson correlation coefficients for the fluxes, soil moisture, soil temperature, and initial CH_4 concentrations (in chambers) indicated that the negative CH_4 fluxes were most strongly correlated to initial CH_4 concentrations (Pearson $r = 0.99$). Also, the important influence of CH_4 concentration can be seen in a multiple linear regression expression ($r^2 = 0.98$) that was developed using these same three variables and an ordinary least squares (OLS) procedure: [negative] CH_4 flux = 0.001 45 (initial CH_4 concentration) – 0.000 191 (soil moisture, %) + 0.000 009 99 (soil temperature, °C) + 0.0037.

Composite soil gas profiles can be developed by plotting the geometric mean of probe data (4, 13). The resulting gradients can infer the direction of net diffusive flux following production and consumption processes, but profiles reflecting production and consumption processes cannot be used to directly calculate diffusive fluxes by using Fick's law. Profiles for several gases compared with each other are also helpful to suggest the vertical zonation of various processes for subsequent modeling. Figure 1 shows the geometric mean profiles for CH_4 , O_2 , and Ar with error bars representing 1 geometric standard deviation. Proximal CH_4 was uniformly low with values of 1–2 ppmv to depths of greater than 100 cm; distal CH_4 was low only in the surface CH_4 oxidation zone, increasing about 2 orders of magnitude to more than 100 ppmv at a depth of 100 cm. The general shapes of the CH_4 curves were identical to those from the preliminary spring 1994 study (4); however, at that time, the distal mean value at 100 cm was approximately 1000 ppmv, compared with 100

ppmv in the present study. In addition to the negative CH_4 flux being highly correlated to initial (atmospheric) CH_4 concentration (previous regression equation), it was also correlated to shallow (25 cm) soil gas CH_4 . This correlation was best for ΔCH_4 flux (change from previous temporal observation) compared with the delta CH_4 concentration at 25 cm ($r^2 = 0.77$ proximal and 0.93 distal). For the proximal area, a decline in CH_4 downward to 50 cm can be seen; for the distal area, a slight decline to only 7 cm occurs. These curves indicate the approximate depth of optimum CH_4 oxidation at their respective inflection points. Concentrations below 2 ppmv were characteristic of the proximal profile to a depth of greater than 50 cm; this was identical to the geometric mean profile for the previous 1994 data. These figures also show spatial changes in shallow soil gas Ar. Soil gas Ar concentrations in the shallow profiles were typically close to their mean atmospheric value (about 1 vol %), indicating extremely well-aerated soils. We have generally found that argon as an inert gas is superior to both O_2 and N_2 as an indicator of aeration status.

Temporal Trends and Whole-Landfill Oxidation Experiment. Temporal trends for the negative CH_4 fluxes indicated the rapid response of methanotrophic CH_4 oxidation to altered operation of the engineered gas recovery system. In general, higher absolute values for the negative fluxes were associated with higher ambient atmospheric CH_4 levels during infrequent shutdowns. This association was seen most clearly during the longest shutdown in October 1995 when the system was shut down from about 2 a.m. on October 17 to about 9 a.m. on October 18. This shutdown provided a whole-landfill oxidation experiment when more intensive monitoring of fluxes was conducted (five monitoring events over a 28 h period). Figure 2 compares the negative fluxes (static chamber

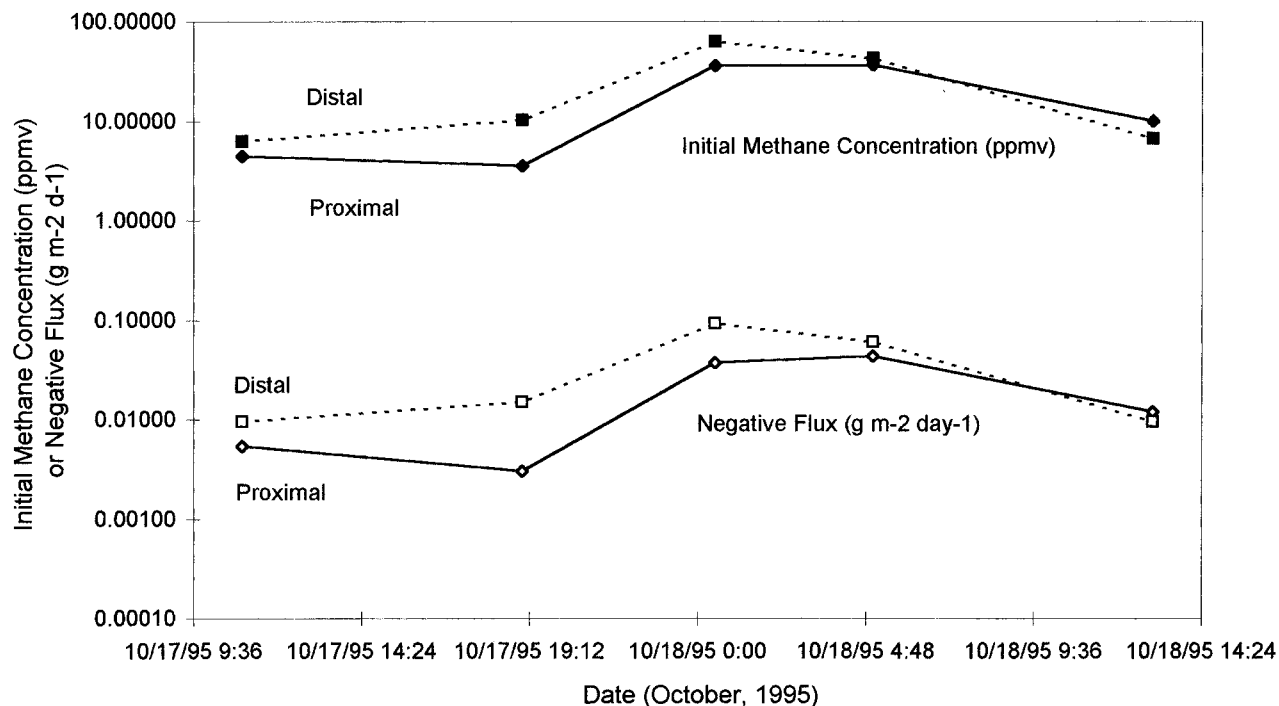


FIGURE 2. Relationships between CH_4 oxidation rates (as measured by negative chamber fluxes) and initial CH_4 concentrations during whole-landfill experiment. Dates are averages of replicates for proximal and distal locations.

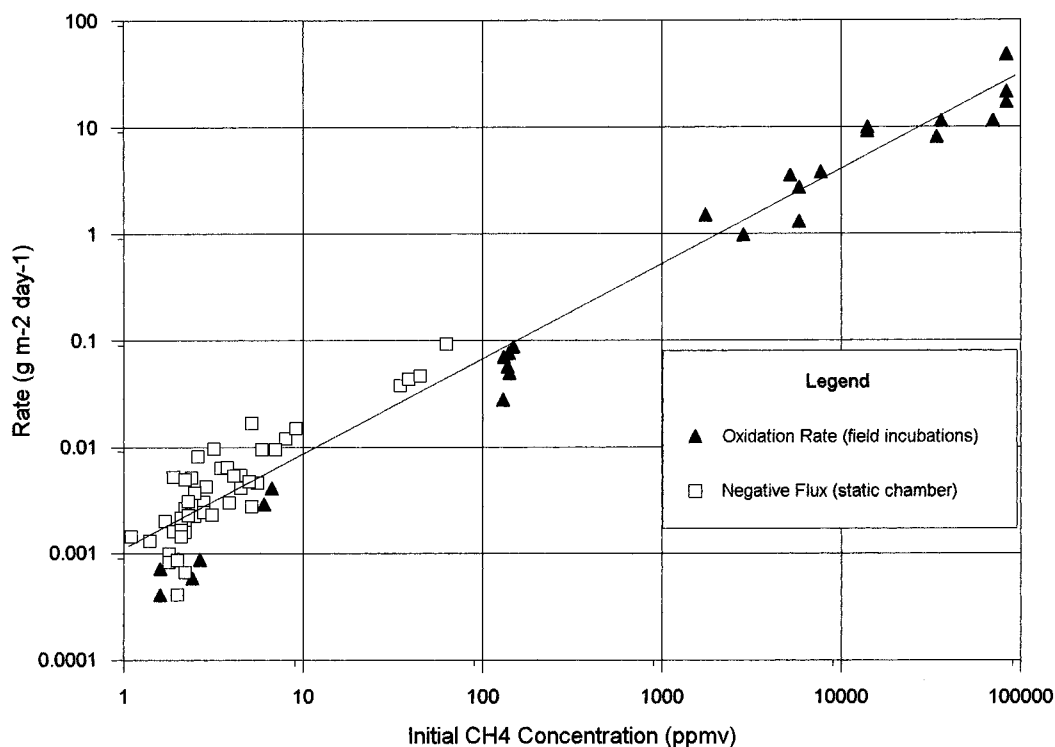


FIGURE 3. Relationship between initial CH_4 concentration and CH_4 oxidation rate; composite plot for static closed chamber measurements (negative fluxes) and field incubations. Fitted line on log-log plot corresponds to $y = 0.001x^{0.0921}$ ($r^2 = 0.9644$).

measurements) to initial CH_4 concentrations in the chambers during this 2 day period. This figure shows the rapid response of CH_4 oxidation to ambient CH_4 concentrations during both an increase and a decrease in available CH_4 , which indicates (1) the high capacity for oxidation in cover soils and (2) the rapid response of CH_4 -oxidizing populations to changing CH_4 concentrations. The relationship between initial CH_4 concentration and the negative fluxes over this period was linear over 2 orders of magnitude ($r^2 = 0.98$). The systematic differences between the proximal and distal data in Figure 2 can be attributed to their relative locations. The distal area

was located directly across the road and upslope from the flare station, which was passively venting large quantities of CH_4 to the atmosphere during the shutdown. As shown in the figure, initial CH_4 concentrations in distal chamber air attained values greater than 60 ppmv during this period. The negative fluxes were maintained throughout this period, even though soil gas CH_4 concentrations were also elevated. The maximum soil gas CH_4 concentrations were observed at the distal location at the 25 cm depth at midday on October 18, 1995, just after the recovery system had been turned on again. At this time, a strong increasing CH_4 gradient from the surface

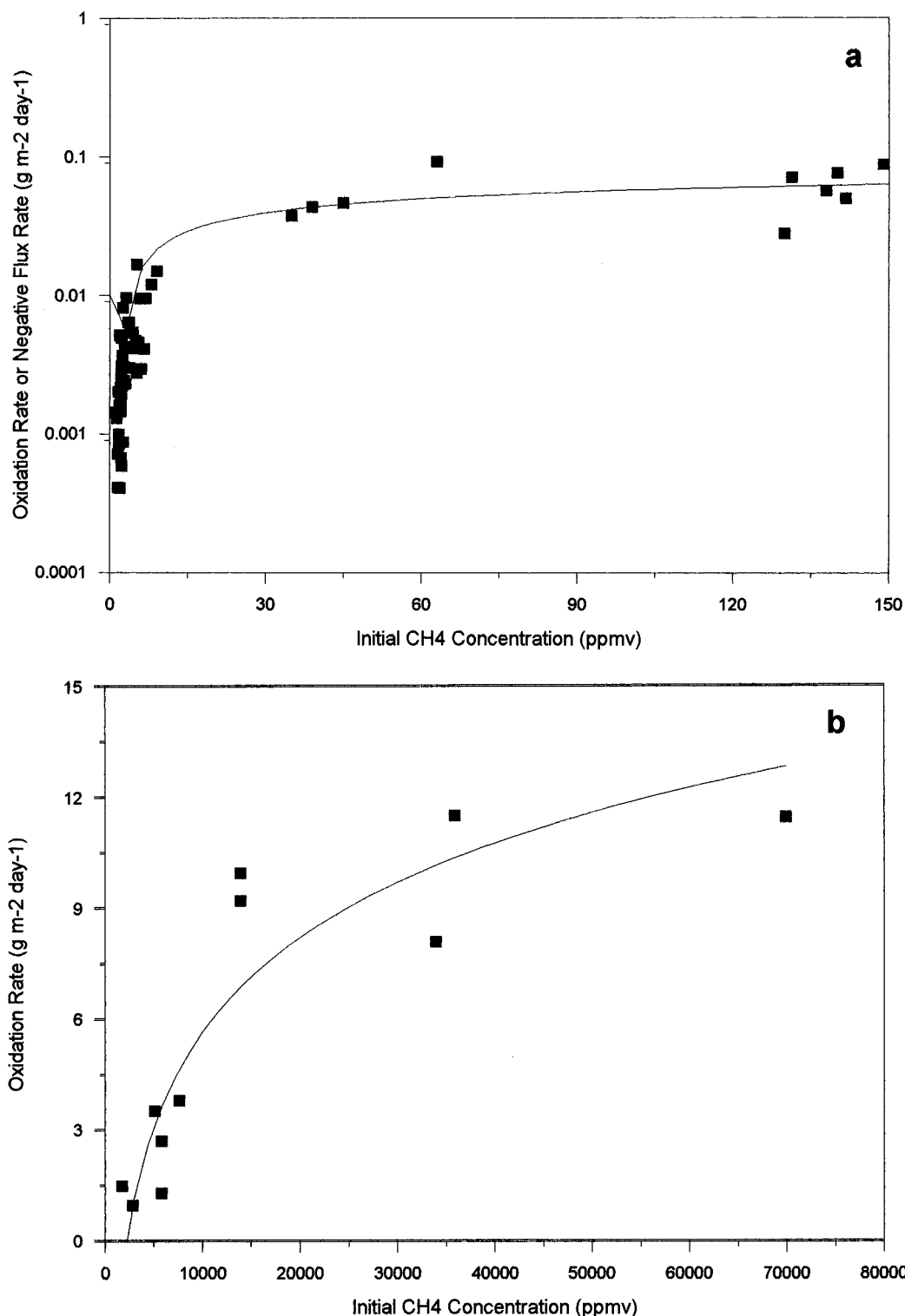


FIGURE 4. Kinetic plots for initial CH₄ concentration vs CH₄ oxidation rate. Units for CH₄ oxidation are standardized on an area basis (g m⁻² day⁻¹) to facilitate comparison of incubation results with static chamber measurements. An approximate conversion to mass-based units can be made using the following empirical equation developed from the site-specific incubation data: [rate in g m⁻² day⁻¹] = 0.0137 [rate in nmol h⁻¹ (g of dry soil)⁻¹] + 0.427 ($r^2 = 0.97$). (a) Low CH₄ values only (composite of chamber fluxes and field incubations). Fitted curve corresponds to $y = 0.0148 \ln(x) - 0.011$ ($r^2 = 0.82$). (b) High CH₄ values only (field incubations). Fitted curve corresponds to $y = 3.684 \ln(x) - 28.31$ ($r^2 = 0.72$).

downward to a depth of 25 cm in the distal area (CH₄ in soil gas was 1.4 ppmv at 7 cm and 4.4 vol % at 25 cm) and a strong decreasing gradient occurred below 25 cm (CH₄ in soil gas was 3.3 ppmv at 100 cm). In the proximal area at the same time, soil gas CH₄ concentrations were generally lower, with the highest observed soil gas CH₄ at the 50 cm depth (12.1 ppmv), decreasing to the 100 cm depth (1.7 ppmv). Methane concentrations in the ambient air at the same time had

decreased to 5–9 ppmv (both locations). These data demonstrate the potentially rapid dynamics of CH₄ oxidation in soil settings where order-of-magnitude rate changes are possible over extremely short time frames. Moreover, such data also emphasize the importance of natural controls (CH₄ oxidation) functioning in tandem with engineering controls.

CH₄ Oxidation Kinetics. A composite plot of initial CH₄ concentration vs CH₄ oxidation rate (in g m⁻² day⁻¹) is given

in Figure 3. Data from the four field incubations were composited with the 1995 negative CH₄ fluxes (measured by chamber techniques). Methane consumption relative to soil mass, soil volume, soil surface area, moisture, and temperature was also determined for each set. The data shown are inclusive of all temperature and moisture conditions. For low initial CH₄ concentrations (<10 ppmv), the larger concentration of data points represents the clustering of incubation results with the 1995 negative fluxes from static chambers. The cores were taken from a shallow depth of 5–15 cm and were thus comparable to “surface” oxidation. The highest observed rate of CH₄ oxidation was 48.0 g m⁻² day⁻¹, corresponding to an initial CH₄ concentration of 8.4 vol %.

Dissecting the wide range of observed oxidation rates shown in Figure 3, separate kinetic trends emerge for low and high values of initial CH₄ concentration. Figure 4a shows initial CH₄ concentration and oxidation rates for only the lower values of initial concentration (less than 160 ppmv). In this figure, the shape of the curve approaches an expected shape for enzymatic kinetics with initially increasing oxidation rates paralleling increasing concentrations followed by a higher rate that no longer shows a concentration dependence (zero order). Figure 4b shows a similar plot for only the high concentration range (1 vol % < CH₄ < 8 vol %). Values for the highest initial CH₄ concentrations (8.4 vol %) were omitted from this plot; we suspected that diffusional limitations in the incubation jars led to widely divergent values for CH₄ oxidation rates (from 16 to 48 g m⁻² day⁻¹).

The previous figures show that considerations of scale become very important for understanding processes where observed rates vary over several orders of magnitude; furthermore, it may be necessary to dissect data to examine embedded relationships that may be obscured in broader views. The data here suggest that as a minimum two major groups of methanotrophs coexist in landfill cover soils. The first group favors low CH₄/high O₂ settings (CH₄ less than about 160 ppmv; O₂ near ambient atmospheric concentrations), with oxidation rate limited by available CH₄. The second group favors higher CH₄/lower O₂ (CH₄ about 1–7%; O₂ about 15–18%). The second group is probably limited by O₂ in the presence of abundant CH₄. The activity of each group individually (as measured by CH₄ oxidation rates) appears to approximate expected enzymatic kinetics. Considering current results and previous literature, some implications for landfill soils are proposed below:

(1) The first group is continuously active in shallow landfill soils, which thus have a capacity for continuous CH₄ oxidation that rapidly responds to a wide range of dynamic CH₄ concentrations. The only exception would be times of periodic surface saturation. Previous literature (17) indicates that methanotrophs are microaerophilic, e.g., flourishing at subambient levels of O₂. The second group best fulfills this requirement. Other methanotrophic groups may also coexist (suggested by finer dissection of the low CH₄ data), and CH₄ oxidation may be partially accomplished by N cycle bacteria. Both the MMO and the ammonia monooxygenase are relatively nonselective, permitting oxidation of ammonia by methanotrophs and oxidation of CH₄ by nitrifiers (17, 18).

(2) As shown by previous literature (5, 6, 16–18), rates of CH₄ oxidation are also dependent on temperature, moisture, and other variables. Nevertheless, in a well-aerated landfill soil over short time frames where a wide dynamic range of CH₄ oxidation rates is possible, the primary controlling variable appears to be CH₄ concentration and, secondarily, aeration status (O₂ availability). This is supported by both the incubation data, which demonstrated CH₄ oxidation rates over 4 orders of magnitude in direct and rapid response to initial CH₄ concentrations, and the negative flux data, which showed primary dependencies on initial CH₄ concentration

TABLE 1. Comparison of Kinetic Coefficients

K _M (ppmv)	V _{max} (nmol h ⁻¹ g ⁻¹ of dry soil)	reference	notes
45.0	5.6	this study ^a	composite of low CH ₄ incubations plus fluxes
25 380	743	this study ^a	high CH ₄ incubations
19.9	6.8	16	grassland soil
17.2	7.4	16	forest soil
32, 43	0.61, 0.76	19	cultivated soil
28, 46	0.74, 1.05	19	meadow soil
22	3.6	19	forest soil
1800	136	9	landfill cover
40–2594	195–5847	50	landfill cover

^a Data were fitted to a generalized form of the Michaelis–Menten equation [Briggs–Haldane] (49): $V_0 = (V_{max}[S]) / ([S] + K_M)$, where V_0 = initial velocity (m t⁻¹ per unit m of soil), [S] = substrate concentration (m L⁻³), V_{max} = rate at substrate saturation (m t⁻¹ per unit m of soil), K_M = the Michaelis constant, or substrate concentration at $V_{max}/2$ (m L⁻³ or mixing ratio for gases).

TABLE 2. Comparison of LMEM Results to Field Data (grams per squared meter per day)^a

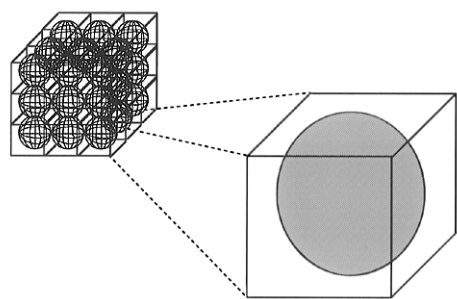
landfill site	measured field rate (mean) static chamber method	calculated rate (LMEM)
Brea–Olinda (1988) southern California no gas recovery sandy silt cover	1119	605
Brea–Olinda (1994) with gas recovery	4.03	2.54
Mallard Lake (1994) proximal	–0.001	–0.008
distal	–0.002	–0.004
Mallard Lake (1995) proximal	–0.007 ^b	–0.003
distal	–0.010 ^b	–0.0001

^a Data from this study and refs 4, 13, 22, and 51. ^b Proximal value is equal to –0.003 and distal value is equal to –0.004 if October 17 and 18, 1995, shutdown data are excluded.

rather than on temperature and moisture. It should be noted, however, that although temperature varied widely between midsummer and winter conditions, soil moisture varied only between about 15 and 25% under field conditions during this study. For the chamber fluxes alone, an empirical logarithmic relationship between gravimetric soil moisture (x , in percent) and negative flux (y , in grams per squared meter days) was developed as follows: $y = 0.2158e^{-0.771x}$ ($r^2 = 0.81$). Temporal changes in moisture status would also drastically affect aeration status (O₂ availability) for CH₄ oxidation.

(3) Previous stable carbon isotopic measurements for deep landfill CH₄ below the cover materials (47, 48) suggest that CH₄ oxidation is also important, at least periodically, in deeper landfill settings. A plot of the $\delta^{13}C$ for landfill CH₄ vs $\delta^{13}C$ for CO₂ using composited data from many landfill sites suggests a CH₄ oxidation trend (48). Here, we postulate that the previously described group (high CH₄/low O₂), or a third group able to function very close to a lower limiting value for O₂, may also be active at CH₄ concentrations greater than 10 vol %.

Table 1 compares calculated kinetic coefficients for the low and high initial CH₄ values in this study to selected values from the literature. As in the above figures, flux data and incubation data with initial CH₄ < 60 ppmv were composited separately from the data with higher initial CH₄. For the high values, a double reciprocal plot (Lineweaver–Burk) of 1/substrate concentration vs 1/oxidation rate was used to linearize the Briggs–Haldane equation; this plot is character-



Potential Fates of Methane Through Node of Model

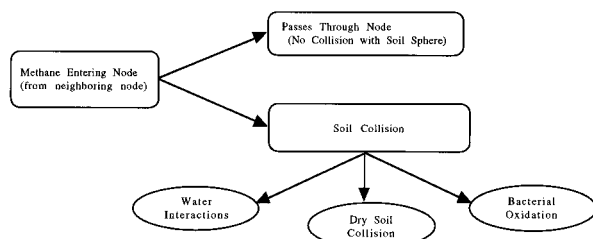


FIGURE 5. Representation of the porous medium for the LMEM model, including possible pathways for CH₄ transport through a given node.

ized by a y -intercept of $1/V_{\max}$ and a slope of K_m/V_{\max} (49). For the low values, where the oxidation rate ranged over more than 2 orders of magnitude, the K_m was obtained by setting the first derivative of the hyperbolic fit ($r^2 = 0.86$) to zero and solving for V_{\max} .

Table 1 shows a broad range of values for the various soils examined. The V_{\max} value for low rates in this study was similar to the values for V_{\max} in the laboratory study of Czepiel et al. (16); however, the K_m in this study for the low initial CH₄ tests was more than double, indicating significantly lower values of substrate saturation. The landfill cover values reported by Whalen et al. (9) fell in the middle of data for this study with respect to both V_{\max} and K_m , but a plot of their rates for CH₄ oxidation vs CH₄ concentration will overlap the data trend shown in Figure 3. The low and high kinetic coefficients (K_m and V_{\max}) from this study and the wide ranges from studies by others also suggest multiple trophic groups that may individually approximate enzymatic kinetics within given ranges of initial substrate concentration.

Landfill Methane Emissions Model (LMEM). Field measurements from the Mallard Lake site (DuPage County, IL) and the Brea–Olinda site (Orange County, CA) were used in model verification, with the initial goal of order-of-magnitude predictive capability for net CH₄ fluxes to the atmosphere. Brea–Olinda was the site of a previous Argonne study where identical field methods were used for static closed chamber measurements and soil gas concentration profiles (4, 51).

Table 2 summarizes the average CH₄ emissions from these sites as determined from static closed chamber measurements (ref 4 and this study), along with the corresponding LMEM results. Model inputs were limited to the generalized site geometry for portions of each site (length, width, depth, and soil cover thickness), mean values for soil moisture and gas-filled porosity, and the soil gas profiles (geometric mean) through the cover material (see ref 22, Figure 2). Atmospheric gas concentrations were assumed at the landfill surface, and landfill gas below the cover soil was assumed to consist of equimolar portions of CH₄ and CO₂. As can be seen from the table, the LMEM results were generally within the same order-of-magnitude as the measured emissions. In addition, the LMEM was able to model negative CH₄ fluxes, or net oxidation of atmospheric CH₄. Because rates for both gaseous transport and CH₄ oxidation may vary by several orders of magnitude, order-of-magnitude predictive capability from limited field data may be sufficient for many sites as input to engineering considerations related to site closure activities and regulatory

compliance. The LMEM also facilitates hypothetical modeling of alternative cover designs under various moisture content scenarios (see Appendix). Given the data to date, current U.S. regulatory models (52), which estimate CH₄ emissions strictly from theoretical models of CH₄ generation without consideration of field measurements of CH₄ emissions or CH₄ oxidation, should be reconsidered and replaced. The high observed rates of CH₄ oxidation also argue against geomembrane covers for control of gaseous emissions, because methanotrophic CH₄ oxidation is dependent on diffusion of atmospheric O₂ to the site of microbial activity. Additional focused monitoring and modeling at individual sites are needed for both improved understanding of emissions and the development of innovative cover designs that consider both natural and engineered control strategies.

Acknowledgments

We gratefully acknowledge the financial support of the U.S. Department of Energy through the National Renewable Energy Laboratory with supplemental support provided by Browning–Ferris Gas Services, Inc. (Houston, TX). Site assistance from Mallard Lake personnel and the Forest Preserve District of DuPage County, the owner of the Mallard Lake site, is most appreciated. Argonne National Laboratory is operated by the University of Chicago for the U.S. Department of Energy under Contract W-31-109-Eng-38.

Appendix A: Landfill Methane Emissions Model (LMEM)

A (3D) finite-difference model was developed to simulate both the mass movement of methane through landfill cover materials and net emissions of CH₄ to the atmosphere. Programmed in C++, the model is PC-based with graphical user interfaces; minimum requirements for the current version are a Windows-compatible 386 or higher PC with a math coprocessor. This model relies on the use of a modified chemical potential gradient with numerous mass balance checks for individual gases (CH₄, CO₂, and O₂) and, as discussed below, is inclusive of numerous CH₄ transport, retention, or reaction (CH₄ oxidation) pathways at a given node during a given time step (39). Although gas movement through soil is controlled by the combination of convective and diffusive processes, gaseous diffusion is regarded as the primary mechanism of gaseous transport through the unsaturated zone (53, 54). Small-scale convective influences due to transport inhomogeneities may also become important because of localized pressure gradients at a given node. The LMEM simulates gas movement through a mass gradient approach based on the sum of the kinetic and potential energy of the gas fluid. This approach conveniently accounts for mass movement due to both concentration gradients (diffusion) and pressure gradients, because the latter can be considered mass gradients (e.g., more gas molecules per unit volume at higher pressures). This strategy also facilitates future expansion to more rigorous inclusion of temperature gradients (increased kinetic energy) and more complex gas mixtures.

For model development, the first task was the geometric representation of the porous medium for diffusional transport of CH₄ in three dimensions (Figure 5). The landfill is modeled as a 3D arrangement of cubic nodes based on the length, width, and cover thickness of the landfill (or portion of a landfill) under consideration. A simple rectangular prism geometry is assumed because it is more expedient running a PC-based model several times for differing portions of a given site than developing site-specific models with complex geometries and several sets of initial conditions. The landfill cover is modeled as a set of 3D nodes with a constant 1 cm dimension and 1 cm³ volume. Required inputs from the user consist of

(a) Length, width, and cover thickness of the region being modeled

(b) Total porosity and volumetric soil moisture of each layer within the cover (three layers possible)

(c) Gas concentration profiles through the cover for CH₄, CO₂, and O₂ (default profiles also available)

The program scales the framework of nodes to the length, width, and cover thickness entered by the user; thus, a landfill cover with dimensions of 50 m × 100 m × 3 m thick would result in a modeled porous medium of 5000 × 10000 × 300 nodes.

The soil matrix is modeled in each cubic node by assuming that all of the soil solids are present in a solid sphere in the node, thereby leaving the remaining open pore space in a given node to represent the total gas-filled porosity of that node. The advantage of a single sphere model is that the partitioning of soil moisture and bacterial growth related to CH₄ oxidation on the solid sphere can be accomplished much more readily than with a multisphere or alternative pore structure model. Furthermore, with this framework, all gaseous transport occurs through free air in each node rather than requiring modification of the diffusion coefficients for a soil matrix; this provides a more reliable mathematical formulation for the final net CH₄ emissions from the surface.

The mass transfer of CH₄ is modeled in 3D by first calculating the mass transfer coefficients across each of the six surfaces of the node of interest in succession:

$$MT_x = (\mu_{x,y,z} - \mu_{x-1,y,z}) + (\mu_{x+1,y,z} - \mu_{x,y,z}) \quad (A1)$$

$$MT_y = (\mu_{x,y,z} - \mu_{x,y-1,z}) + (\mu_{x,y+1,z} - \mu_{x,y,z})$$

$$MT_z = (\mu_{x,y,z} - \mu_{x,y,z-1}) + (\mu_{x,y,z+1} - \mu_{x,y,z})$$

where MT is the Mass Transport Coefficient for x, y, or z; $\mu_{x,y,z}$ is the modified chemical potential for node x, y, z, and the modified chemical potential is given by

$$\mu = KE + PE \quad (A2)$$

$$KE = \frac{m(\overline{w}\alpha)^2}{2} \quad (A3)$$

$$PE = mg\Phi \quad (A4)$$

where KE is the kinetic energy; PE is the potential energy; $\overline{w} = (8kT/\pi m)^{1/2}$; α is the ratio of mean free path to nodal dimension (1 cm³), corrected for porosity, or $\{[(2)^{1/2}\pi d^2 n]/\rho\phi\}^{-1}$; Φ is the node number; m is the mass of gas molecule; d is the diameter of gas molecule; n is the total number of molecules present in node; g is the gravitational constant; T is the absolute temperature; and \overline{w} is the average velocity. The net flux of gas at a given node for a given time step is

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial \mu}{\partial x} + \frac{\partial \mu}{\partial y} + \frac{\partial \mu}{\partial z} \right] = D |MT|_t \quad (A5)$$

The mass transport coefficients represent the normalized driving force possible for gas movement into or out of each cubic face. This driving force is the result of one or more of the following processes: diffusion, convection, microbial consumption or production, and the aqueous solubility of individual gases into soil moisture. At each time step, the mass transfer coefficients are normalized to give the relative driving force of CH₄ for the 3D matrix and to provide a 3D probability distribution for CH₄ movement. Then the probability of collisional interactions is calculated, based on the gas-filled porosity that controls the size of the sphere in each node. A collisional parameter (CL) is developed, based on the ratio of the sphere's surface area in two dimensions (circle) to a nodal surface area of 1 cm²:

$$CL_i = (\pi r^2)/(1 \text{ cm}^2) = \pi \{ [3\pi(1 - \phi)]/4 \}^{3/2} \quad (A6)$$

All gases are modeled through the free air space in each node with a sequence of calculations to partition the transported CH₄ from the collisional CH₄. The transported CH₄ is the mass of CH₄ that completely passes through the node because of the mass transport gradient given above and which does not collide with the sphere (soil) within the node. The collisional CH₄ is defined as that CH₄ which collides with the surface of the sphere (soil). An additional algorithm simulates the collisions of CH₄ molecules with the soil sphere to partition the collisional CH₄ into three groups (Figure 5):

(1) CH₄ that collided with dry soil

(2) CH₄ that collided with moisture on the surface of the sphere

(3) CH₄ that collided with a bacterial colony on the sphere.

The dry soil collisional CH₄ remains in the gas-filled porosity (air space) of a given node. For collisions with water, the assumption is made that surface moisture can only absorb the maximum amount of CH₄ and other gases allowed by Henry's law partitioning coefficients. This calculation may result in a loss of CH₄ from the node.

The oxidation of CH₄ is modeled via the growth of bacteria on the surface of the soil sphere. The user selects a growth rate speed that is linear (slow), quadratic (medium), or exponential (fast) for methanotrophic bacterial colonies, according to the following generalized equations:

linear

$$[BC]_T = \zeta [BC]_{T-1} + [BC]_{T-1} \quad (A7)$$

quadratic

$$[BC]_T = [BC]_{T-1}^{\zeta} + [BC]_{T-1} \quad (A8)$$

exponential

$$[BC]_T = [BC]_{T-1} e^{4\zeta} \quad (A9)$$

where ζ is the [free surface area on sphere/total surface area on sphere][mass fraction O₂].

A specific microbial growth equation is user-selected for a given model run. The three options above were developed to allow the user to examine a range of growth rates as determined from available literature where various microbial growth kinetic relationships exist (55–57). The exponential or fast growth rate may be most suitable for older landfill sites, which have a high capacity for CH₄ oxidation, whereas a new site might be more appropriately simulated by using a linear relationship. The soil moisture is also partitioned on the surface of the sphere in each node. After each time step, a check is made to determine if all available sites are used; if not, a growth phase is started which follows the growth relationship selected by the user. This growth step controls the locations on the sphere that are to be filled with new bacterial colonies during each time step. These locations are used as input to the soil collisional routine to divide the CH₄ into three groups (discussed above). A mass balance check is performed to confirm that there is sufficient O₂ present in the node for the oxidation to occur. If so, then the model calculates the mass of CH₄ that could be oxidized by the mass of O₂ present in the node. In a given node, "lost" CH₄ is the sum of the CH₄ oxidized, the CH₄ dissolved in moisture collisions, or the CH₄ which passes through the node entirely. Figures 6 and 7 illustrate model sensitivity to selected values of soil moisture and porosity during standard runs for the following landfill cover configuration. Top layer (top-soil): total porosity 0.40; gravimetric soil moisture varying between 0 and 20% (wt H₂O/dry wt soil); thickness 20 cm.

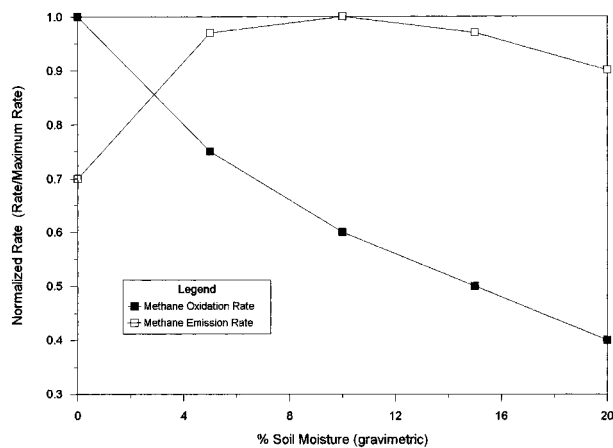


FIGURE 6. Sensitivity of simulated CH₄ emissions and oxidation to gravimetric soil moisture using LMEM. Plot of gravimetric soil moisture (wt H₂O/dry wt soil) to normalized rate (ratio of rate to maximum rate).

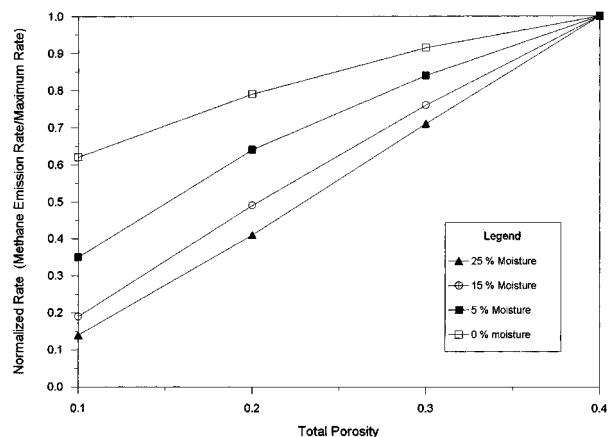


FIGURE 7. Sensitivity of simulated CH₄ emissions to both gravimetric soil moisture and total porosity. Plot of gravimetric soil moisture and total porosity to normalized CH₄ emission rate (ratio of rate to maximum rate).

Middle layer: total porosity 0.30; gravimetric soil moisture 15%; thickness 40 cm. Bottom layer: total porosity 0.33; gravimetric soil moisture 10%; thickness 40 cm. Concentration profile: 2 cm depth = 2 ppmv CH₄; 350 ppmv CO₂; 19.5 vol % O₂. 40 cm depth = 10 vol % CH₄; 10 vol % CO₂; 5 vol % O₂. 100 cm depth (base of cover) = 50 vol % CH₄; 50 vol % CO₂.

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Received for review October 23, 1996. Revised manuscript received April 21, 1997. Accepted April 23, 1997.[⊗]

ES960909A

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1997.