

Methane Oxidation in Landfill Cover Soils, is a 10% Default Value Reasonable?

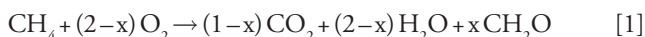
Jeffrey P. Chanton* and David K. Powelson Florida State University

Roger B. Green Waste Management Inc.

We reviewed literature results from 42 determinations of the fraction of methane oxidized and 30 determinations of methane oxidation rate in a variety of soil types and landfill covers. Both column measurements and in situ field measurements were included. The means for the fraction of methane oxidized on transit across the soil covers ranged from 22 to 55% from clayey to sandy material. Mean values for oxidation rate ranged from 3.7 to 6.4 mol m⁻² d⁻¹ (52–102 g m⁻² d⁻¹) for the different soil types. The overall mean fraction oxidized across all studies was 36% with a standard error of 6%. The overall mean oxidation rate across all studies was 4.5 mol m⁻² d⁻¹ ± 1.0 (72 ± 16 g m⁻² d⁻¹). For the subset of 15 studies conducted over an annual cycle the fraction of methane oxidized ranged from 11 to 89% with a mean value of 35 ± 6%, nearly identical to the overall mean. Nine of these studies were conducted in north Florida at 30° N latitude and had a fraction oxidized of 27 ± 4%. Five studies were conducted in northern Europe (~50–55° N) and exhibited an average of 54 ± 14%. One study, conducted in New Hampshire, had a value of 10%. The results indicate that the fraction of methane oxidized in landfill greater than the default value of 10%. Of the 42 determinations of methane oxidation reported, only four report values of 10% or less.

THE process of methane oxidation reduces the emissions of methane and other volatile hydrocarbons from the surface of landfills (Bogner et al., 1995; Börjesson and Svensson, 1997; Kjeldsen et al., 1997; Scheutz et al., 2003; Huber-Humer et al., 2008). The quantification of methane oxidation is one of the major uncertainties in estimating national or global CH₄ emissions from landfills (Bogner and Spokas, 1993). Landfill gas (LFG) that is not collected or vented passes through landfill cover soils before being released to the environment. Bacteria near the landfill surface consume methane and other volatile hydrocarbons that are produced by decomposition in the underlying waste by reacting it with oxygen. These bacteria harness the energy from these enzyme-catalyzed chemical reactions to fuel their respiration. A portion of the methane is also incorporated into the biomass of the microbial cells (Hanson and Hanson, 1996).

Most biological methane oxidation is performed by a group of ubiquitous aerobic soil bacteria called methanotrophs. Although found everywhere in soil, methanotrophs are concentrated above anaerobic regions of wetlands where CH₄ is produced. They are also found at high concentrations in the rhizosphere of wetland plants (Chanton et al., 1992; King 1992; Hanson and Hanson, 1996). They can even be found in forest soils where they consume methane directly from the atmosphere (1.7 μL L⁻¹ CH₄, Tyler et al., 1994). Biological CH₄ oxidation is similar to chemical CH₄ oxidation except that the reaction is catalyzed by enzymes and some energy is used to produce biomass (represented as CH₂O):



Although known since the early 1900s, the widespread activity of methanotrophs in the environments of lakes, marine settings and rice paddies was not appreciated until the 1970s (Hanson and Hanson, 1996; Reeburgh, 1976; Reeburgh and Heggie, 1977; Rudd and Hamilton, 1975; Rudd et al., 1976, Rudd and Taylor, 1980; Hanson, 1980, Kiene, 1991; King, 1992). The first journal publication to report the activity of methanotrophs in landfill cover soils was Whalen et al. (1990), who found the highest rates of environmental methane oxidation observed in any soils before that time (45 g or 3 mol m⁻² d⁻¹). Whalen et al. worked in California landfill soils. Several years later, Kightley et al. (1995) observed that coarse sandy landfill soils permeated with methane for 6 mo oxidized 10.4 mol of CH₄ m⁻² d⁻¹. Whalen et al. (1990) estimated that methane oxidation consumed approximately 50% of methane produced in landfills.

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*Corresponding author (jchanton@fsu.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

J.P. Chanton, and D.K. Powelson, Dep. of Oceanography, Florida State Univ., Tallahassee, FL 32306-4320; R.B. Green, Waste Management Inc., 2956 Montana Ave, Cincinnati, OH 45211.

Currently, the default value for landfill cover CH₄ oxidation is set between 0 and 10% of generated CH₄ (IPCC, 2006, USEPA, 2004). The 10% value was proposed at an IPCC workshop in Washington in 1995. At an international seminar in Chicago in 1997 it was agreed to use 10% as a standard value (IPCC, 2000). The results of comprehensive studies in New Hampshire were just being made available at that time. To our knowledge, the earliest government document making reference to a 10% value for landfill CH₄ oxidation is in USEPA (1998). In this document EPA cites the New Hampshire studies of Liptay et al. (1998) and Czepiel et al. (1996a, 1996b) who published seasonally averaged annual values of 10% CH₄ oxidation. The 10% value for this landfill was subsequently confirmed in air plume studies by Chanton et al. (1999). A report conducted by the USEPA in 2004 stated that “average oxidation of methane (on a volumetric basis) in some laboratory and case studies on landfill covers have indicated ranges from 10% to more than 25% with the lower portion of the range being found in clay soils and higher in topsoils” (USEPA, 2004). Due to the uncertainty involved and the lack of a standard method to determine oxidation rate, the USEPA recommended the default factor of 10% by volume methane oxidation for landfill cover soils.

A value of 0 to 10% oxidation is also recommended by the Intergovernmental Panel on Climate Change (IPCC, 2006) guidelines for national greenhouse gas inventories. The 1996 IPCC Guidelines for National Greenhouse Gas Inventories lists the default for methane oxidation as zero but included it in the calculation as placeholder to facilitate the use of nonzero values in the future based on ongoing work (IPCC, 2006). The 2006 IPCC Guidelines for National Greenhouse Gas Inventories still lists zero oxidation as the default but states, “The use of the oxidation value of 0.1 is justified for covered, well-managed solid waste disposal sites to estimate both diffusion through the cap and escape by cracks/fissures. The use of an oxidation value higher than 0.1, should be clearly documented, referenced, and supported by data relevant to national circumstances.”

The purpose of this review is to compile flux-based methane oxidation rates per unit area in mol CH₄ m⁻² d⁻¹, and the fraction of methane transported through the soil that is oxidized (fraction oxidized as a percent) in landfill cover materials. We examined and reviewed column experiments and in situ field studies. The strengths and weaknesses of these approaches are reviewed. Best estimates of methane oxidation rate and fraction oxidized are presented and discussed.

Methods

Approaches to determine methane oxidation are summarized in Table 1 and discussed below.

Column Measurements

The most realistic laboratory microcosm is a large undisturbed soil column where CH₄ and CO₂ are applied at a known rate to the bottom and the top is open to air. The CH₄ emission from the top is monitored periodically by enclosing the headspace and measuring the increase in CH₄ concentra-

tion within the enclosure (chamber method, Hutchinson and Livingston, 2002). From the CH₄ influx (J_{in} , mol m⁻² d⁻¹) and outflux (or emission, J_{out} , mol m⁻² d⁻¹) the flux-based oxidation rate or mass balance determined flux loss due to oxidation (J_{oxf}) and fraction oxidized (f_{ox}) can be directly calculated:

$$J_{oxf} = J_{in} - J_{out} \quad [2]$$

$$f_{ox} = J_{oxf} J_{in}^{-1} \quad [3]$$

It is sometimes difficult to obtain an undisturbed column due to gravel, wood, etc. in the cover material, and there is likely to be considerable variability between undisturbed columns. For these reasons some research is conducted with repacked columns where soil is dug out and sieved before being packed in a column. This method allows better control of soil composition, but the disruption of soil structure may mean that repacked columns are not representative of field conditions, because they lack cracks and other soil structure that form after a few years in field conditions.

Flask Incubations

In addition to column and field studies, methane oxidation rates can be determined from flask incubations. In vitro incubations are primarily used to determine the Michaelis-Menton kinetic parameters (V_{max} and K_m):

$$V = V_{max} S / (K_m + S) \quad [4]$$

where V is the CH₄ loss rate and S is the aqueous CH₄ concentration (usually determined from gas-phase CH₄ concentration and Henry's law). Sieved and homogenized soil is typically used to minimize variability. A small amount of soil is placed in a flask along with CH₄ in air so that gas diffusion is rapid throughout the soil, and measurements of V are taken as quickly as possible to minimize growth of methanotrophs. The Michaelis-Menton equation was intended for use with a constant amount of an enzyme (Tabatabai, 1994), so enzyme production or loss through changes in the bacterial condition or numbers are confounding factors. It is theoretically possible to calculate an oxidation rate (J_{oxv}) from V_{max} (mol g⁻¹ d⁻¹), field bulk density (ρ_b , g m⁻³), and oxidation depth (z , m):

$$J_{oxv} = V_{max} \rho_b z \quad [5]$$

This approach assumes oxygen is not limiting throughout the depth. Czepiel et al. (1996a) found that maximum CH₄ oxidation occurred when volumetric O₂ concentration was >10% and oxidation did not decline sharply until O₂ was <3%.

Field Methods

Calculation of methane oxidation rate is straightforward (Eq. [2]) if the influx to the bottom of the oxidation region (J_{in}) is known. Christophersen et al. (2001) used the mass balance of CH₄ and CO₂ to estimate J_{in} in steady-state conditions. Knowing the total outflux of CH₄ and CO₂ and the CH₄ and CO₂ concentrations below the zone of oxidation, J_{in} can be calculated:

$$J_{CH4+CO2} = J_{CH4out} + J_{CO2out} = J_{CH4in} + J_{CO2in} \quad [6]$$

Table 1. Summary of methods to determine methane oxidation.

Method	Description	Strengths/Weaknesses	Reference examples
Laboratory methods			
Column	Methane flow from below at a known rate. Methane emission measured at top of column	Controlled study. Precise determination. Does not account for cracks and heterogeneity in landfill soil	Humer and Lechner (1999) De Visscher et al. (1999, 2004)
Flask incubation	Measure methane uptake rate in closed system. Extrapolate to field rate using bulk density and depth of active layer.	Controlled study. Uncertainty of bulk density. Uncertainty of depths to apply to.	Czepiel et al. (1996a)
Field methods			
Mass balance of CO ₂ and CH ₄	Assumes a carbon mass balance in the aerobic zone where excess CO ₂ is due to CH ₄ oxidation.	Simple approach. CO ₂ affected by plant respiration, soil respiration and differential solubility in water.	Christophersen et al. (2001)
Isotopic fractionation			
Chamber approach	Emitted CH ₄ that has been exposed to oxidation is collected in a chamber. The δ ¹³ C of this methane is compared to anoxic zone methane δ ¹³ C using Eq. [12] or [13].	Simple method to apply. Can be applied to specific areas. Results in a conservative estimate. Uncertainty in fractionation factor.	Liptay et al. (1998) Chanton and Liptay (2000) Börjesson et al. (2001)
Soil gas probe	Similar to the chamber method, but the oxidized CH ₄ is collected within the soil oxidation zone.	Can be applied to specific areas. Uncertainty as to which depth from which to collect the oxidized CH ₄ . Uncertainty in fractionation factor.	Chanton et al. (2008b)
Plume captured CH ₄	Similar to the chamber method, but the oxidized CH ₄ is collected from the air downwind of the landfill. Corrected for upwind CH ₄ .	Integrates over entire landfill. Background correction can be significant. Uncertainty in fractionation factor.	Chanton et al. (1999) Börjesson et al. (2007)

$$J_{CH_4in} = (J_{CH_4out} + J_{CO_2out})[\phi_{CH_4in}/(\phi_{CH_4in} + \phi_{CO_2in})] \quad [7]$$

where ϕ is volumetric gas concentration. The main assumptions in this technique are: there is no net change in CO₂ due to its dissolution in water entering or leaving the oxidation zone, and production of these gases in the soil is negligible. The validity of these assumptions is rather uncertain. One factor is CO₂ generation by oxidation of soil organic compounds other than CH₄. The approach can also be confounded by the presence of surface vegetation that can have a large effect on surface CO₂ emissions. Additionally, CO₂ and CH₄ have vastly different solubility in water and so they may be fractionated by dissolution. The approach has not been widely used.

As a result of the difficulty in estimating J_{in} in the field, C isotope fractionation has been widely used to obtain in situ estimates of methane oxidation in cover soils is by use of subtle shifts in the stable carbon isotope ratio of methane as it passes from anaerobic zones through zones of oxidation. This technique compares the ¹³C/¹²C ratio before and after exposure to methanotrophic bacteria. The advantage of this method is that only gas samples from the anaerobic zone and the surface or shallow subsurface are required, along with the fractionation factor (α_{ox} , Eq. [11]).

There are two stable isotopes of carbon, ¹³C which is about 1% abundant and ¹²C which comprises 99% of carbon atoms. Stable isotopes are useful for determining CH₄ oxidation because as it occurs, the remaining CH₄ becomes ¹³C enriched due to preferential utilization of the lighter ¹²C isotope by bacteria (Coleman et al., 1981). Carbon isotopic composition is expressed in the δ notation, which is defined as follows:

$$\delta^{13}C\text{‰} = ((R_{\text{sample}}/R_{\text{standard}}) - 1) \times 1000 \quad [8]$$

where R_{sample} is the ¹³C/¹²C ratio of the sample and R_{standard} is the ¹³C/¹²C ratio of the marine carbonate standard (PDB, 0.01124). Typical biogenic landfill CH₄ is produced at values of around -55 to -58‰. (Chanton et al., 1999). Following oxidation, CH₄ may exhibit ¹³C enriched values of -30 to -50‰. Typical organic matter is ¹³C enriched relative to CH₄ with a δ¹³C value of -26‰. The negative δ value indicates that the sample is ¹³C depleted relative to the carbonate standard, which by definition equals 0‰. The more negative the value, the more ¹³C depletion is indicated. More positive values indicate δ¹³C enrichment.

Methanotrophic bacteria consume ¹²CH₄ at a slightly faster rate than ¹³CH₄ (Silverman and Oyama, 1960). This results in a shift in the isotopic ratio, or fractionation, as oxidation progresses. It is possible to calculate how much methane oxidation has occurred from the change in isotopic composition of CH₄ before and following CH₄ oxidation and the degree of fractionation by methanotrophs. The rate of oxidation is dependent on the volumetric CH₄ concentration (ϕ) and a first-order rate constant (k) for each isotope,

$$(d\phi_{12}/dt) = -k_{12}\phi_{12} \quad [9]$$

$$(d\phi_{13}/dt) = -k_{13}\phi_{13} \quad [10]$$

where k for ¹²CH₄ is greater than that for ¹³CH₄. The ratio k_{12}/k_{13} is the kinetic isotope effect or fractionation factor α_{ox} . α_{ox} may be obtained by finding the slope of the regression for $\ln \phi$ on the y axis and $\ln(\delta + 1000)$ on the x axis (DeVisscher et al., 2004):

$$\alpha_{ox} = \text{slope}/(1 + \text{slope}) \quad [11]$$

The fraction of methane oxidized in a closed system (f_{ox}) may then be calculated from initial (δ_o) and final (δ) isotope ratios using the simplified Rayleigh equation (Mahieu et al., 2006):

$$f_{\text{ox}} = [(\delta + 1000)/(\delta_0 + 1000)]^{\alpha_{\text{ox}}/(1-\alpha_{\text{ox}})} \quad [12]$$

There are several important issues that must be addressed in the application of this method, however. As will be discussed below, these issues result in the approach yielding a lower limit appraisal of methane oxidation.

First, most researchers do not calculate f_{ox} by the Rayleigh equation (Eq. [12]) because the *closed-system* assumption that a sample of gas moves through soil without mixing with other CH_4 may not be realistic. Instead, they use an open-system equation:

$$f_{\text{oxo}} = (\delta - \delta_0)/[1000(\alpha_{\text{ox}} - \alpha_{\text{trans}})] \quad [13]$$

where α_{trans} is the transport fractionation factor. The open-system equation was adapted from an equation used by Monson and Hayes (1980) to study fatty acid synthesis (Liptay et al., 1998).

The term α_{trans} is difficult to assess, because it depends on the relative importance of diffusion relative to advection in the transport of methane. If methane is transported by advection, which does not result in isotopic fractionation, then α_{trans} is equal to 1 and the solution to Eq. [13] is exact. If diffusion is important, then $\alpha_{\text{trans}} > 1$. It is currently not possible to easily assess the relative importance of diffusion vs. advection in transporting methane from the soil across the surface of a landfill. Advection is an important process, as methane production increases gas volume and this excess pressure is relieved by flow outwards toward the surface. It has been shown that landfill gas emission varies as a function of variations in atmospheric pressure implying that advection is an important process (Czepiel et al., 2003; Bergamaschi et al., 1998). Cover materials are quite variable in terms of their gas permeability so advection/diffusion may vary in their relative importance from location to location. Additionally, landfill gas capture reduces pressure within the landfill reducing outward advection and increasing the importance of diffusion in gas transport toward the surface. Generally, in applying Eq. [13] α_{trans} is assumed to be equal to 1. The effect of this assumption is that the isotopic approach results in lower-limit conservative values for methane oxidation (f_{oxo}) as the denominator in Eq. [13] is overestimated.

The lower limit effect of diffusion in applying the isotope approach results because diffusion, as well as oxidation, fractionates isotopes. $^{12}\text{CH}_4$ diffuses to the atmosphere faster than $^{13}\text{CH}_4$, thereby impacting measured isotope fractionation of surface samples and isotope-derived f_{oxo} (De Visscher et al., 2004). De Visscher et al. (2004) clearly demonstrated that isotopic based measurements, particularly those applied on emitted methane captured in chambers, are lower limit conservative estimates when $\alpha_{\text{trans}} = 1$. The isotope approach consistently underestimates methane oxidation in controlled lab experiments where isotopic and mass balance approaches have been directly compared (Powelson et al., 2007; De Visscher et al., 2004). The diffusion effect likely explains the observation that $\delta^{13}\text{C}$ values from 5- to 10-cm probe samples were less negative than surface samples, which means that subsurface samples had greater calculated oxidation (Chanton et al., 2008b). A combination of the two approaches may be used (Chanton et al., 2008b).

A second weakness of the method is that literature values for the fractionation factor α_{ox} range considerably (Templeton et al., 2006; Chanton and Liptay, 2000), depending on temperature and other factors. Small differences in α_{ox} have a large impact on f_{ox} (Eq. [12] or [13]). Generally α_{ox} is determined for each soil type where oxidation is quantified by the isotopic approach to reduce this source of uncertainty (e.g., Börjesson et al., 2007). A closed system approach is used for this determination (Mahieu et al., 2006). Chanton et al. (2008a) have recently reported observations of α_{ox} as a function of temperature and location.

Third, heterogeneity of soil pore sizes results in a range of CH_4 transport rates. Methane following the slowest routes may be completely oxidized before reaching the surface, and the loss of this isotope signature is an additional factor which results in the underestimation of f_{ox} by the isotope approach (Powelson et al., 2007; Chanton et al., 2008b).

Calculating Rate of Oxidation from Oxidation Fraction and Emission Rate

If the outflux or emission rate of methane (J_{out}) and the fraction of methane oxidized in the cover (f_{ox}) are known it is possible to calculate the rate of methane oxidation:

$$J_{\text{ox}} = J_{\text{out}}/(f_{\text{ox}}^{-1} - 1) \quad [14]$$

where f_{ox} is usually determined by the isotope method. Outflux may be found by the chamber method, where the increase in methane concentrations in a closed chamber covering the soil is determined. Outflux from a large area such as a landfill may be estimated by averaging outflux from numerous locations. It has been found that there is a large spatial variability in methane outflux, which makes it difficult to determine the true mean flux (Czepiel et al., 1996b).

Atmospheric tracers may also be used to find the CH_4 emission (Q_m , mol d⁻¹) from large areas. This involves releasing a tracer gas like SF_6 from evenly spaced locations on the landfill at a known rate (Q_t) and measuring the relative concentrations of the tracer (ϕ_t) and CH_4 (ϕ_m) downwind (Czepiel et al., 1996b). If the released tracer is well mixed with the CH_4 plume, Q_m may be calculated:

$$Q_m = Q_t(\phi_m/\phi_t) \quad [15]$$

The average outflux is Q_m divided by the source area. The main disadvantage of this technique is the expense of the gas and the collection many plume samples downwind over a large area in a short time. It should also be mentioned that SF_6 is the most potent greenhouse gas that the IPCC has evaluated, with a global warming potential 22,200 times that of CO_2 when compared over a 100 yr period (Ramaswamy et al., 2001). Recently other gases such as N_2O or ethylene have been used as a tracer in plume studies (Jacobs et al., 2007; Börjesson et al., 2007).

A new approach involves the use of optical remote sensing to determine methane emissions from large areas of landfills, although it is still prone to considerable uncertainty particularly due to a lack of knowledge about the area contributing to the emis-

sions. The method uses a path-integrated optical remote sensing system in multiple beam configurations to locate “hot spots” and determine emissions (USEPA, 2006; Hater et al., 2007; Chanton et al., 2007; Modrak et al., 2007). A tunable diode laser (TDL) is used as the optical sensor since methane absorbs strongly in the infrared portion of the electromagnetic spectrum. The approach is to turn the landfill into a giant open path spectrophotometer. A series of mirrors is placed across and above the landfill surface to form a three-dimensional set of reflectors. The computer controlled laser rotates automatically from mirror to mirror, directing its beam at each one in turn. The laser signal returns from the mirror to a receiver that measures its strength. The attenuation of the laser beam in relation to the locations of the reflectors in the field are input to the field computer which evaluates the path-integrated methane concentration to produce horizontal and vertical maps of the methane plume above the landfill. Simultaneously a weather station determines wind velocity and speed, and a model is used to estimate the flux of methane emitted from a selected area. Eddy correlation approaches have also been used (Lohila et al., 2007). The TDL method is prone to spatial variability in CH₄ emissions, and there are many uncertainties in using wind speed or eddy correlation to reliably convert concentration to flux. As mentioned above, the area of the footprint is not well known.

Results and Discussion

The results in Table 2 are organized by soil type and method. For covers that have layers of different materials, the material in the upper 30 cm is listed, for this region is where most oxidation is likely to occur (De Visscher et al., 1999). Only column studies and field determinations (sections 2a and 2c) are compiled in Table 2. Organic covers had an average oxidation rate of $3.96 \pm 2.33 \text{ mol m}^{-2} \text{ d}^{-1}$ (\pm standard error = (standard deviation)/ $n^{1/2}$) and fraction oxidized of $40 \pm 9\%$. Clayey soils had an average oxidation rate of $3.88 \pm 2.18 \text{ mol m}^{-2} \text{ d}^{-1}$ with an average fraction oxidized of $22 \pm 5\%$. Sandy soils had the greatest rate of oxidation rate at $6.43 \pm 2.77 \text{ mol m}^{-2} \text{ d}^{-1}$ with fraction oxidized of $55 \pm 9\%$. Composite and other soil materials had an oxidation rate of $3.72 \pm 1.21 \text{ mol m}^{-2} \text{ d}^{-1}$ and $30 \pm 5\%$ fraction oxidized. Generally, the column studies reported greater rates of oxidation and percent oxidation than the in situ field studies. This may be due in part to a lack of cracks and fissures in columns, which in the field allow some CH₄ to bypass oxidation. If field studies are considered alone, the percent oxidation values are organic-34%, clayey-18%, sandy-53%, and other-28%. The in situ field studies are based mostly on the isotope approach and, thus, are lower limit estimates as discussed above. Column studies are based on the mass balance approach, which is more reliable but uncertain in field settings as discussed above.

Sandy soils exhibited the highest oxidation rate and the highest fraction oxidized (Table 2), probably due to better gas permeability. Oxygen is a factor which can limit methane oxidation and it can diffuse into sand more readily than into clay soils due to the higher diffusivity of sand. However, sand is less effective than other materials in blocking methane flow toward the surface and would considerably reduce landfill gas capture efficiency.

Surprisingly, given the interest in using compost as biocovers, organic materials in the field had the lowest oxidation rate ($0.07 \text{ mol m}^{-2} \text{ d}^{-1}$) in the field studies. This is because when compost covers are applied in the field they often limit the gas transmissivity of the underlying clay cover by their moisture holding capacity, thus preserving the hydration of the clay. This effectively reduces methane emissions by a process termed “blockage” (Stern et al., 2007). This value is the average of only two studies, and organic materials had the second highest oxidation rate in laboratory studies ($7.84 \text{ mol m}^{-2} \text{ d}^{-1}$).

We suggest that the best approach to estimating CH₄ oxidation capacity of landfill covers is to use the average appropriate to each soil type. We suggest including laboratory column studies and field methods in the average because each has strengths and weaknesses as discussed above. The column results were determined by mass balance, which produces a more exact estimate while the field studies employed the isotope approach for the most part, which yields a lower limit value for methane oxidation.

There was no trend in the data with oxidation as a function of cover thickness in the studies compiled. There are several reasons why we did not observe this trend. First, oxidation is confined to the surface-most zone of a cover where oxygen penetrates via diffusion from above. Since the oxygen comes in from above, the cover thickness overall does not affect oxygen penetration except that a thicker cover may attenuate methane upward advection that tends to push oxygen out of the soil. Second, the data were compiled from a number of soil covers and includes a variety of factors so any trend might have been obscured by other sources of variability. Additional controlled studies of methane oxidation as a function of cover thickness at a single site needs to be conducted (e.g., Stern et al., 2007). In general, a thicker cover will result in increased retention times for transported CH₄. This increased retention of CH₄ in the landfill soil covers results in lower emission rates and in a higher fraction of CH₄ being oxidized (Stern et al., 2007).

As with other biochemical processes, methane oxidation increases with temperature until enzymes start to become denatured. The data in Table 2 over-represent warmer temperatures; however, temperatures warmer than those of New Hampshire may be representative of conditions found in much of the world. Czepiel et al. (1996a, 1996b) found that oxidation rate increased by about a factor of 33 from 5.5° to 36°C, but no oxidation activity was observed at 45°C. The studies in Table 2 report soil temperatures from -2° to 40°C (temperatures are not necessarily in the active zone, and when temperature was not reported, location and months are listed). For the 15 studies that were conducted for at least a year, the fraction of methane oxidized ranged from 10 to 89% (Table 2 “all year”). The mean value of the all year studies was $35 \pm 6\%$, surprisingly similar to the overall average. While the bulk (9 of 15) of these all-year studies were conducted in north Florida at 30° N latitude and had an average of $27 \pm 4\%$, five were conducted in northern Europe (~55° N) and exhibited an average of $54 \pm 14\%$. This unexpected inverse relationship of fraction oxidized with temperature may illustrate the effect of other environmental factors. Alternatively these results are also influenced by

Table 2. Literature values for methane oxidation rate and fraction oxidized (mean and standard error, SE), sorted by cover material and method (column or field).

Cover material	Method	Oxidation rate —mol m ⁻² d ⁻¹ —	SE rate	Fraction oxidized	SE fraction	Gas collection	Cover depth m	Soil temperature °C or state and month	Reference¶
ORGANIC	COLUMN								
Compost	Repacked column with CH ₄ advection	9.423†	na‡	1.00†	na‡	na‡	0.60	18	Humer and Lechner (1999)
Compost	Repacked column with CH ₄ advection	6.250	0.6250†	0.19	0.019†	na‡	0.50	22	Wilshusen et al. (2004)
		7.836		0.60					AVERAGE
ORGANIC	FIELD								
Compost landfill cover	Isotope fractionation	0.041†	0.0331†	0.55	0.136	yes	1.15	KY Apr to Sep	Barlaz et al. (2004)
Wood chips and sludge	Plume tracer and isotope fractionation	nr‡	nr‡	0.16	0.031	yes	nr‡	7	Börjesson et al. (2007)
Wood chips and sludge	Plume tracer and isotope fractionation	nr‡	nr‡	0.25	0.003	yes	nr‡	17	Börjesson et al. (2007)
Compost	Combination probe and chamber	nr‡	nr‡	0.36	0.06	no	0.47	FL all year	Chanton et al. (2008b)
Mulch 30 cm	Combination probe and chamber	nr‡	nr‡	0.18	0.04	no	0.30	FL all year	Chanton et al. (2008b)
Mulch 60 cm	Combination probe and chamber	nr‡	nr‡	0.50	0.04	no	0.60	FL all year	Chanton et al. (2008b)
Yard-waste compost	Isotope fractionation	0.108	0.0338	0.38	0.031	no	0.50	FL all year	Stern et al. (2007)
		0.074		0.34					AVERAGE
ORGANIC	ALL	3.955	2.3324	0.40	0.0888				AVERAGE of all organic
CLAYEY	COLUMN								
Silty clay landfill cover	Undisturbed column with 135 to 145 µL ⁻¹ v CH ₄ diffusion	0.004†	0.0005†	nr‡	nr‡	na‡	nr‡	IL June,Sept.,Nov.	Bogner et al. (1997)
Silty clay landfill cover	Undisturbed column with 1 to 8% CH ₄ diffusion	1.156†	0.2927†	nr‡	nr‡	na‡	nr‡	IL June,Sept.,Nov.	Bogner et al. (1997)
Clay landfill cover	Repacked column with CH ₄ advection	6.800	0.3000	0.40	0.018	na‡	1.00	19	Kightley et al. (1995)
		2.653		0.40					AVERAGE
CLAYEY	FIELD								
Sandy clay landfill cover	Isotope fractionation	0.564†	0.3420†	0.14	0.039	no	0.15	FL Feb to May	Abichou et al. (2006)
Clay landfill cover	Isotope fractionation	1.216†	0.8693†	0.21	0.056	yes	1.00	KY Apr,June,Sept.	Barlaz et al. (2004)
Clay landfill cover	Isotope fractionation	13.517†	1.8114†	0.14	0.020	no	0.15	FL all year	Chanton and Liptay (2000)
Clayey landfill cover	Combination probe and chamber	nr‡	nr‡	0.21	0.04	no	0.15	FL all year	Chanton et al. (2008b)
		5.099		0.18					AVERAGE
CLAYEY	ALL	3.876	2.1752	0.22	0.0473				AVERAGE of all clayey
SANDY	COLUMN								
Coarse sand landfill cover	Repacked column with CH ₄ advection	10.400	0.1000	0.61	0.006	na‡	1.00	19	Kightley et al. (1995)
Fine sand landfill cover	Repacked column with CH ₄ advection	6.900	0.3000	0.41	0.018	na‡	1.00	19	Kightley et al. (1995)
Loamy sand landfill cover	Repacked column with CH ₄ advection of 4.8 mol m ⁻² d ⁻¹	4.608†	0.0842†	0.96†	0.017†	na‡	1.00	22	Scheutz and Kjeldsen (2003)
Loamy sand landfill cover	Repacked column with CH ₄ advection of 65 mol m ⁻² d ⁻¹	23.725†	1.7299†	0.37†	0.027†	na‡	1.00	22	Scheutz and Kjeldsen (2003)
Sandy soil	Repacked column with CH ₄ advection	4.366†	0.2634†	0.44†	0.033†	na‡	1.20	30 to 40	Visvanathan et al. (1999)
		10.000		0.56					AVERAGE
SANDY	FIELD								
Sand landfill cover	Isotope fractionation	0.172†	0.2771†	0.42	0.095†	no	0.3 to 0.8	0.4 to 24.8 all year	Börjesson et al. (2001)

(cont'd)

Table 2. Continued.

Cover material	Method	Oxidation rate —mol m ⁻² d ⁻¹ —	SE rate	Fraction oxidized	SE fraction	Gas collection	Cover depth m	Soil temperature °C or state and month	Reference¶
Sand adjacent to landfill	CH ₄ and CO ₂ mass balance	1.097†	0.4969†	0.89	nr‡	nr‡	na‡	2 to 25 all year	Christophersen et al. (2001)
Sand adjacent to landfill	Isotope fractionation	0.149†	0.1372†	0.28	0.152	nr‡	na‡	2 to 25 all year	Christophersen et al. (2001)
		0.473		0.53					AVERAGE
SANDY	ALL	6.427	2.7701	0.55	0.0886				AVERAGE of all sandy
OTHER MATERIAL	COLUMN								
Sandy-clay loam landfill cover	Incubation and model§	1.830†	0.2642†	0.10	nr‡	no	1.0 to 2.0	5 to 36 all year	Czepiel et al. (1996a)
Loamy agricultural soil	Repacked column with CH ₄ advection	8.236†	0.2725†	0.61†	0.020†	na‡	0.60	22	De Visscher et al. (1999)
Sandy loam landfill cover	Repacked column with CH ₄ advection	15.000	0.2725†	0.65	0.020†	na‡	0.60	22	De Visscher et al. (1999)
Sandy loam landfill cover	Repacked column with CH ₄ advection	3.535	0.0757	0.21	0.005	na‡	0.31	22	Hilger et al. (2000)
Sand with clay landfill cover	Undisturbed column with CH ₄ diffusion	3.813	0.2914	nr‡	nr‡	na‡	0.10	25	Whalen et al. (1990)
		6.483		0.39					AVERAGE
OTHER MATERIAL	FIELD								
Sandy loam landfill cover	Isotope fractionation	0.456†	0.2158†	0.25	0.028	no	0.45	FL Sept to Feb	Abichou et al. (2006)
European landfill covers	Isotope fractionation	4.239†	1.5460†	0.84	0.023†	yes	1.00	Germany and Netherlands all year	Bergamaschi et al. (1998)
Sandy loam landfill cover	Isotope fractionation	3.795†	2.6892†	0.26	0.048†	yes	0.4 to 1.0	–0.3 to 26.8 all year	Börjesson et al. (2001)
Sewage sludge and mineral soils	Plume tracer and isotope fractionation	nr‡	nr‡	0.07	0.023	yes	nr‡	6	Börjesson et al. (2007)
Sewage sludge and mineral soils	Plume tracer and isotope fractionation	nr‡	nr‡	0.15	0.011	yes	nr‡	–2	Börjesson et al. (2007)
Mineral soil	Plume tracer and isotope fractionation	nr‡	nr‡	0.40	0.026	yes	nr‡	9	Börjesson et al. (2007)
Mineral soil	Plume tracer and isotope fractionation	nr‡	nr‡	0.38	0.032	yes	nr‡	5	Börjesson et al. (2007)
Mulch and topsoil landfill cover	Isotope fractionation	1.678†	0.2114†	0.26	0.040	no	1.09	FL all year	Chanton and Liptay (2000)
Loamy landfill cover	Combination probe and chamber	nr‡	nr‡	0.22	0.04	no	0.35	FL all year	Chanton et al. (2008b)
Sandy-clay loam landfill cover	Chambers and estimated fraction oxidized	0.906†	0.2506†	nr‡	nr‡	no	1 to 2	NH Sept to Oct	Czepiel et al. (1996b)
Sandy-clay loam landfill cover	Plume tracer and estimated fraction oxidized	1.031†	0.0586†	nr‡	nr‡	no	1 to 2	NH Sept to Oct	Czepiel et al. (1996b)
Landfill “A” cover	Isotope fractionation	nr‡	nr‡	0.28	0.108	nr‡	nr‡	21 to 30	Liptay et al. (1998)
Landfill “B” cover	Isotope fractionation	nr‡	nr‡	0.19	0.014	nr‡	nr‡	20 to 28	Liptay et al. (1998)
Sandy-clay loam landfill cover	Isotope fractionation	nr‡	nr‡	0.68	0.093	nr‡	nr‡	22 to 29	Liptay et al. (1998)
Rochester landfill cover	Isotope fractionation	nr‡	nr‡	–0.03	0.035	nr‡	nr‡	NH Aug	Liptay et al. (1998)
Springfield landfill cover	Isotope fractionation	nr‡	nr‡	0.01	0.042	nr‡	nr‡	14 to 18	Liptay et al. (1998)
Wayland landfill cover	Isotope fractionation	nr‡	nr‡	0.32	0.053	nr‡	nr‡	18 to 23	Liptay et al. (1998)
Fine sandy loam landfill cover	Isotope fractionation	0.141	0.0281	0.19	0.027	no	0.35	FL all year	Stern et al. (2007)
		1.749		0.28					AVERAGE
OTHER MATERIAL	ALL	3.722	1.2133	0.30	0.0521				AVERAGE of all other material
ALL MATERIALS	ALL	4.505	1.001	0.36	0.06				OVERALL AVERAGE

† Estimated. Methods listed by reference below.

‡ na = not applicable; nr = not reported.

§ Not a column study, but a “hybrid” study that incorporated laboratory incubation and field measurements in an oxidation model.

¶ References:

(cont'd)

Table 2. Continued.

Abichou et al. (2006). Oxidation rates (J_{ox}) calculated from emission fluxes (J_{out} , their Table 1) and oxidation fractions (f_{ox} , their Table 2):

$$J_{ox} = J_{out} / (f_{ox} - 1) \quad [f1]$$

Barlaz et al. (2004). Oxidation rates calculated using eq. f1 from Supplemental Information using the average emission fluxes in Tables S3 and S4 and the oxidation fractions in Table S6.

Bergamaschi et al. (1998). The oxidation rate and SE had to be approximated by averaging the emission fluxes, and the SE approximated by using the average, minimum, and maximum fluxes listed for covered areas in their Tables 7 and 8. The oxidation rate SE accounted for propagation of error:

$$s_{rel,a} = (s_{rel,b}^2 + s_{rel,c}^2)^{1/2} \quad [f2]$$

where s_{rel} is the relative standard deviation (s mean⁻¹) and in this case a, b, and c refer to oxidation rate, emission flux rate, and fraction oxidized, respectively (Christian, 1986). The fraction oxidized SE was estimated from the relative SD of emitted $\delta^{13}C$.

Bogner et al. (1997). Oxidation estimated from their Fig. 3 for two ranges of initial CH_4 concentration: 135 to 145 $\mu L L^{-1}$ and 1 to 8% by volume.

Borjesson et al. (2001). The oxidation rates and standard errors were calculated by averaging data in their Table 3 and 5 and the propagation of error for the averages was accounted for by:

$$s_{avg} = (s_1^2 + s_2^2 + \dots)^{1/2} \quad [f3]$$

where s_{avg} is the standard deviation of the average and s_1, s_2 , etc. are standard deviations of the values contributing to the average (Christian, 1986).

Chanton and Liptay (2000). The reported average oxidation rates were used with each average CH_4 emission flux over the course of a year (estimated from their Fig. 1) to calculate oxidation rate.

Chanton et al. (2008b). Emitted fraction oxidized from closed-system equation (their Table 1). SEs estimated from $\delta^{13}C$ SEs. Subsurface samples taken from 5 to 10 cm depth with probes.

Christophersen et al. (2001). For the mass-balance method, the reported average oxidation rate for the Field transect, 89%, was used with each Field average CH_4 emission flux (their Table 1) to calculate oxidation rate. For the isotope fractionation method, the fraction oxidized for three locations (their Table 3) was used with the corresponding emission flux to calculate oxidation rate.

Czepiel et al. (1996a). Jar incubations of homogenized soil to find oxidation rate. Oxidation flux loss estimated from their Fig. 1 (5–15 cm depth) and assuming bulk density of 1.7 $g cm^{-3}$. Fraction oxidized was modeled over a year using oxidation rates “in soil columns” adjusted for field temperature and moisture content and field-measured outflux. Standard errors or other measure of confidence were not given.

Czepiel et al. (1996b). Both chamber and plume emissions converted to oxidation rates (eq. f1) using their estimated oxidation fraction of 0.20.

De Visscher et al. (1999). There are no true replicates; mean and standard error for the agricultural soil were estimated from repeated sampling from one column shown in their Fig. 1. Data for the landfill cover column were not shown; the landfill standard error was assumed to equal that for the agricultural column.

Hilger et al. (2000). Oxidation values are for steady state (their Table 1, Exp. 1, Live + LFG). Oxidation rate calculated from column parameters.

Humer and Lechner (1999). Oxidation values are for steady state in a single column where there was complete oxidation.

Scheutz and Kjeldsen (2003). Oxidation estimated from their Fig. 5 at inlet flow rates of 0.24 and 3.18 $m^3 m^{-2} d^{-1}$.

Visvanathan et al. (1999). Oxidation rates estimated from their Fig. 6.

Whalen et al. (1990). Oxidation rate is Michaelis-Menton V_{max} reported on an area basis (their Table 1).

Wilshusen et al. (2004). Oxidation values are for steady state. SE was estimated from final values of three columns in their Fig. 2 (the low, nonsteady-state column was excluded).

two studies Christophersen et al. (2001) and Bergamaschi et al. (1998) which used somewhat different approaches. The CO_2/CH_4 ratio approach employed by Christophersen et al. yielded 89% oxidation vs. 28% oxidation by the stable isotope technique in the same cover. Bergamaschi et al. used a combined Rn-stable isotope technique and determined 89% oxidation in a landfill cover. As stated above the isotope method described by Liptay et al. (1998) and Chanton and Liptay (2000) yields conservative estimates.

It is also important to consider how methane oxidation rates are expressed. Currently oxidation is generally expressed as a percent of the transported methane that is oxidized, that is, a constant fraction of landfill production (J_{in}). In this scenario, the amount of CH_4 oxidized increases linearly as emissions (J_{out}) increase (Eq. [14]). Recent studies, however, show that the percent oxidation is an inverse function of the rate of emission (Stern et al., 2007; Chanton et al., unpublished data, 2008). At lower rates, the methanotrophs in the soil cover can consume a larger portion of the methane delivered to them, oxidizing up to 95 to 100% (Humer and Lechner, 1999, 2001; Huber-Humer et al., 2008; Powelson et al., 2006, 2007; Kjeldsen et al., 1997). As outflux rates increase, their percent oxidation decreases and they can become overwhelmed with methane. As methane emission increases, percent oxidation decreases (Powelson et al., 2006, 2007).

It is necessary to know the rates of methane uptake associated with different cover types and variations in seasonal moisture and temperature for the purposes of constructing landfill covers that eliminate CH_4 emissions in conjunction with gas collection systems (Huber-Humer et al., 2008). Gas collection systems may not be able to capture 100% of produced methane. A landfill designer could eliminate the CH_4 flux by constructing a gas collection system and soil barrier that limit the upward flux to a range less than or equal to the oxidation capacity of the cover system. A reasonable goal would be a functionally layered cover system in which the bottom layer regulates landfill gas flux as a barrier (typically clay soil). The upper layer would function as an oxidation medium and work in tandem with the underlying barrier layer (e.g., Stern et al., 2007).

Table 3 lists four studies where oxidation rate determined from V_{max} (section 2b) is compared to flux-based oxidation rate (J_{oxf}) with the same soil material. Two of the studies show similar results, but the other two studies have 22.2 and 33.6 times greater oxidation rates using the V_{max} method. This might be expected because V_{max} is a theoretical maximum oxidation rate where CH_4 and O_2 are optimal for the entire depth z , which is not likely to be the case for J_{oxf} . Furthermore, the incubated soil is broken up, which allows gases better access to methanotrophs, and nutrients are mixed and more available. Because there is considerable uncertainty in applying V_{max} to field conditions

Table 3. Comparison of oxidation rates calculated from V_{\max} or maximum V and flux.

Material	V_{\max}	Bulk density	Oxidation rate from V_{\max} (J_{oxv}) [†]	Oxidation rate from flux (J_{oxf})	$J_{\text{oxv}}/J_{\text{oxf}}$	Reference [§]
	mol Mg ⁻¹ d ⁻¹	Mg m ⁻³	mol m ⁻² d ⁻¹	mol m ⁻² d ⁻¹		
Coarse sand	24.0	1.65‡	11.86	10.40	1.14	Kightley et al. (1995)
Sandy-clay loam	62.3	1.63‡	30.44	0.91	33.59	Czepiel et al. (1996a, 1996b)
Loamy agricultural soil	22.5	1.00	6.72	8.24	0.82	De Visscher et al. (1999)
Compost	720.0	0.64	138.46	6.25	22.15	Wilshusen et al. (2004)

[†] $J_{\text{oxv}} = (V_{\max})$ (Bulk Density) (Depth). An oxidation depth of 0.3 m was assumed.

‡ Bulk density estimated from saturated water content of the soil texture (Leij et al., 2002) and a mineral density of 2.65 g cm⁻³, except for compost which was estimated from leaf compost (Wilshusen et al., 2004).

§ References:

Czepiel et al. (1996a, 1996b). J_{oxf} from average of chamber outflux and assumed f_{ox} of 0.2.

De Visscher et al. (1999). V_{\max} averaged from most active depths of agricultural soil.

Wilshusen et al. (2004). J_{oxf} from steady-state rate in repacked compost column.

and in determining z , this method of estimating oxidation rate is likely to be less reliable than other methods. These results are reported in Table 3 for the purpose of comparison, but they are not included in any reported averages.

Conclusions

The overall mean oxidation rate across all studies was 4.5 mol m⁻² d⁻¹ with a standard error of 1.0 (72 ± 16 g m⁻² d⁻¹), and the overall mean oxidation was 36% with a standard error of 6%. All-year studies (subset of 15) ranged from 10 to 89% oxidation with averages of 27 and 54% at 30° (nine studies) and 55° N latitude (five studies), respectively. The mean value of the seasonal studies was 35 ± 6% and includes the 10% New Hampshire value. The literature summarized in this paper indicates that the fraction of methane oxidized in cover soils is probably greater than the default value of 10%. Of the 42 determinations of methane oxidation reported in Table 2, only four report values of 10% or less. The Czepiel et al. study (1996a) reports a value of 10%. This study was the first to report a well constrained value for the fraction of methane oxidized in a specific landfill, and because of this, it has received undue weight. The default value of 10% should be updated based on technological advancements in soil engineering and state-of-the-practice applications in cover design as well as recent studies detailed above.

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