Characterization of Methane Flux and Oxidation at a Solid Waste Landfill

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Abstract: Methane emissions were measured at several locations at a typical solid waste facility using a static chamber technique. At the entire facility, methane flux varied from −13.6 to 1,755 g m^{-2} day^{-1}. The flux data had an arithmetic mean value of 71.3 g m^{-2} day^{-1} and a geometric mean value of 18.6 g m^{-2} day^{-1}. At this site, methane emission was generally lower on the side slopes relative to the flat areas of the landfill. The spatial variability of methane flux was characterized by point kriging and inverse distance weighing (IDW) in an intensive study of a 61×61-m area. The geospatial means in this area obtained by both methods were almost identical (20.9 versus 20.8 g m^{-2} day^{-1}). These geospatial means for the area were also similar to the arithmetic mean (24.5 g m^{-2} day^{-1}), but 3.4 times the geometric mean (6.5 g m^{-2} day^{-1}). Methane oxidation was evaluated at the surface of the landfill and at several depths within the cover soil using stable isotope techniques. The $\delta^{13}C$ of CH_4 averaged −55.4% in the anoxic zone. Methane collected in chambers and in surficial soil probes exhibited more ^{13}C enriched values, ranging from −55.4 to −34.5%, due to the preferential uptake of $^{12}CH_4$ by methanotrophic bacteria. Methane oxidation at the landfill averaged 22% and occurred in the upper 70 cm of the landfill cover soil. Oxidation occurred in all tested locations of the landfill and for all ages of buried waste.

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Introduction

Methane is a greenhouse gas with an infrared activity 25 times that of CO_2. Its concentration has increased in the atmosphere by a factor of 2 over the last century. Mitigating landfill gas emissions can play an important role in reducing overall greenhouse gas emissions. Landfills are point sources and techniques to reduce the flux of methane from them are readily achievable (Chanton and Liptay 2000; Humer and Lechner 2001; Barlaz et al. 2004).

Landfills are significant sources of atmospheric methane with rates frequently measured in the range of grams CH_4 per square meter per day (Bogner and Spokas 1993; Bogner et al. 1995; Czepiel et al. 1996; Borjesson and Svensson 1997; Chanton and Liptay 2000). Bogner and Matthews (2003) used a model based on per capita waste generation (per capita energy consumption) and produced a best estimate of global methane of 16.4–18.1 Tera gram per year. On a landfill surface, emissions are highly variable in space and have been reported to vary over seven orders of magnitude from less than 0.0004–4,000 g m^{-2} day^{-1} (Bogner et al. 1997). However, field measurements of methane emissions from landfills are quite limited (Borjesson et al. 2001).

Because landfill gas is generated primarily by the decomposition of solids in the waste, the resulting gas expands to a substantially larger volume leading to pressure buildup within the landfill. The pressure inside a landfill at the bottom of the waste column has been reported to vary from slightly above atmospheric to 4 atm (Prosser and Janachek 1995). Since pressure inside a landfill is greater than atmospheric, convection tends to be the primary mechanism governing the rate of methane emission from landfills, at least those without vacuum gas collection systems (Qian et al. 2002).

Due to the heterogeneity of soil cover and waste, the spatial variations of landfill emissions are difficult to quantify. It is therefore challenging to scale up emissions obtained from flux chambers to the entire covered waste mass. Borjesson et al. (2000) made 83 flux measurements on a 3-ha landfill with 7.4-L chambers and interpolated these values by kriging to estimate the overall flux. Simultaneously a tracer gas technique was used and the flux calculated by this method was more than 4 times higher than that obtained by using chambers and kriging. This is probably because the chamber method only captures methane emissions across the soil cap whereas emissions from the entire landfill as measured by the tracer technique may be dominated by a few point sources such as large cracks, holes, or vents not covered by the chambers. Spokas et al. (2003) recognized the need to use a

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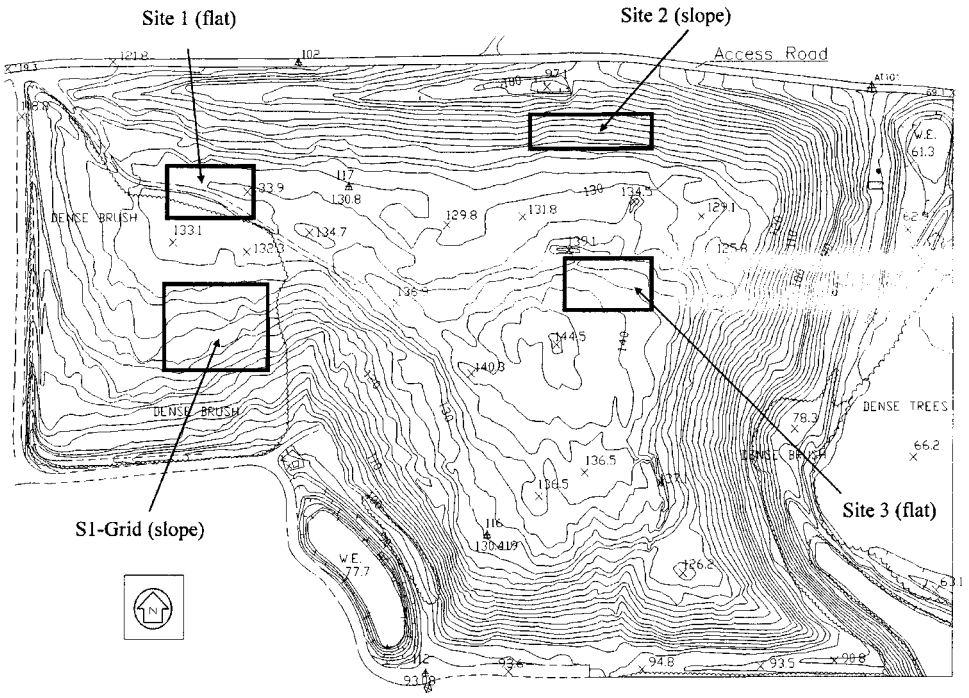

Fig. 1. Elevation contour and location map of test sites

spatial model to estimate methane flux from landfills rather than using the arithmetic mean, which may be overly influenced by "hot spots." They measured landfill methane flux with a 0.25-m^2 chamber at about 20-m intervals over 250 ha, and compared kriging and inverse distance weighing (IDW) interpolations.

Methane oxidation also affects the variability of emissions measured at the landfill surface, and may be the largest unknown variable in preparing global estimates of landfill methane emissions. Methanotrophic bacteria found in agricultural soils, forest soils, and bogs are capable of oxidizing CH_4 to carbon dioxide and also sequestering it as cell biomass (Whalen et al. 1990; Borjesson et al. 2001). These bacteria are important in controlling emissions of methane from landfill covers (Bogner et al. 1997; Dammann et al. 1999; Humer and Lechner 1999; Straka et al. 1999).

Objectives

Research is underway at the Leon County Landfill to develop techniques to mitigate greenhouse gas emissions via the biooxidation of methane at the surface of soil cover. One aspect of this research is the designing and testing of biocovers consisting of a compost layer overlying a dispersant layer to be placed on the landfill surface. Before such an effort can begin, methane emissions and oxidation at the landfill had to be well characterized. Therefore, our overall goal was to characterize the methane emission from and oxidation within the cover soil at this landfill prior to initiating biocover experiments to mitigate methane emission (Chanton and Liptay 2000; Humer and Lechner 2001; Barlaz et al. 2004). Mapping of emissions is the first step toward that goal, and is necessary to investigate if patterns of emissions vary for different locations of the landfill. Emission flux maps will then be used to engineer a placement scheme of biocover materials in accordance with the methane flux emission contours.

The objectives of this study were (1) to characterize the emissions of methane at several locations of a typical solid waste facility; (2) measure methane oxidation associated with landfill covers; and (3) test the methodology to describe the spatial variation of methane emissions from landfills.

Materials and Methods

Landfill Description

Measurements were performed at a municipal solid waste (MSW) landfill in Leon County, Fla. (Fig. 1), from June 2003 to February 2004. Previously, Chanton and Liptay (2000) studied the seasonal variation of methane flux and oxidation at a single site at this landfill. The landfill study section is lined and at the time of this study there was no gas collection system, so waste gases escaped through the cover or through the leachate collection pipes. The cover soil is sandy clay, varying in depth from approximately 15 to 100 cm, with an overlay of approximately 15 cm of sandy loam on the S1-Grid area (Table 1). The gravimetric soil moisture (6–10 cm depth) ranged from 0.005 to 1.0 g/g with a mean of 0.092 g/g; the soil temperature (8 cm depth) ranged from 8.4 to 37.3 °C with a mean of 22.3 °C. We chose four sites for investigation. Sites 1 and S1-Grid are areas where the waste was covered 7 years prior to the measurement period. The covers in Sites 1 and S1-Grid consisted of a 45-cm-thick (on average) interim soil layer. Vegetation was not well established on these two sites. Site 2 consisted of a 14-year-old waste mass covered by a well-vegetated soil cover (nearly 100% coverage of native grasses and herbs). The average thickness of the cover in Site 2 was 45 cm. Site 3 consisted of newly placed waste covered by only daily cover. The daily cover was 15–30-cm thick and had no vegetation. Sites 1 and 3 were located on top of the landfill. Sites 2 and S1-Grid were located on the side slopes of the landfill.

Table 1. Summary of Properties and Flux Results at all Sites

Properties	Site 1	Site 2	Site 3	S1-grid	All sites
Age of latest waste (year)	7	14	1	7	1–14
Cover thickness (cm)	30–60	45	15–30	21–119	15–119
Slope aspect	Flat	Slope	Flat	Slope	
First sampling date	June 18, 2003	June 23, 2003	June 26, 2003	September 29, 2003	June 18, 2003
Last sampling date	September 22, 2003	July 16, 2003	November 26, 2003	February 16, 2004	February 16, 2004
Flux ($g\ m^{-2}\ day^{-1}$)					
n	62	18	28	112	220
Maximum	1,754.8	63.1	5,21.2	3,42.5	1,754.8
Median	24.0	2.1	32.7	0.72	4.8
Minimum	−13.6	−2.3	0	−6.1	−13.6
Mean	167.0	8.6	87.0	24.5	71.3
s	332.3	16.4	143.5	63.4	198.5
Mean_g[a]	43.8	3.4	24.9	6.5	18.6
s_g[a]	4.6	2.8	6.1	2.5	3.2

[a]Geometric mean (mean_g) and standard deviation (s_g) are defined in Eqs. (6)–(8).

Methane Emission Rates and Gas Analysis

Methane emission rates from the landfill surface were determined using a static chamber technique. The chamber technique was more suitable for this research than large-scale tracer dilution methods since eventually we will be comparing emissions and oxidation in biocover and control test beds. Methane samples were collected from each chamber sequentially over a 20-min period using 60-mL disposable syringes (Becton, Dickinson, and Co., Franklin Lakes, N.J.) fitted with plastic stopcocks (Cole Parmer Instrument Co., Franklin Lakes, N.J.). Samples were analyzed on a gas chromatograph equipped with a flame ionization detector within 24 h of collection. Methane flux was determined from concentration data (C in parts per million per volume) plotted versus elapsed time (t in minutes). The methane concentration within the chambers generally increased linearly, in which case dC/dt is the slope of the fit to the data. This change in volumetric concentration was converted to a mass flux by using the ideal gas law. The methane flux, F ($g\ m^{-2}\ day^{-1}$), is calculated as follows:

$$F = PVMU(dC/dt)/(ATR) \tag{1}$$

where P=pressure (1 atm); V=chamber volume (80 L); M=molar mass of methane (16 g/mol); U=units conversion factor [0.00144 L min/(μL day)]; A=surface area covered by the chamber (0.4 m^2); T=chamber temperature (K); and R=gas constant [0.08205 L atm/(K mol)]. The slope of the line, dC/dt, was determined by linear regression between CH_4 concentration and elapsed time. The median r^2 value for the flux data was 0.95. Following the approach of Barlaz et al. (2004), a nonzero flux was reported only if there were 90% confidence ($p<0.1$) in the correlation between CH_4 concentration and time, otherwise a zero flux is reported.

Gas probes constructed from 9.5-mm stainless steel tubing and closed by valves at the top were installed at Sites 1, 2, and 3 to sample gas at depths ranging from 15 to 91 cm. Gas concentrations were determined using a Shimadzu 8A gas chromatograph (Shimadzu, Kyoto, Japan) with a thermal conductivity detector. Scott Specialty gases were used as standards (0.1 and 100% for methane).

A Stable Isotope Technique for Determination of Methane Oxidation

Recently stable isotope tracing has been employed to quantify the oxidation of methane in landfill cover soils (Bergamaschi et al. 1998; Liptay et al. 1998; Chanton and Liptay 2000; Borjesson et al. 2001; Christophersen et al. 2001). There are two stable isotopes of carbon, ^{13}C, which is about 1% abundant and ^{12}C, which comprises 99% of carbon atoms. Carbon isotopic composition is expressed in the δ notation (δ ^{13}C), which is defined as follows:

$$\delta\% = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1{,}000 \tag{2}$$

where $R_{\text{sample}} = {}^{13}C/{}^{12}C$ ratio of the sample and $R_{\text{standard}} = {}^{13}C/{}^{12}C$ ratio of the marine carbonate standard (Pee Dee Belemnite, $R_{\text{standard}}=0.01124$). Typical microbial CH_4 is produced at values below −55%. Following oxidation, CH_4 may exhibit ^{13}C enriched values from −30 to −50%. Typical organic matter is ^{13}C enriched relative to CH_4 with a δ ^{13}C value of −25%. The negative δ value indicates that the sample is ^{13}C depleted relative to the carbonate standard. The more negative the value, the more ^{13}C depletion is indicated.

In order to calculate the isotope ratio of the methane emitted (δ_E) from the soil during flux sampling it was necessary to account for the local atmospheric methane present in the air within the chamber at the initiation of the emission measurement

$$\delta_E = \frac{(\delta_F c_F) - (\delta_I c_I)}{c_F - c_I} \tag{3}$$

where δ_I and c_I=methane δ and concentration for the initial gas sample taken from the chamber; and δ_F and c_F=final sample.

Significant isotopic fractionation occurs when methane is oxidized. Microbial culture studies have shown that methanotrophic organisms preferentially consume CH_4 containing the lighter isotope ^{12}C, leaving residual CH_4 enriched in ^{13}C (Coleman et al. 1981; Barker and Fritz 1981). With an estimate of the preference of the bacteria for the lighter isotope, α_{ox}, one may calculate the extent of oxidation from the isotopic difference between the unaffected (as produced by methanogens, in this case) and the

residual (or left over) methane which has been exposed to oxidation but not itself oxidized. The percentage of CH_4 oxidized in transit through the cover soil ($f_o\%$) is determined by the following equation which describes isotopic fractionation in an open system:

$$f_o\% = 0.1(\delta_E - \delta_A)/(\alpha_{ox} - \alpha_{trans}) \quad (4)$$

where $\delta_A = \delta\,^{13}C$ value of anoxic zone CH_4 (−55.4% determined from probe data); α_{ox}=isotopic fractionation factor for bacterial oxidation; and α_{trans}=isotopic fractionation associated with gas transport. To the extent that gas transport is dominated by advection of gases across the landfill cap, as discussed previously, α_{trans} will approach 1. However, if diffusion plays a significant role in gas transport, α_{trans} will be greater than 1 causing this approach to yield conservative values of methane oxidation if α_{trans} is assumed to be 1 (De Visscher et al. 1999, 2004). The fractionation factor (α_{ox}) depended on soil temperature (t, °C) using a regression equation for clay soil (Chanton and Liptay 2000)

$$\alpha_{ox} = -0.000433t + 1.0421 \quad (5)$$

Stable isotopic ratios were determined using a Hewlett Packard gas chromatograph (Hewlett Packard, Palo Alto, Calif.) coupled via a combustion interface to a Finnegan Mat Delta S isotope ratio mass spectrometer (GCC-IRMS) (Thermo Electron Corporation, Waltham, Mass.) following methods adapted from Merrit et al. (1995). For chamber samples, a cryogenic focusing device was used on the front end of the gas chromatograph. The standard deviation of replicate analyses is generally about 0.15%. Stable isotopic ratios for the anoxic gases and soil gas profile were determined using direct injection on the GCC-IRMS.

Spatial Variability

One of the most challenging aspects of estimating methane emissions from a landfill is scaling up isolated chamber measurements to describe emissions from an entire landfill surface. The S1-Grid site was designed for intensive sampling. The grid was 60.8 m (200 ft) on a side and was divided into 64 squares, 7.6 by 7.6 m (25 by 25 ft). Methane emissions were measured in the middle of each square. Six squares had additional sampling locations in each quadrant as well as one in the middle. In these squares the minimum separation distance between sampling locations was 2.69 m (8.84 ft).

Sampling was conducted in Summer and Fall of 2003. Repeated sampling of 12 of the grid squares showed no temporal trend in methane flux during the study period. Consequently, the data were treated as if temporal variations were minimal and samples for the entire period could be used for the spatial variability analysis. Two methods of interpolating between data points were compared, kriging and IDW. For both methods all the data were used; i.e., there was no limit to the search neighborhood.

In kriging, a model of the overall variance structure was used to generate the interpolated contours. The variance structure is shown as a variogram with half the variance of the difference between values on the y axis and sample separation distance on the x axis. Key variables for a variogram are the nugget (unexplained or error variance), sill (total model variance, equal to nugget plus "scale"), and range (distance where the variance reaches the sill) (Yates and Warrick 2002). Point kriging was used with the variogram model to construct flux contours.

In IDW the interpolation contours are calculated by weighing neighboring data using the inverse of the separation distance to a power (*SURFER* 2002; Spokas et al. 2003). A power of two was used. IDW is considered an exact interpolator because each data point is treated as the true value and the surrounding estimates grade toward it. These contours show "bull's eye" peak-and-valley patterns around spatially variable individual points.

Results

Methane Flux Emissions

A total of 220 methane flux measurements were taken during this study (Table 1). The distribution of total methane fluxes was similar to the distributions obtained at each individual site and all distributions were highly skewed. Since the data were not distributed normally, they were transformed to log-normal distributions to determine geometric means and standard deviations. It was necessary to shift the flux distributions by a threshold value so that zero and negative fluxes could be included in log transformation (*SAS* 2002)

$$F_{ln} = \ln(F - F_{min} + 1\,\text{g m}^{-2}\,\text{day}^{-1}) \quad (6)$$

where F_{ln}=transformed flux; and F_{min}=minimum value for F. The use of 1 g m^{-2} d^{-1} as a constant in this transformation was chosen after it was found to produce the most normal distribution. The geometric mean ($mean_g$) was calculated from the mean of the F_{ln} distribution ($mean_{ln}$), and adding back the threshold value

$$mean_g = \exp(mean_{ln}) + F_{min} - 1\,\text{g m}^{-2}\,\text{day}^{-1} \quad (7)$$

Geometric standard deviation (S_g) was calculated from standard deviation of the F_{ln} distribution (S_{ln})

$$S_g = \exp(S_{ln}) \quad (8)$$

Methane flux for the entire data set varied from −13.6 to 1,755 g m^{-2} day^{-1} (Table 1). The negative flux here indicates that in some areas, the surface of the landfill acts as a methane sink, consuming the elevated atmospheric methane at the landfill. The chamber emission flux data had a geometric mean of 19.3 g m^{-2} day^{-1}, a median of 4.8 g m^{-2} day^{-1}, and an arithmetic mean of 71.3 g m^{-2} day^{-1}. The large variability of methane flux is consistent with the observations of Bogner et al. (1997), Borjesson et al. (2000), and Spokas et al. (2003). Site 2 and S1-Grid had the lowest geometric means of 3.4 and 6.5 g m^{-2} day^{-1}, respectively. Sites 1 and 3 had higher geometric means of 43.8 and 24.9 g m^{-2} day^{-1}, respectively.

Analyses of variance (ANOVAs) were performed to determine significant differences in flux among the four sites. Sample sizes were different; consequently unbalanced, one-way ANOVAs were performed using the general linear models procedure (SAS 2002). The natural logarithm of the flux data [F_{ln}, Eq. (5) F_{min}=−13.58 g m^{-2} day^{-1}] was used to normalize the distributions. There were significant difference in F_{ln} between sites (F value=13.18; df=3, 216; p=<0.0001). A Duncan multiple range test (p=0.05) showed that Site 1 was not significantly different from Site 3, Site 2 was not significantly different from the S1-Grid, and Sites 1 and 3 had significantly more flux than Sites 2 and S1-Grid. This analysis can only be considered approximate because the usual ANOVA assumption of independent measures is not met (the variogram shows some spatial correlation). Further, it is not possible to isolate the source of the variability because age of waste, cover thickness, slope aspect, and sampling dates varied between sites. Nevertheless, the common factor in this difference appears to be slope aspect; methane emissions tend

Table 2. Summary of Stable Isotope and Oxidation Results at all Sites

	Site 1	Site 2	Site 3	S1-grid	All sites
n	22	2	6	31	61
$\delta\ ^{13}C-CH_4$					
Maximum	−38.6	−42.9	−46.9	−34.5	−34.5
Median	−50.8	−49.1	−50.6	−49.0	−49.5
Minimum	−55.4	−55.4	−54.8	−54.8	−55.4
Mean	−50.0	−49.1	−50.4	−47.6	−48.8
s	5.0	8.8	3.2	5.1	5.0
Oxidation (%)					
Maximum	60.4	53.2	26.3	63.9	63.9
Median	16.6	26.6	14.7	20.9	18.8
Minimum	0	0	1.7	2.0	0
Mean	19.5	26.6	14.4	25.2	22.1
s	18.1	37.6	8.8	15.7	16.8

to be lower on slopes as opposed to top of this landfill regardless of cover. This might be due to the fact that in wet climate, gas migration through landfill covers is governed by bubbling. That is, as water ponds on the flat areas, the shear strength of the soil decreases and therefore landfill gas is able to bubble through the cover soil. On the other hand, water does not pond on the slopes but rather fills up the pores blocking advective flow. Since soil on the slopes is not as soaked as soil on the flat areas, it has a higher strength and therefore less likely to allow bubbling.

Methane Oxidation at the Landfill Surface

Table 2 shows summary statistics of the measured fraction oxidized, or percent oxidation, for all the sites. For all sites the mean δ_A was −55.4%, δ_E was ^{13}C enriched and ranged from −55.4 to −34.5% with a mean of −48.8%, and oxidation ranged from 0 to 63.9%. The peak oxidation of 63.9% was measured in a location of the S1-Grid, confirming the fact that high CH_4 oxidation can occur in vegetated soil covers. A histogram of

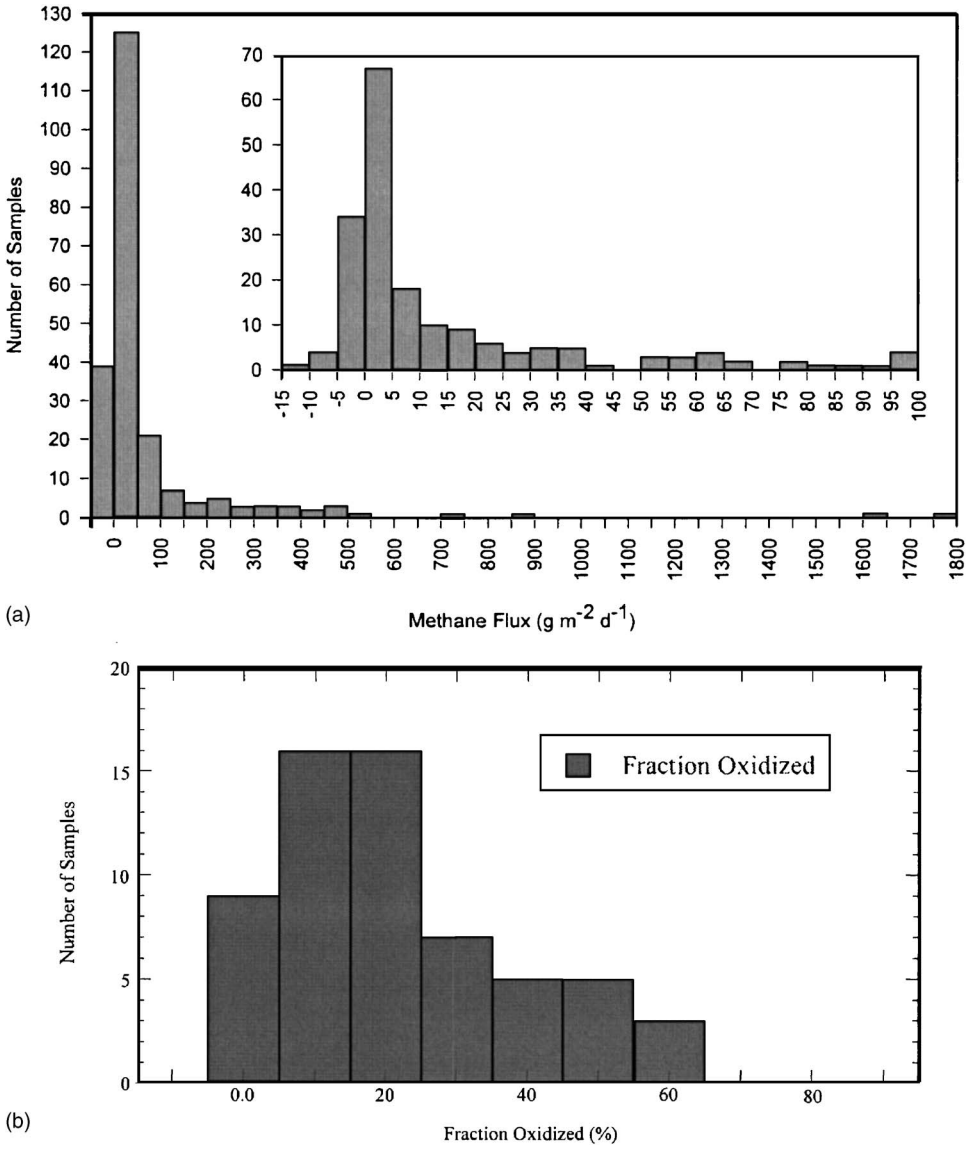

Fig. 2. (a) Histograms of all methane fluxes. The outer graph shows all fluxes and the inner graph shows fluxes from −15 to 100 g m^{-2} day^{-1}. (b) Histogram of all oxidation results at all sites.

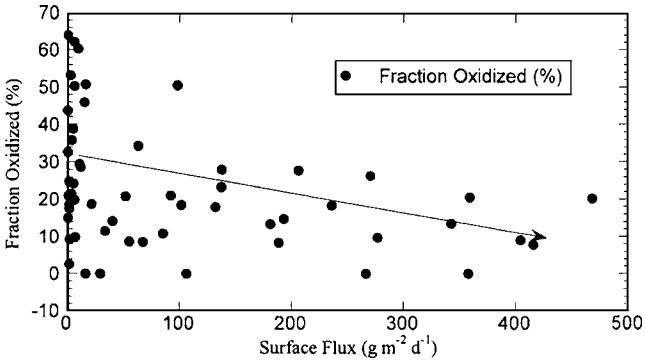

Fig. 3. Nonzero positive flux versus fraction oxidized at all sites

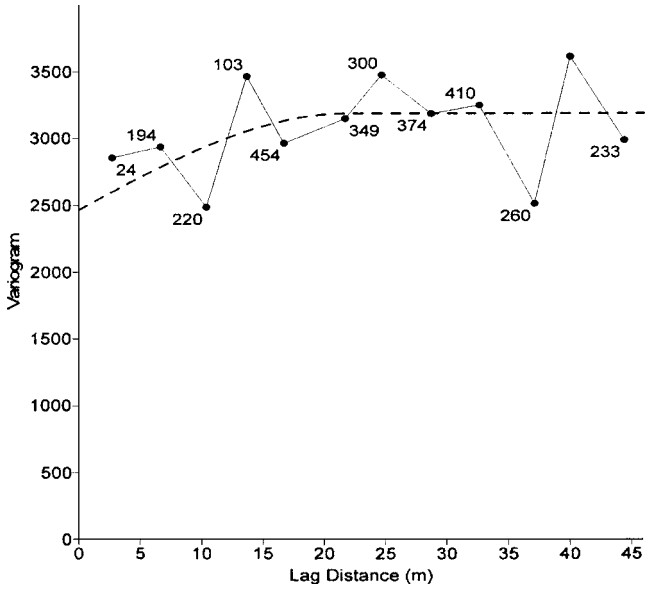

Fig. 4. Variogram of methane flux data for the S1-Grid site along with a spherical model (parameters listed in Table 2).

the CH_4 oxidation data set [$n=61$, Fig. 2(b)] shows that the distribution is not as skewed as the distribution of the flux data [Fig. 2(a)]. The histogram shows a central tendency and has a mean of 22.1%, a median of 18.8%, and a standard deviation of 16.8%. The mean percent oxidation was 25.2% for Site S1-Grid, 19.5% for Site 1, 26.6% for Site 2, and 14.4% for Site 3. The median oxidation measured was 20.9% for S1-Grid, 16.6% for Site 1, 26.6% for Site 2, and 14.7% for Site 3. These medians were very similar to the means, a further indication of the central tendency of the distribution of the oxidation data. The lowest oxidation values (mean and median) were measured in the area covered with daily cover (Site 3). However, when an analysis of variance was performed on the oxidation data, the ANOVA analysis showed that there were no significant differences in oxidation between the four sites (F value was 0.99; $df=3, 57$; $p=0.405$).

Fig. 3 shows fraction oxidized versus measured surface flux. In general, higher oxidation is associated with lower surface flux. Fraction oxidized higher than 20% did not occur when surface flux was higher than 300 g m^{-2} day^{-1}. Fraction oxidized higher than 30% did not occur when surface flux was higher than 200 g m^{-2} day^{-1}. No correlation was observed between oxidation and either water content or soil temperature. However, the lack of correlation is probably due to the fact that the data were collected from several sites and during a limited time period. Additional measurements are being performed in the S1-Grid site to investigate the effects of water content and temperature on oxidation.

Spatial Variability

Methane fluxes from landfills are not spatially uniform; rather there are hot spots where gas bubbles can often be seen in wet conditions. Consequently, taking the average of flux measurements may not accurately represent flux from a large area. Some method of accounting for spatial variability is required. IDW and kriging are two commonly used interpolation methods.

The spatial structure of methane flux in S1-Grid was evaluated by fitting a model to the variogram (Fig. 4); and using the model (Table 3) to generate an interpolated contour plot by kriging (Fig. 5). *SURFER* (2002) software was used for the variogram and contour plots. The range was 35 m in the anisotropy direction (100.1°, ratio=1.6). This anisotropy indicates that fluxes were more similar in the 100.1° direction, which in this case is E10.1°N. Anisotropy indicates there is a directional component of the source or transmission of methane, for example, how waste was placed in the landfill. The variance between sample locations was high even at the closest separation (2.69 m), resulting a nugget that is 77% of the model sill. A similarly large relative nugget appeared to be used by Borjesson et al. (2000), although the exact parameters were not reported. Spokas et al. (2003) used a nugget that was 42% of the sill, although there were serious deviations in the model at short lag distances. Point kriging was used with the variogram model to construct the flux contours for the entire S1-Grid (Fig. 5). Kriged contours do not reach the highest peaks and valleys of the data, because one of the underlying assumptions in kriging is that a nugget indicates uncertainty about the true value of the data points, giving more influence to the overall variance.

IDW parameter values listed in Table 3 were used with the same flux data to generate the contours shown in Fig. 6. In this case the general flux level is between 10 and 30 g m^{-2} day^{-1} with numerous valleys of lower flux and a few peaks of very high flux. It is likely this pattern is artificial because the spacing of the peaks and valleys are set by the sampling interval, not the natural spatial structure. IDW provides a good estimate of the local spatial structure around individual points.

Table 3. Comparison of Kriging and IDW Methods of Interpolating Spatial Methane Flux Data for S1-Grid

Parameters	Kriging	IDW
Model	Spherical	Inverse distance squared
Nugget	2,468	NA
Scale	724	NA
Range (m)	35	NA
Anisotropy angle (deg)	100.1	100.1
Anisotropy ratio	1.6	1.6
Geospatial mean[a] (g m^{-2} day^{-1})	20.92	20.80
Cross-validation residual mean square[b]	4,392	3,301
Model residual mean square[b]	2,342	0.6[c]

Note: NA=not applicable.

[a]Volume enclosed by the model divided by the area.

[b]See the text for definitions.

[c]IDW has zero model residual by definition; the small calculated residual is due to computing errors.

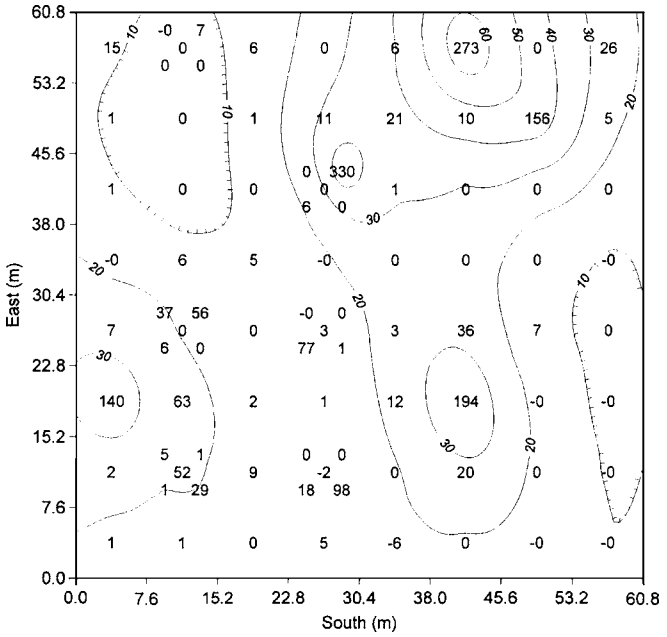

Fig. 5. Methane flux contours for the S1-Grid obtained using kriging

The quality of kriging and IDW interpolation methods were evaluated by comparing geospatial means (the volume enclosed between the model surface and zero, divided by the area), and by cross validation and model residuals (Table 3). For the S1-Grid, the geospatial means were almost identical (20.9 g m^{-2} day^{-1} with kriging and 20.8 g m^{-2} day^{-1} with IDW), indicating that there is little difference between kriging and IDW by this measure. In cross validation, model errors were calculated by removing an observation from the data set, and using the remaining data and the model to interpolate a value at that location. The error or residual is the difference between the interpolated value and the observed value (*SURFER* 2002). The mean square of the IDW cross-validation residuals was about 75% of that for kriging

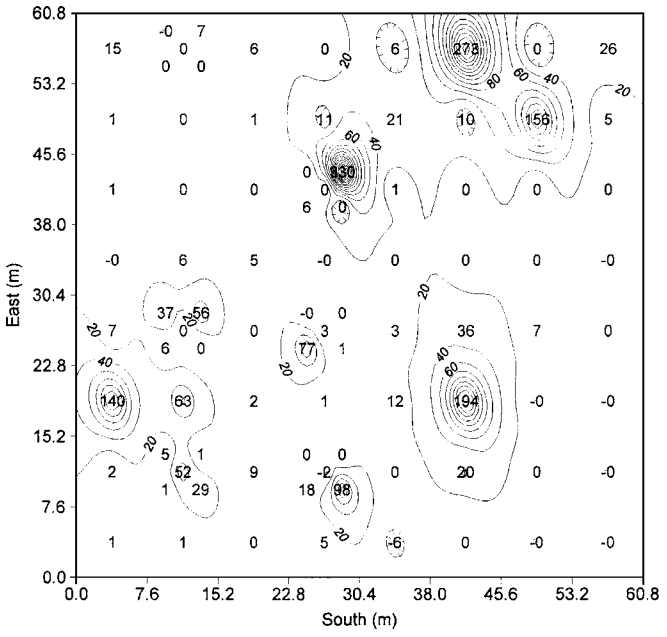

Fig. 6. Methane fluxes contours for the S1-Grid obtained using IDW

(Table 3). This indicates that the IDW contours are less dependent than kriging on single-point measurements, are more representative of the overall data, and have better predictive ability. Model residual mean square is a goodness-of-fit indicator (the model residual is the difference between the measured and model value for each point). The IDW surface intersects each measured point resulting in essentially no model residuals, whereas the nugget effect in kriging moderates surface fluctuations resulting in large residuals.

IDW did better than kriging in both residual comparisons (Table 3), indicating that it is the better model for this data set. This is in agreement with the results of Spokas et al. (2003). However, use of a variogram and kriging provide more information about the overall spatial structure and more natural-looking contours. Also, because these data have substantial variability at the smallest separations, the variogram had a large nugget resulting in many poor fits of the kriged contours with the measured values.

There is often a need to find a single number that represents the central tendency of a distribution. Five measures of flux (g m^{-2} day^{-1}) have been presented for the S1-Grid: the median (1.35), the mean (24.5), the geometric mean (6.5), the geospatial mean by kriging (20.9), and the geospatial mean by IDW (20.8). We have the most confidence in the IDW geospatial mean because it accounts for spatial correlation and IDW provided a better fit to these data than kriging. The geospatial mean assumes that nearby values will be highly correlated, which is usually, but not always the case. The arithmetic mean is only 11% greater than the geospatial mean, whereas the geometric mean is 71% less. Statisticians generally recommend using the geometric mean to represent the central value for log-normally distributed, uncorrelated data for the purpose of statistical tests (e.g., Ott 1995). But in this study of log-normally distributed spatial data that was obtained from a uniform grid, the arithmetic mean may be a better indicator of the central value than the geometric mean.

The spatial variability in fluxes over the intensively sampled S1-Grid may be due to underlying methane generation or variations in cover. Because the pressure in the landfill is usually greater than atmospheric, any differences in gas conductivity of the cover will result in great differences in advective macropore flow. Surface cracking of the cover soil was observed, particularly in dry periods. Trash penetration of the cover may also serve as conduits for gas flow. Depth of cover was variable, with depth ranging from 21 to 119 cm in just the 0.37-ha S1-Grid. It is also possible that rainfall softened the clayey cover enough in some areas that the landfill gas pushed vents through it. Shallow depressions in the cover filled with water after a rain, and gas bubbles were observed coming from the bottom of these puddles. This process may explain the significant differences in flux between the top and sides of the landfill. The top is nearly level and probably has greater rainfall infiltration than the sloping sides.

Gas Concentration Profiles

The composition of gas samples collected from the gas probes installed at Sites 1, 2, and 3 provides a snap shot of gas concentration profiles with depth (Fig. 7). Fig. 8 shows variation of the $\delta\ ^{13}C$ and the CH_4 oxidation with depth. All three profiles in Fig. 7 show that at a depth of 70 cm the oxygen concentration is very low indicating the presence of anaerobic conditions. The shape of the concentration curves are similar to results obtained by other researchers such as Scheutz et al. (2003). At Sites 1 and 3, the concentration of methane decreased to less than 1% at a depth of

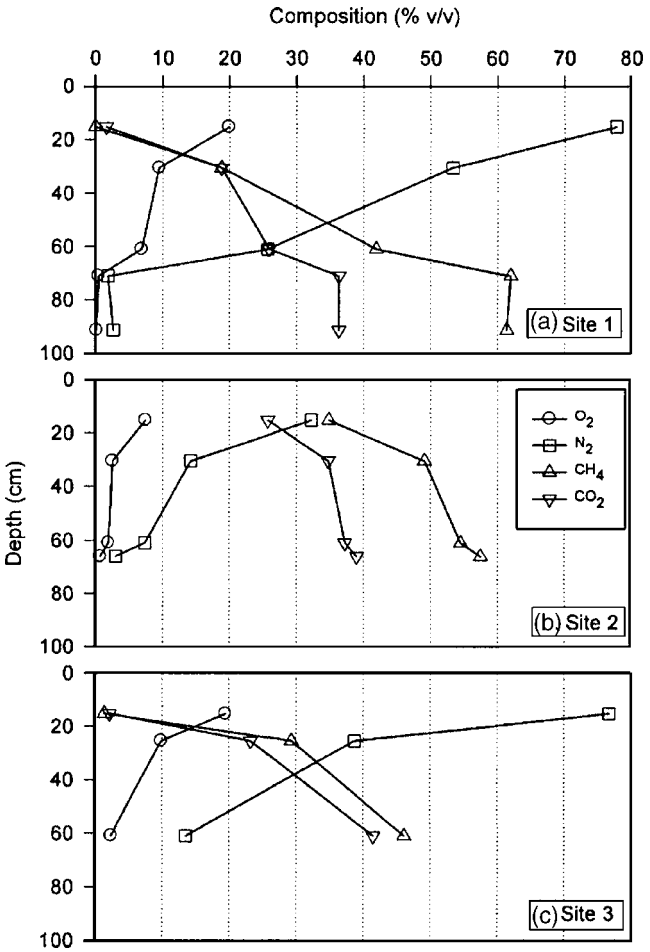

Fig. 7. Profiles of soil gas composition, for Sites 1, 2, and 3

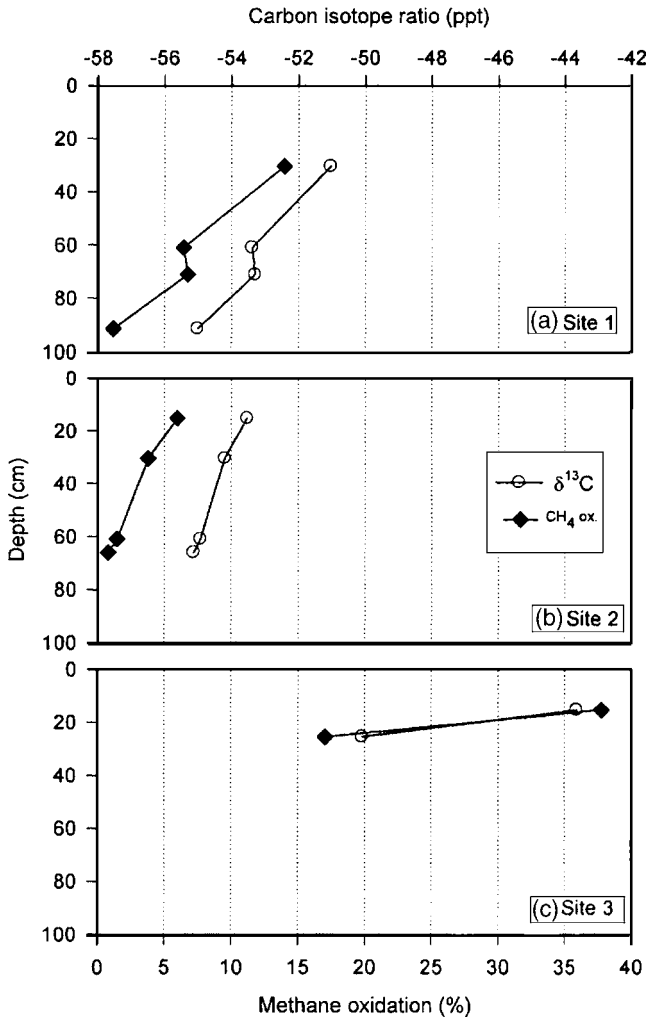

Fig. 8. Profile of δ ^{13}C and methane oxidation for Sites 1, 2, and 3

15 cm, whereas at the same depth in Site 2 it only decreased to around 30%. This is not consistent with the fact that the mean methane oxidation was only 26.6% in Site 2 as compared to 19.5% in Site 1 and 14.4% in Site 3.

The δ ^{13}C of methane increased in the upward direction for all gas probes. δ ^{13}C increased from −55% at a depth of 90 cm to −51% at a depth of 30 cm in Site 1. δ ^{13}C increased from −55% at a depth of 70 cm to −53% at a depth of 15 cm in Site 2. In Site 3 however, δ ^{13}C varied from −50% at a depth of 25 cm to −43% at a depth of 15 cm. No information was available at deeper depths. The increase in δ ^{13}C from bottom to top of the profiles confirms the presence of oxidation in the landfill covers.

In a landfill profile there is an optimum zone for methane oxidation, where oxygen, methane, and moisture concentrations promote methanotrophic growth. In our study the steepest decline in methane concentration may indicate the zone of optimum methane oxidation. Sites 2 and 3 had a relatively shallow optimum zone from approximately 15 to 30 cm, whereas Site 1 had a deep zone from approximately 15 to 70 cm (Fig. 7). Czepiel et al. (1996) tested the oxidation rate in different soil depths with the incubation test and found that the maximum oxidation occurred in the 5–10-cm depth. Visvanathan et al. (1999) found that the maximum oxidation occurs in the depth of 15–40 cm below ground level. Several other researchers found different maximum methane oxidation zones [from 3 to 12 cm (Whalen et al. 1990); between 40 and 60 cm (Nozhevnikova et al. 1993; Borjesson and Svensson 1997); from 20 to 30 cm (Kightley et al. 1995)]. Humer and Lechner (2001) found that in their field scale test the maximum zone to methane oxidation was between 40 and 90 cm in sewage sludge compost and MSW compost.

Practical Implications

The soil cover presently in place on this landfill is oxidizing 22% of the methane passing through it. Certainly there is room for improvement in the efficiency of oxidation by this cover with innovative design approaches and engineering. Before engineering a scheme to improve methane oxidation at the landfill surface, flux an oxidation were characterized. In testing new soil cover designs the chamber technique is currently the most cost effective method of evaluating methane emissions from a relatively confined experimental area. Methane flux varied from −13.6 to 1,755 g m^{-2} day^{-1} in a highly skewed distribution with a mean of 72.3 g m^{-2} day^{-1}. Scaling up these chamber measurements can be accomplished with either kriging or IDW. Geospatial means generated using point kriging and IDW were almost identical, about 11% less than the arithmetic mean, and about 3.4 times the geometric mean. IDW had lower cross validation and model mean square residuals and was considered the more appropriate model and it is easier to use.

Methane emissions were higher (p=0.05) in flat top areas of

the landfill as compared to the sloped areas. The spatial variability in fluxes may be due to variations in underlying methane generation or cover. The cover was observed to crack in dry periods and bubble gas (due to loss of soil cohesion) in wet periods. Trash penetration of the cover may also serve as conduits for gas flow. Because the pressure in the landfill is usually greater than atmospheric, any differences in gas conductivity of the cover will result in great differences in advective macropore flow.

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