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Improved Field Methods to Quantify Methane Oxidation in Landfill Cover Materials Using Stable Carbon Isotopes

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Stable carbon isotopes provide a robust approach toward quantification of methanotrophic activity in landfill covers. The field method often applied to date has compared the $\delta^{13}\text{C}$ of emitted to anaerobic zone CH_4 . Recent laboratory mass balance studies have indicated that this approach tends to underestimate CH_4 oxidation. Therefore, we examined the CH_4 - $\delta^{13}\text{C}$ at various soil depths in field settings and compared these values to emitted CH_4 . At 5–10 cm depth, we observed the most enrichment in CH_4 - $\delta^{13}\text{C}$ (–46.0 to –32.1‰). Emitted CH_4 - $\delta^{13}\text{C}$ was more negative, ranging from –56.5 to –43.0‰. The decrease in CH_4 - $\delta^{13}\text{C}$ values from the shallow subsurface to the surface is the result of processes that result in selective emission of $^{12}\text{CH}_4$ and selective retention of $^{13}\text{CH}_4$ within the soil. Seasonal percent oxidation was calculated at seven sites representing four cover materials. Probe samples averaged greater ($21 \pm 2\%$, $p < 0.001$, $n = 7$) oxidation than emitted CH_4 data. We argue that calculations of fraction oxidized based on soil derived CH_4 should yield upper limit values. When considered with emitted CH_4 values, this combined approach will more realistically bracket the actual oxidation value. Following this guideline, we found the percent oxidation to be $23 \pm 3\%$ and $38 \pm 16\%$ for four soil and three compost covers, respectively.

Introduction

Methane (CH_4) is an important greenhouse gas: the total positive climate forcing attributed to CH_4 over the last 150 years is 40% that of carbon dioxide (CO_2) (1). Over a 20-year time frame, a molecule of CH_4 in the atmosphere has a global warming potential (GWP) approximately 23 times higher than a molecule of CO_2 (2). The high GWP of CH_4 coupled with a relatively short atmospheric lifetime (about 10 years) indicates that current reductions in atmospheric CH_4 sources can significantly lower atmospheric concentrations on decade or shorter time scales. The imbalance between sources and

sinks of CH_4 in the global budget is less than 6% of the total of global sources or perhaps even approaching balance (3, 4). Thus a small decrease in CH_4 emissions could result in stabilization of atmospheric CH_4 or, possibly, a reduction in the atmospheric concentration (5, 6). Because CH_4 is a more potent greenhouse agent than is CO_2 , lowering the atmospheric CH_4 concentration is a very realistic and worthwhile goal. The relatively short residence time of CH_4 in the atmosphere (7–10 years) relative to CO_2 (100 years) means that the effects of mitigation efforts would be rapidly observed.

The 2007 IPCC report (2) indicates that the entire waste sector is responsible for <5% of total global greenhouse gas emissions including CO_2 , CH_4 , N_2O , and other gases. Landfills are responsible for about 3–7% of global CH_4 emissions (5, 7) and are the largest anthropogenic CH_4 source in the United States (8). Landfills represent point sources of CH_4 to the atmosphere and thus are excellent targets for mitigation. At modern larger facilities, gas capture for flaring or power generation reduces emissions significantly. But fugitive emissions from all landfills and total emissions from older and smaller landfills without gas collection systems can be minimized by methanotrophic bacteria in soil layers (biocovers) and biofilters (9, 10). Recently, the approach has received considerable attention (11) including recognition from environmental agencies in Germany and Finland.

Engineers require a reliable approach to quantify the effect of these bacteria so that they may design soil covers to maximize their activity. It is difficult to determine the relative effectiveness of soil cover mitigation, the fraction of CH_4 oxidized. In controlled laboratory experiments, mass balance approaches can be used. With this approach both the CH_4 flux to the bottom of the cover soil (J_{in}) and outflux or emissions (J_{out}) from the surface must be evaluated (12, 13). Another approach is to compare the rate of J_{out} from control and treated areas (9, 14) to estimate changes in the efficiency of CH_4 oxidation by difference. This method suffers from the large spatial and temporal variability observed in CH_4 emissions (13, 15, 16).

One of the most promising ways to estimate the fraction of CH_4 oxidized (f_{ox}) is by the use of stable isotopes (17, 18). The CH_4 stable carbon isotope ratio ($\delta^{13}\text{C}$ ‰) is calculated by (eq 1)

$$\delta = 1000 \left(\frac{R_{\text{sam}}}{R_{\text{std}}} - 1 \right) \quad (1)$$

where R_{sam} is the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample and R_{std} is the ratio for standard Vienna Pee Dee Belemnite (0.01124). Methanotrophic bacteria oxidize $^{12}\text{CH}_4$ at a slightly more rapid rate than that for $^{13}\text{CH}_4$ (19). Calculation of f_{ox} requires only gas samples from the gas source (anoxic zone) and the location of interest and knowledge of the isotope fractionation factor caused by oxidation (α_{ox}).

There are two approaches to calculating f_{ox} from $\delta^{13}\text{C}$ values, both of which rely assumptions about the behavior of the mass of CH_4 . If it is assumed that CH_4 moves as a closed system between source and sampling point and does not mix with other CH_4 , the “simplified Rayleigh approach” (eq 2) (20) may be used to calculate the fraction oxidized at depth z ($f_{\text{ox},z}$)

$$f_{\text{ox},z} = 1 - \left(\frac{\delta_z + 1000}{\delta_{\text{anox}} + 1000} \right)^{\frac{\alpha_{\text{ox}}}{1 - \alpha_{\text{ox}}}} \quad (2)$$

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where δ_{anox} and δ_z are standard $\delta^{13}\text{C}$ isotope ratios for the anoxic zone and sample depth z or emitted CH_4 . Alternatively, if it is assumed that CH_4 in the porous media is well mixed, an open-system equation (eq 3) (17) may be used to calculate fraction oxidized ($f_{\text{oxo},z}$)

$$f_{\text{oxo},z} = \frac{\delta_z - \delta_{\text{anox}}}{1000(\alpha_{\text{ox}} - \alpha_{\text{trans}})} \quad (3)$$

where α_{trans} is the isotope fraction factor from transport ($\alpha_{\text{trans}}=1$ for purely advective transport and $\alpha_{\text{trans}} > 1$ where diffusion is important (12)). Use of both the closed-system and open-system equations will be examined in this paper.

In controlled laboratory-scale column and biofilter experiments, where J_{in} could be evaluated and CH_4 oxidation directly measured by mass balance, CH_4 oxidation was found to be greater than predicted by isotopic determinations on these same systems. The isotope method using eq 3 gave results that were only 0.25–0.50 of the mass balance (12). Similarly, Powelson et al. (21), in a biofilter study, found that the isotope method using eq 2 gave results that were only 0.36–0.75 of the mass balance. Both studies found differences between fractional oxidation determined by mass balance and by stable carbon isotopes.

In this study, $\delta^{13}\text{C}$ values from CH_4 taken from various depths in landfill covers and biocovers were compared to $\delta^{13}\text{C}$ emitted from the surface. The fraction oxidized was calculated from both data sets. We hypothesized that CH_4 oxidation calculated from samples collected at shallow depths within the soil would be greater than those values obtained from calculations using emitted CH_4 $\delta^{13}\text{C}$ values. We will examine different conceptual models for this hypothesis and propose that determination of the isotopic composition of CH_4 within the soil oxidation layer in addition to the isotopic composition of CH_4 released from the soil can fine tune the isotopic approach to give a better estimate of the extent of CH_4 oxidation for application to future field studies.

Methods

Landfill and Cover Description. Measurements were performed at two areas (sites 1 and 4) at the municipal solid waste landfill in Leon County, Florida, from July 2004 to July 2006 (22–25). The landfill study section was clay-lined, and there was no gas collection system, so waste gases escaped through the cover or the leachate collection pipes. Samples were taken for isotopic analysis approximately monthly for the first year and bimonthly for the second year.

Both sites 1 and 4 had control and treatment plots. At site 1, the waste had been covered for 8 years, had a two-layer interim cover, and was well vegetated. The lower cover consisted of clayey subsoil from Orangeburg soil series ((26), fine-loamy, kaolinitic, thermic Typic Kandudults, average depth 38 cm), which was overlain by 35 cm (average depth) of loamy dredge-spoil from a local lake. The experimental area within site 1 consisted of two rows of three 7.6×7.6 m plots separated by at least 7.6 m. In one row, three “deep compost” biocover plots (dC2, dC4, and dC6) were created by putting a 10 cm gas dispersion layer on each plot and covering the whole row with 47 cm of compost. The dispersion layer consisted of gravel-sized glass cullet from recycled bottles, and the compost was made from chipped yard waste that had been windrowed for three years. In the control row, the three “no compost” control plots (nC2, nC4, and nC8) were simply marked off on the existing cover. Each plot had one probe nest and four surrounding chamber collars. This experiment will be referred to as the site 1 compost study. In this paper, our objectives are to compare the $\delta^{13}\text{C}$ of subsurface CH_4 with the $\delta^{13}\text{C}$ of emitted CH_4 . As emissions were only infrequently observed at compost cells dC4 and dC6, we will not consider them further.

In the second study area (site 4, Mulch study), the waste had been covered for 1 year, had a 15 cm temporary cover, and was poorly vegetated. The cover material was clayey Orangeburg subsoil. The experimental area consisted of three adjacent 32×18 m plots. The deep mulch biocover plot (dM) had a 13 cm gas dispersion layer, overlain by 60 cm of mulch. The shallow mulch biocover plot (sM) had a 13 cm gas dispersion layer overlain by 30 cm of mulch. The no-mulch control plot (nM) had nothing over the existing cover. The gas dispersion layer consisted of thin glass chips from crushed fluorescent tubes, and the mulch consisted of freshly chipped yard waste. One probe nest and three surrounding chamber collars were established in each plot.

Sampling and Analysis. The probes consisted of stainless-steel tubing that varied from 3.2 to 9.5 mm outer diameter. The bottom of the tubes were crimped and cut to a point, and small holes were drilled in the side just above the bottom to permit collection of gas. The probes were hammered to the desired depth, ranging from 5 to 122 cm. The probes were separated horizontally by 5–10 cm. After the probes were flushed, 30 mL gas samples were injected into evacuated vials.

The chambers consisted of two aluminum sections: a lower collar that was inserted approximately 5 cm into the cover and left in place and an upper chamber that was sealed to the collar when flux measurements were made. The collars enclosed an area of 63×63 cm. The upper chamber had a battery-powered fan to mix the enclosed gas and a sampling tube. Samples were collected using the static chamber method. Two samples for isotope analysis were taken from the chamber at each sampling time: the initial sample as soon as the chamber was sealed to the collar and the final sample after 30–45 min. The chamber isotope ratio emitted at the surface (δ_0) was determined from the initial and final samples (eq 4)

$$\delta_0 = \frac{\delta_F \varphi_F - \delta_I \varphi_I}{\varphi_F - \varphi_I} \quad (4)$$

where δ_I and δ_F are the initial and final carbon isotope ratios, respectively, and φ_I and φ_F are the initial and final CH_4 volume fractions, respectively. Samples for CH_4 volume fraction determination were kept in 60 mL plastic syringes and analyzed within 6 h using a Shimadzu 14A gas chromatograph with a flame ionization detector and Carbosphere column. Scott Specialty gas was used as a standard. Samples for isotope analysis were injected into evacuated vials. δ was measured by a Hewlett-Packard gas chromatograph coupled via a combustion interface to a Finnigan Mat Delta S isotope ratio mass spectrometer (GCC-IRMS).

Results and Discussion

Samples from the deepest probes had the lowest $\delta^{13}\text{C}$ values, representing landfill gas before oxidation in the cover, δ_{anox} . These values remained relatively constant, ranging from -56.6 to -52.8‰ (Table 1). For use in eqs 2 and 3, δ_{anox} was determined for each location separately by averaging the deepest measured δ value. The value used for α_{ox} (1.024) was determined from incubation experiments using mulch and soil inoculated with water from the study site (24).

At more shallow depths, the $\delta^{13}\text{C}$ of CH_4 usually increased, with the highest values occurring at the 5 and 10 cm depths, ranging from -46.0 to -32.1‰ (Figure 1). The $\delta^{13}\text{C}$ values for captured emitted CH_4 (circled point at 0 depth, Figure 1) were consistently more negative than those observed at shallow (5 to 10 cm) depths, and ranged from -56.5 to -43.0‰ . It is somewhat surprising that emitted CH_4 - $\delta^{13}\text{C}$ was more negative than shallow subsurface CH_4 - $\delta^{13}\text{C}$, because one would expect additional oxidation in the soil between the soil–air surface and the shallow subsurface. For brevity, only

TABLE 1. Summary Statistics of $\delta^{13}\text{C}$ and Estimated Fraction of CH_4 Oxidized by Closed-System (f_{oxc}) and Open-System (f_{oxo}) Equations for the Compost and Mulch Studies^a

location and depth (cm)	material	n	mean $\delta^{13}\text{C}$ (‰)	std error $\delta^{13}\text{C}$ (‰)	mean f_{oxc}	mean f_{oxo}
no compost control site 1						
0	emitted	99	-50.56	0.67	0.1198	0.1540
9	sediment	30	-44.26	1.58	0.3138	0.4119
16	sediment	37	-44.28	1.35	0.3171	0.4113
28	sediment	43	-47.93	0.85	0.2251	0.2614
41	subsoil	48	-49.64	0.98	0.1545	0.1913
51	subsoil	42	-50.18	0.85	0.1449	0.1693
73	subsoil	62	-52.40	0.40	0.0731	0.0784
107	waste	17	-54.31	0.15	-0.0004	0.0000
deep compost site 1						
0	emitted	22	-43.80	2.24	0.2877	0.3978
10	compost	9	-39.56	2.02	0.4410	0.5716
20	compost	9	-44.97	1.93	0.2941	0.3500
40	compost	12	-49.72	1.78	0.1284	0.1550
60	sediment	11	-48.33	2.58	0.1549	0.2120
110	subsoil	6	-53.51	0.64	-0.0021	0.0000
no mulch control site 4						
0	emitted	30	-50.67	0.73	0.0776	0.0879
5	subsoil	8	-42.92	3.00	0.3170	0.4054
10	subsoil	12	-42.58	1.91	0.3383	0.4193
20	waste	16	-48.59	1.44	0.1473	0.1730
30	waste	14	-50.62	0.81	0.0854	0.0898
40	waste	11	-51.02	0.59	0.0729	0.0732
60	waste	10	-51.12	0.46	0.0704	0.0693
80	waste	4	-52.81	0.51	-0.0008	0.0000
shallow mulch site 4						
0	emitted	21	-56.46	1.01	-0.0146	0.0061
5	mulch	13	-46.02	1.10	0.3655	0.4342
10	mulch	14	-46.44	1.22	0.3505	0.4168
20	mulch	14	-51.05	1.35	0.2014	0.2281
30	glass cullet	15	-53.30	0.75	0.1302	0.1358
41	subsoil	15	-54.08	1.19	0.0883	0.1038
70	waste	14	-55.54	0.23	0.0458	0.0438
101	waste	15	-56.61	0.07	-0.0001	0.0000
deep mulch site 4						
0	emitted	21	-45.37	1.10	0.3988	0.4933
5	mulch	14	-33.64	2.45	0.5695	0.8580
10	mulch	13	-32.06	2.83	0.5938	0.9225
20	mulch	15	-41.37	1.42	0.4252	0.5410
30	mulch	15	-42.00	1.86	0.4009	0.5151
40	mulch	15	-43.34	2.23	0.3574	0.4603
50	mulch	14	-46.62	1.09	0.2854	0.3257
62	glas cullet	18	-48.08	1.03	0.2363	0.2659
100	waste	5	-53.28	2.33	0.0349	0.0528
122	waste	18	-54.57	0.42	-0.0032	0.0000

^a No compost combines the three no-compost control plots (nC2, nC4, and nC8), and deep compost is just dC2 because dC4 and dC6 did not have adequate emitted methane. Slightly negative f_{oxc} values at depth are due to the nonlinear form of eq 2.

data from site 1 are shown in Figure 1. Site 4 results appeared to be very similar.

Paired t tests were performed to ensure that the difference between surface and subsurface CH_4 - $\delta^{13}\text{C}$ were significant (Figure 2). In these tests, only values that were taken on the same date were paired. Consequently, variability from environmental factors was minimized by this method, but not all the data could be paired and used because of occasional missing values. The difference, $\delta_z - \delta_0$, is the average difference and is negative if the CH_4 - $\delta^{13}\text{C}$ value for emitted CH_4 is more positive than the value at a particular depth, as should be expected if oxidation alone is driving isotopic variability. This is generally the case up to a depth of about 30 cm (Figure 2). Above this point, $\delta_z - \delta_0$ was greater than zero in every case, and this difference was significant in 12 of 19 t tests indicating some other process was controlling the isotopic distribution in addition to methanotrophy. De Visscher et al. (12) also observed a

maximum $\delta^{13}\text{C}$ in the shallow subsurface in column and field measurements.

Three possible mechanisms for the decrease in CH_4 - $\delta^{13}\text{C}$ from shallow depth to the surface are: (1) diffusive fractionation, (2) bypass mixing, and (3) differential flow path oxidation. Each of these cases could result in an isotope effect such that a sample of soil gas CH_4 collected with a shallow subsurface probe will be ^{13}C enriched relative to a sample of CH_4 emitted from the surface collected with a chamber. Each case will be discussed below.

(1) De Visscher et al. (12) attributed the subsurface peak in soil CH_4 - $\delta^{13}\text{C}$ relative to emitted CH_4 as being caused by diffusive fractionation. The $^{12}\text{CH}_4$ diffuses from the soil at a 1.9% faster rate than $^{13}\text{CH}_4$ because of a difference in their respective diffusion coefficients in air. This leads to the preferential release of $^{12}\text{CH}_4$ and results in the underestimation of CH_4 oxidation rates based upon the difference between anoxic zone CH_4 and emitted CH_4 . If $^{12}\text{CH}_4$ is released from

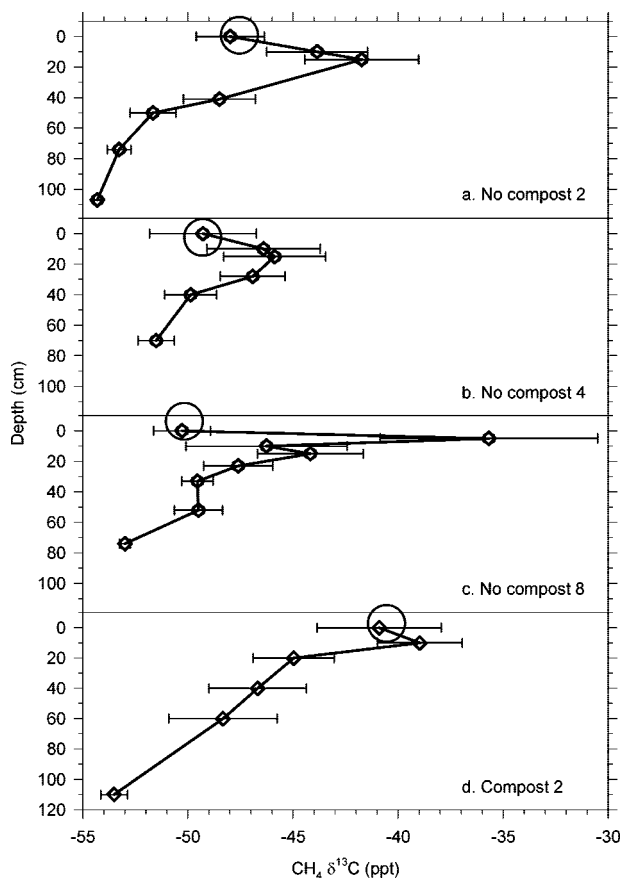


FIGURE 1. Methane seasonally averaged $\delta^{13}\text{C}$ depth profiles and standard error bars for three plots (a, b, c) in the site 1 control area (no compost) and in the site 1 compost plot where CH_4 was emitted (d). The circled symbol at “0” cm depth represents emitted CH_4 , captured within a closed chamber, while other symbols represent probe-collected gas from soil. Replicates represent 7–10 separate sampling dates from July 2004 to May 2006. Methane concentration profiles are shown in the Supporting Information.

the soil preferentially, then residual, left-behind soil- CH_4 is enriched in ^{13}C by this mechanism. If the ^{13}C enrichment of CH_4 in soil–air is caused by the combination of both CH_4 oxidation and diffusive fractionation then probe samples provide upper limit estimates of CH_4 oxidation.

Similar effects have been observed in the lacunar spaces of aquatic macrophytes that transport CH_4 from CH_4 rich wetland soils via diffusive transport (27, 28). Within these plants, enrichment of $\delta^{13}\text{C}$ has been frequently observed, yet CH_4 emitted from the plants is more negative than the lacunal CH_4 . Harden and Chanton (29) demonstrated that mass-dependent fractionation was controlling this behavior using a gas mixture of ethane and propane injected into lacunar spaces. Ethane was emitted preferentially while propane was left behind and enriched within internal spaces.

(2) It is also possible that emitted CH_4 - $\delta^{13}\text{C}$ is controlled by the mixture of oxidized CH_4 (enriched $\delta^{13}\text{C}$) released from the soil matrix and anoxic CH_4 (depleted $\delta^{13}\text{C}$) that reaches the surface through macropores, thereby bypassing methanotrophic oxidation. The probe samples may not have included macropore flow because the process of hammering in the probes compressed the soil around the tip, thereby sealing any macropores. Bypass flow can also occur along the sides of soil columns, which could also explain the decline in δ from subsurface to emitted values observed in ref 12.

(3) Finally, considering that the gas migration may occur by multiple flow paths, if a portion of the gas sampled at

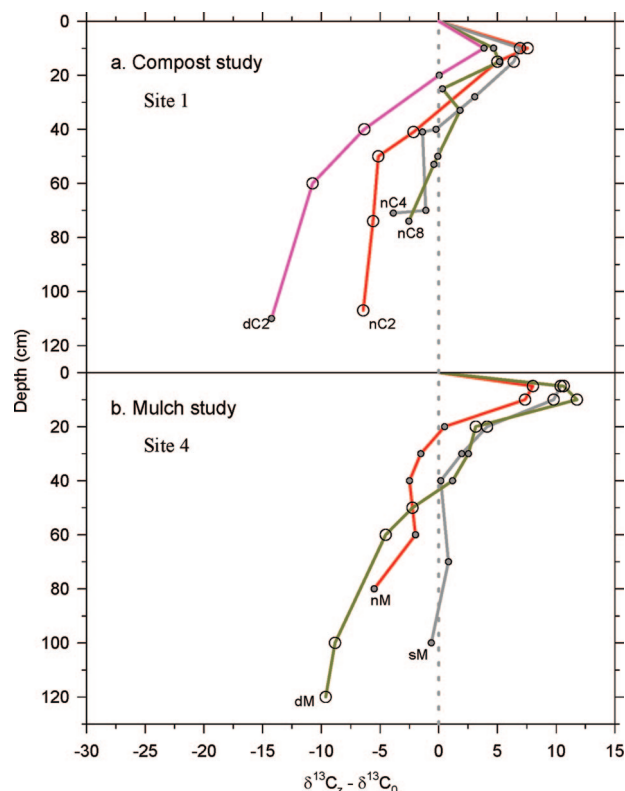


FIGURE 2. Difference between $\delta^{13}\text{C}$ - CH_4 at a given depth ($\delta^{13}\text{C}_2$) and the emitted $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_0$) for the site 1, compost (upper panel a) and site 4, mulch (lower panel b) studies. The open circles indicate that the difference is significant (paired t test, $p = 0.05$), and the small dots indicate that the difference is not significant. Treatments are labeled near the bottom of each curve (nC2, nC4, and nC8 are no-compost plots; dC2 is the compost plot; nM is no mulch; sM is shallow mulch; and dM is deep mulch). Difference represents data from 7–10 separate sampling dates from July 2004 to May 2006.

shallow depths was completely oxidized before reaching the surface, the very high $\delta^{13}\text{C}$ value of this gas (just before it was used up) would not contribute to the emitted CH_4 - $\delta^{13}\text{C}$ value. Complete oxidation of a portion of the flow would thus result in more negative emitted CH_4 isotopic values than are truly representative of the amount of CH_4 actually oxidized. Completely oxidized or “dead end” flow is not represented in the emitted CH_4 and also represents the slowest path of gas transport, in contrast to bypass flow, which represents the fastest path. Completely oxidized flow can be a significant portion of J_{in} , from 48% to 62% (21). This factor is more important in low-flow situations than in higher-flow experiments (12, 21). Complete oxidation of one flow path is not necessary to impact oxidation calculations. If flow paths are oxidized to different extents, the mixing will be nonlinear, and the less-oxidized flow path will be over-represented because of its larger amount of CH_4 , causing an underestimate of CH_4 oxidation.

For the three reasons listed above, a more realistic value of CH_4 oxidation in landfill cover soils may be obtained by sampling both emitted and below-ground CH_4 . We hypothesize that the capture and determination of emitted CH_4 yields a lower-limit estimate, while the probe samples yields an upper limit estimate.

Examination of CH_4 oxidation for site 1 (Figure 3) calculated with eq 2 for chamber and probe CH_4 captured simultaneously support our hypothesis. Methane oxidation percents calculated from probe samples are consistently greater than percents calculated from emitted CH_4 isotopic values by averages over the study period of 23, 22, 22, and

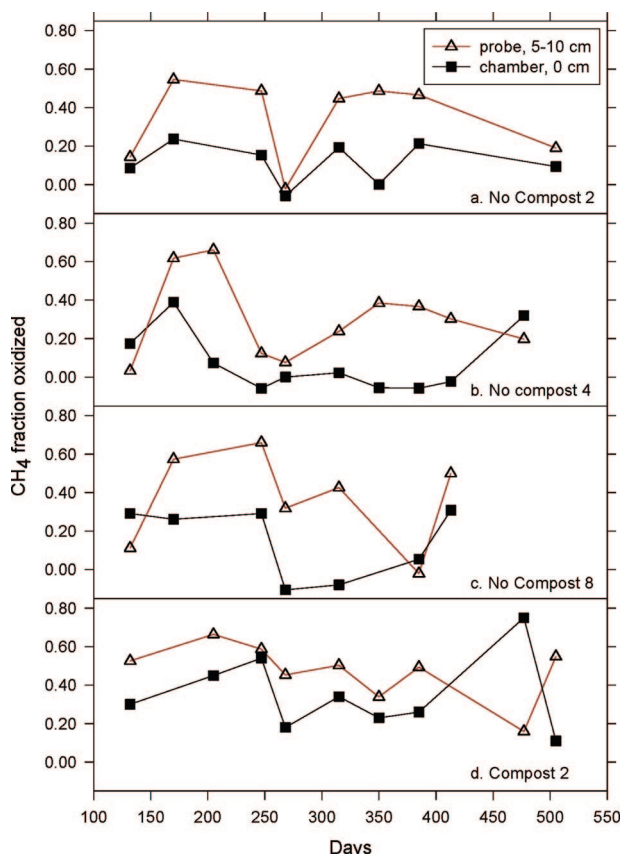


FIGURE 3. Time series of CH_4 fraction oxidized (f_{oxc}) versus days after application of compost at site 1 area dC2. f_{oxc} was calculated with $\alpha_{\text{ox}} = 1.0244$ and $\delta_{\text{anox}} = -54.55$. (eq 2). Dates run from July 2004 to May 2006. The probe values (open triangles) were not replicated. Emitted methane (chamber) values represent 1–4 replicates as follows: panel a from left to right 1,2,4,4,3,4,4,4; panel b 1,2,3,3,2,3,3,3,1; panel c 1,1,4,3,2,2,3; panel d 2,1,2,4,3,3,2,1,3.

TABLE 2. Percent Oxidation Calculated with Eq 2 for Emitted (Chamber Collected) CH_4 , Surface Soil Probe-Collected CH_4 and Difference^a

location	emitted	probe	difference	significant
site 1				
2B control	11.5	34.3	22.8	yes, $p < 0.001$
4B control	7.8	30.3	22.2	yes, $p = 0.008$
8B control	14.6	36.7	22.1	yes, $p = 0.035$
2D compost	35.8	47.5	12.4	no, $p = 0.155$
site 4				
NM control	15.1	35.0	20.8	yes, $p < 0.001$
SM mulch	7.0	36.3	29.4	yes, $p < 0.001$
DM mulch	43.4	62.0	18.6	yes, $p < 0.001$

^a The data represent seven different sites and four different cover types. All values are averaged over the study period. Difference is (percent oxidation probe) – (percent oxidation chamber) averaged over each monthly sampling. All values are in percent. The average of the differences between probe and emitted methane oxidized was significant, $21 \pm 2\%$, paired t test $p < 0.001$, $n = 7$.

12% for areas 2B, 4B, 8B, and 2D, respectively (Table 2). For site 4 (data not presented graphically), the percent oxidation average over the study period shallow probe results were 21, 29, and 19% greater than the average percent oxidation calculated from emitted CH_4 - $\delta^{13}\text{C}$ for areas nM, sM, and dM (Table 2). These differences were significant in six of seven cases (Table 2). These results represent seasonally averaged

data from seven different sites and four different cover materials. Taking the data set as a whole (the mean of the averaged results from the seven sites), the probe samples yielded significantly greater ($21 \pm 2\%$, paired t test $p < 0.001$) percent oxidation than emitted CH_4 data.

We conclude that emitted CH_4 - $\delta^{13}\text{C}$ consistently indicates less CH_4 oxidation than CH_4 captured 5–10 cm deep in the soil. As argued above, emitted CH_4 may provide an underestimate of CH_4 oxidation, while probe CH_4 may provide an overestimate. We hypothesize that the true extent of CH_4 oxidation occurring in the soil is bracketed by the values in Table 2. Using the average of the emitted and probe determined percent oxidation for each cover (Table 2), we find that seasonal percent oxidation varied from 19–23% in the site 1 control areas (2B, 4B, 8B), was 25% at the site 4 control area (NM), and was 22% (site 4, SM), 42% (site 1, 2D), and 52% (Site 4, DM) at the compost and mulch treated areas. Overall, we found the percent oxidation to be $23 \pm 3\%$ and $38 \pm 16\%$ for soil and compost covers, respectively. The treatment covers were 30, 47, and 60 cm thick, respectively. The mean percent oxidation for the two thicker compost covers was 47%. The thicker biocovers covers had double the percent oxidation of the soil covers. The 30 cm mulch cover was not effective.

We recommend that field programs that wish to quantify CH_4 oxidation should immediately begin to collect probe samples in parallel with chamber samples. Next to each chamber, a probe samples should be collected at 10 cm depth. Methane oxidation should be evaluated from the combination of these values.

Acknowledgments

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Supporting Information Available

Methane seasonally averaged concentration profiles and standard error bars for three plots (a, b, c) in the site 1 control area (no compost) and in the site 1 compost plot where methane was emitted (d). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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