

Methane Oxidation in Biofilters Measured by Mass-Balance and Stable Isotope Methods

D. K. POWELSON* AND J. P. CHANTON
*Department of Oceanography, 0102 OSB, West Call Street,
 Florida State University, Tallahassee, Florida 32306*

T. ABICHOU

*Department of Civil and Environmental Engineering, The
 Florida A&M University and Florida State University College
 of Engineering, 2525 Pottsdamer Street, Tallahassee, Florida
 32310*

Simultaneous flux and isotope measurements on compost and sand biofilters showed that the fraction of CH₄ oxidized, calculated from δ¹³C measurements using a closed system model ($f_{\text{oxir,C}}$), averaged only 0.455 of the fraction oxidized based on mass-balance measurements (f_{oxm}). The discrepancy between f_{oxm} and $f_{\text{oxir,C}}$ may be partly due to complete oxidation of a portion of the inflow gas, thereby eliminating its contribution to the emitted methane on which isotopic measurements are conducted. To relate $f_{\text{oxir,C}}$ and f_{oxm} a simple binary closed-system model is proposed that assumes that $f_{\text{oxir,C}}$ refers to only part of the inflow, P , and that the remainder of inflow $(1 - P)$ is completely oxidized before reaching the outlet. This model is compared to the standard open-system model. The H-isotope fraction oxidized ($f_{\text{oxir,H}}$) was determined for a subset of samples and found to be not significantly different from $f_{\text{oxir,C}}$. The carbon isotope fractionation factor, $\alpha_{\text{ox,C}} = 1.0244$, and the H-isotope fractionation factor, $\alpha_{\text{ox,H}} = 1.2370$, were determined by incubation studies. δ¹³C measurements indicated that the emitted flow was more strongly oxidized by the compost biofilters ($f_{\text{oxir,C}} = 0.362$, $f_{\text{oxm}} = 0.757$) than the sand biofilters ($f_{\text{oxir,C}} = 0.222$, $f_{\text{oxm}} = 0.609$).

Introduction

Methane emissions from landfills need to be reduced because a mole of CH₄ has 23 times the global warming potential of a mole of CO₂ over the next 20 years (1), and landfills are responsible for about 7% of CH₄ emissions (2). Biofilters can be used to oxidize landfill gas from point sources such as vents and are especially useful to treat landfill emissions that are not oxidized by flaring or power generation (3). Non-point sources of landfill gas such as a landfill surface may be treated with biocovers (4). Biofilters and biocovers use methanotrophic bacteria to convert CH₄ and O₂ to CO₂, H₂O, and biomass.

Better methods are needed to evaluate treatments that reduce landfill CH₄ emissions. The most rigorous method is to find the mass-balance or flux-based fraction oxidized (f_{oxm}) from influx (J_{in} , g m⁻² d⁻¹) and out-flux (J_{out} , g m⁻² d⁻¹) measurements of CH₄:

$$f_{\text{oxm}} = 1 - \frac{J_{\text{out}}}{J_{\text{in}}} \quad (1)$$

For pipe-fed contained biofilters J_{in} can be determined using flow and concentration measurements. It can sometimes be difficult to determine biofilter J_{in} in a field setting, however, because of large short-term variations in flow (5). Methods to determine J_{out} are well established, including dynamic and static chambers (6), and can be applied to biofilters. The relative effectiveness of biocovers is more difficult to determine because J_{out} for a large area must be estimated. One approach is to compare samples of J_{out} from control and treated areas (3, 4). This method suffers from the large spatial and temporal variability of J_{out} (7, 8). Atmospheric tracer dilution (7, 9) and micrometeorological measurements (10) have been used to estimate methane emissions from large areas, and laser infrared adsorption is being developed to measure the integrated methane concentration that can be combined with vertical wind velocity to determine J_{out} (11). There is still a need to compare emission rate to input rate to determine methane oxidation, and we are not aware of any way to directly measure J_{in} for landfill biocovers.

One of the most promising ways to determine the fraction of CH₄ oxidized without measuring J_{in} or J_{out} is by the use of stable isotopes (12–14). Methanotrophic bacteria oxidize CH₄ with lighter isotopic composition faster than CH₄ with heavier isotopic composition (15). Qualitatively, the greater the difference between the isotope ratios of input and output samples, the greater the amount of oxidation has occurred. Only input and output gas samples and the isotope fractionation factor, α_{ox} , are required. If it is assumed that CH₄ moves as a closed system between inlet and outlet and does not mix with other CH₄, the “simplified Rayleigh approach” (16) may be used to calculate the fraction oxidized:

$$f_{\text{oxir}} = 1 - \left(\frac{\delta_{\text{out}} + 1000}{\delta_{\text{in}} + 1000} \right)^{\alpha_{\text{ox}}/1 - \alpha_{\text{ox}}} \quad (2)$$

where δ_{in} and δ_{out} are the input and output standard isotope ratio. The carbon isotope ratio (‰) is calculated by:

$$\delta^{13}\text{C} = 1000 \left(\frac{R_{\text{sam}}}{R_{\text{std}}} - 1 \right) \quad (3)$$

where R_{sam} is the ¹³C/¹²C ratio of the sample and R_{std} is the ratio for standard Vienna Pee Dee Belemnite (0.01124). The hydrogen isotope ratio, δ²H, is calculated in the same way using the ²H/¹H ratio for standard mean ocean water (0.0001558) for R_{std} . f_{oxir} can be calculated for C or H.

Alternatively, if it is assumed that CH₄ in the biofilter or soil is well mixed, an open system equation may be used to calculate fraction oxidized (12, 15, 17):

$$f_{\text{oxio}} = \frac{\delta_{\text{out}} + \delta_{\text{in}}}{1000(\alpha_{\text{ox}} - \alpha_{\text{trans}})} \quad (4)$$

where α_{trans} is the isotope fraction factor due to transport ($\alpha_{\text{trans}} = 1$ for purely advective transport and $\alpha_{\text{trans}} > 1$ where diffusion is important (15)). Spokas et al. (18) used eq 4 and carbon isotopes from three landfills, and found oxidation in the cover ranged from 4% to 50%.

De Visscher et al. (15) found that f_{oxio} was always less than f_{oxm} when α_{trans} was assumed to equal one, with $f_{\text{oxio}}/f_{\text{oxm}}$ ranging from 25 to 50%. They used $\alpha_{\text{trans}} > 1$ to reconcile f_{oxio} to f_{oxm} by accounting for the effect of diffusion on the isotopic

* Corresponding author phone: 850-645-6925; fax: 850-644-2581; e-mail: powelson@end.fsu.edu.

composition of emitted methane. Diffusion will reduce the measured difference between δ_{out} and δ_{in} for the same amount of oxidation, thus resulting in a lower calculated value of f_{oxio} (eq 4), if it is not accounted for, that is if α_{trans} is assumed to be 1. Their model is based on dilution of the emitted isotope ratio by $^{12}\text{CH}_4$ that diffuses from the biofilter faster than $^{13}\text{CH}_4$, thereby reducing the isotopic fractionation observed. This approach is elaborated in De Visscher and Van Cleemput (19) to include methanotrophic growth. Diffusive fractionation of CH_4 in biofilters undoubtedly occurs, and can explain the smaller oxidation percentage calculated from isotopic data using eq 4 and assuming $\alpha_{\text{trans}} = 1$. However, in this paper we describe a second possibility: that flow partitioning in an advective transport system also impacts calculation of the isotope-based fraction oxidized.

This study made simultaneous measurements of methane f_{oxm} and C and H isotopic composition of inflow and outflow gas in two types of biofilter. C and H isotope fractionation factors, α_{oxC} and α_{oxH} , were determined by incubation studies to calculate f_{oxir} and f_{oxio} , and these were compared to f_{oxm} . Because f_{oxir} and f_{oxio} ($\alpha_{\text{trans}} = 1$) were almost always less than f_{oxm} , we propose a model that partitions gas flow into completely oxidized and partially oxidized streams to correct for the difference.

Materials and Methods

Incubation Study. Four 1-L flasks were used in two incubation studies to determine α_{oxC} and α_{oxH} . Two flasks contained media from the sand biofilters (dry mass 142 g each and water content $0.120 \text{ g g}_{\text{dry mass}}^{-1}$) and two contained media from the compost biofilters (dry mass 43.2 g each and water content $0.825 \text{ g g}_{\text{dry mass}}^{-1}$). The flasks were dosed with 6% CH_4 in air weekly for a month before the experiment to increase the population of active methanotrophs. The first incubation study was designed to start with 7% CH_4 and the second was designed to start with 24% CH_4 in air to approximate conditions in the active oxidation zone of a landfill biofilter after diffusive mixing. These initial concentrations required some way to control the gas volume and pressure in the flask to prevent large changes in pressure after adding CH_4 and due to the consumption of oxygen. Over- or under-pressures affect dissolved gas concentrations and thus the availability of CH_4 and O_2 to methanotrophs. To achieve this control, a water-filled helium-quality latex balloon was suspended in the flask and connected to a manometer outside the flask (Supporting Information, Figure S1). The flasks were incubated at 22°C and six samples were taken in vials over the next 23 h after restoring the flasks to atmospheric pressure with oxygen before sampling.

Methane concentrations were determined by injecting subsamples from the vials into a TCD-GC (Shimadzu GC-8A with CRT 1 column). Further subsamples were used for isotopic analysis. The isotope fractionation factor due to oxidation, α_{ox} , was calculated by plotting the logarithm of CH_4 concentration (ppmv) on the y -axis and $\log(\delta + 1000)$ on the x -axis, and finding the slope of the regression (15):

$$\alpha_{\text{ox}} = \frac{\text{slope}}{1 + \text{slope}} \quad (5)$$

Biofilters. Two biofilter designs located at an outdoor facility were used in this study: a compost-based design (2 replicates, N and S) and a water-spreading sand design (2 replicates, E and W). Details of the biofilter methods and full flux results are given in Powelson et al. (20). A compost biofilter consisted of a 1:1 mixture of compost and polystyrene pellets in a 238-L barrel. A roof over the barrel shed rain but allowed air circulation. A water-spreading sand biofilter consisted of finer sand over coarser sand in a mounded ridge design that was open to rainfall. The two-layer arrangement

“spread” water vertically by using capillarity to make the upper layer wetter and the lower layer drier than would occur in a uniform one-layer design. The average air temperature during the study was 25.8°C . The biofilters were fed from below with artificial landfill gas ($53 \pm 2\% \text{CH}_4$ by volume) by mixing the flow from compressed tanks of CH_4 and CO_2 . Oxygen passively diffused in from the top. Methane influx (J_{in} , $\text{g m}^{-2} \text{d}^{-1}$) was determined by measuring flow rate and concentration. Methane out-flux (J_{out} , $\text{g m}^{-2} \text{d}^{-1}$) was determined from the change in methane concentration in the biofilter headspace by the static chamber technique (6) and stochastic diffusion model (21). Sampling for flux determination lasted 86 days, but isotope sampling did not begin until day 21 and only the results from days 21–86 will be discussed in this paper.

Stable Isotope Testing. Biofilter samples for isotopic analysis were taken at the end of flux measurement and inflow isotope samples were taken for each new CH_4 tank. There were 22 flux sampling occasions during the 65-day study ($n = 88$), but for the outflow C-isotope $n = 79$ because 9 samples were not taken or the vials leaked. The H-isotope ratio was determined for inflow samples and for just 13 outflow samples because only CH_4 concentrations greater than about 3% could be analyzed.

Stable C-isotope ratios ($\delta^{13}\text{C}$, eq 3) were measured by direct injection into a Hewlett-Packard gas chromatograph coupled via a combustion interface to a Finnigan Mat Delta S isotope ratio mass spectrometer (GCC-IRMS) following Merritt et al. (22). The hydrogen isotope ratio ($\delta^2\text{H}$) was determined on a Finnigan Mat Delta XP in continuous flow mode.

Statistical Analyses. Statistical comparisons were made by ANOVAs (23). In order to use ANOVAs to compare biofilter parameters it was assumed that the measurements were independent and not correlated in time. When averages are reported, the mean \pm the standard error of the mean is used unless the probability of the confidence interval is stated. Curve fitting was done with SigmaPlot (24).

Results and Discussion

Incubation Study. There was no significant difference in α_{ox} for the two biofilter media ($p > 0.05$, Supporting Information, Figure S2). In the first incubation experiment the initial CH_4 concentration was 6–8%, and $\alpha_{\text{oxC}} = 1.0180 \pm 0.0005$ and $\alpha_{\text{oxH}} = 1.1608 \pm 0.0114$. In the second incubation experiment the initial CH_4 concentration was 23–24%, and $\alpha_{\text{C}} = 1.0244 \pm 0.0006$ and $\alpha_{\text{H}} = 1.2370 \pm 0.0049$. Note that H-isotopes are more strongly fractionated than C-isotopes during CH_4 oxidation and could potentially be a more sensitive measure of oxidation. The values of α_{oxC} determined here are less than that determined by Chanton and Liptay (8) for mulch in incubation studies ($\alpha_{\text{oxC}} = 1.0315$ at 22°C) and greater than those determined by Snover and Quay (25) for forest soil in chamber studies (α_{oxC} ranged from 1.0158 to 1.0172 at 21°C). It is not known why α_{ox} differed between the two experiments; it is possible that the bacterial metabolism changed during the 12 intervening days. The α_{ox} results from experiment 2 will be used in the following analysis because the higher initial CH_4 concentration was closer to that expected during methane oxidation in the biofilters.

Comparison of Biofilter Methane Oxidation Calculations. The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of methane emitted from the biofilters was enriched in the heavier isotope relative to the inflow due to bacterial oxidation that removed relatively more $^{12}\text{C}^1\text{H}_4$ than $^{13}\text{C}^1\text{H}_4$ or $^{12}\text{C}^2\text{H}^1\text{H}_3$. $\delta^{13}\text{C}$ enrichment was greater for the compost biofilters ($10.62 \pm 0.51 \text{‰}$) as compared to the water spreading biofilters ($5.82 \pm 0.38 \text{‰}$), suggesting that more oxidation occurred in the compost biofilters (Supporting Information, Figure S3). The average difference between $f_{\text{oxir,C}}$ and $f_{\text{oxir,H}}$ (closed system interpretation, eq 2) was not

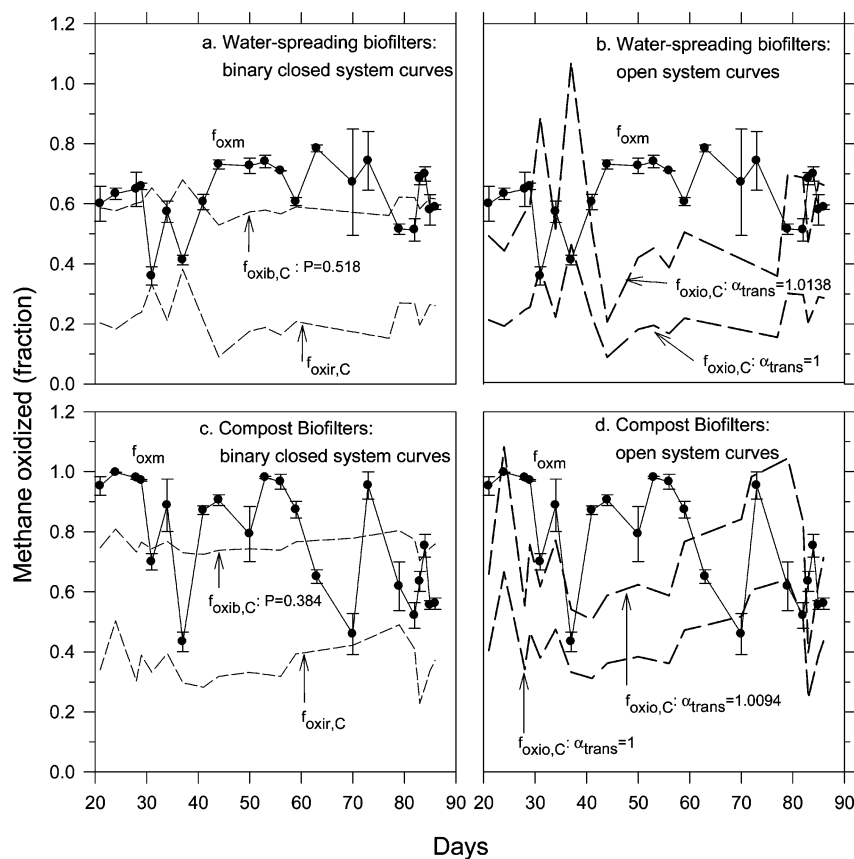


FIGURE 1. Fraction of CH_4 oxidized in biofilters determined from mass balance (average $f_{\text{oxm}} \pm$ standard error) and from carbon isotopes. f_{oxm} for water-spreading biofilters (a) is repeated in (b), and f_{oxm} for compost biofilters (c) is repeated in (d) to facilitate comparison of the binary closed-system and the open system model results. The two broken lines in the binary closed system graphs (a and c) show no partitioning ($f_{\text{oxir,C}}$) and average P ($f_{\text{oxib,C}}$) calculations. The two broken lines in the open system graphs (b and d) show no transport fractionation ($f_{\text{oxio,C}}, \alpha_{\text{trans}}=1$) and average α_{trans} ($f_{\text{oxio,C}}, \alpha_{\text{trans}}=1.0094$) calculations. The f_{oxm} curves were previously published (20, reprinted by permission of Sage Publications Ltd.).

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significant ($f_{\text{oxir,C}} - f_{\text{oxir,H}} = 0.0643 \pm 0.0649$, $p = 0.05$, $n = 11$, Supporting Information, Table S1).

$f_{\text{oxir,C}}$ was almost always less than f_{oxm} (Figure 1a and c). Out of 79 cases, each type of biofilter had only two cases where $f_{\text{oxir,C}}$ was greater than f_{oxm} . Overall $f_{\text{oxir,C}}$ was only $45.5 \pm 2.4\%$ of f_{oxm} , and ranged from 8 to 110%. For the water-spreading biofilter $f_{\text{oxir,C}} = 0.222 \pm 0.012$ and $f_{\text{oxm}} = 0.609 \pm 0.017$; and for the compost biofilter $f_{\text{oxir,C}} = 0.362 \pm 0.014$ and $f_{\text{oxm}} = 0.757 \pm 0.032$. There was considerable variation in the fraction oxidized which may have been due in part to changes in J_{in} , which ranged from 17 to $723 \text{ g m}^{-2} \text{ d}^{-1}$ (20). $f_{\text{oxio,C}}$ is also plotted in Figure 1b and d, for $\alpha_{\text{trans}} = 1$, to illustrate how it differs from $f_{\text{oxir,C}}$ and to show that it also usually underestimates f_{oxm} . Values of f_{oxio} were larger than f_{oxir} , except when $\delta^{13}\text{C}_{\text{out}} - \delta^{13}\text{C}_{\text{in}} < 2.9\text{‰}$. Overall $f_{\text{oxio,C}}$ was $52.3 \pm 3.1\%$ of f_{oxm} and ranged from 8 to 141%. The other lines in Figure 1 will be discussed in the Flow Partitioning section below.

The oxidation ratio ($f_{\text{oxir,C}}/f_{\text{oxm}}$) for the compost biofilters increased with J_{out} (Figure 2). De Visscher et al. (15) also found that $f_{\text{oxio,C}}/f_{\text{oxm}}$ (with $\alpha_{\text{trans}} = 1$) increased with increasing CH_4 flux and accounted for this by decreasing α_{trans} with increasing flux. The oxidation ratio for the water-spreading biofilters did not have as clear a relationship with J_{out} (Supporting Information, Figure S4) because of four outlying points, but most of the data had a trend similar to that of the compost biofilters.

Model Description. The usual mismatch between f_{oxm} and f_{oxir} or f_{oxio} (with $\alpha_{\text{trans}} = 1$) indicated that something was missing in the isotope-based equations for fraction oxidized. The effect of diffusion, which De Visscher et al. (15) used to modify α_{trans} (eq 4), may not be the only process that needs

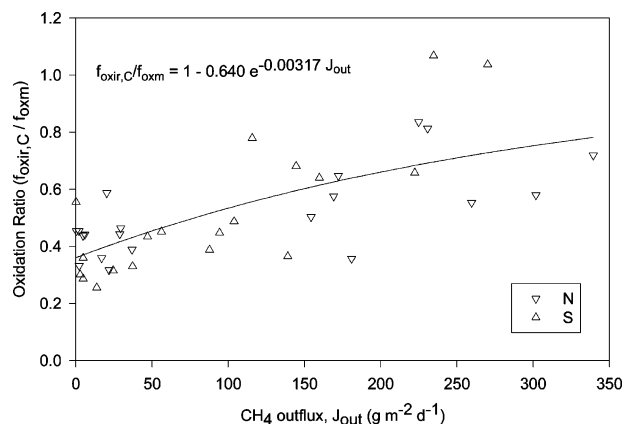


FIGURE 2. Fraction of CH_4 oxidized calculated from isotopes ($f_{\text{oxir,C}}$) as a proportion of the fraction oxidized calculated from flux measurements (f_{oxm}) versus methane outflux (J_{out}) for the two compost biofilters. $f_{\text{oxir,C}}/f_{\text{oxm}}$ increased with increasing J_{out} . The parameters of the least-squares-fitted equation were 0.640 ± 0.0355 and -0.00317 ± 0.000613 (value \pm asymptotic standard error, (24)), and the average absolute value of the residuals (mean absolute error) was 0.106.

to be accounted for. Calculation of f_{oxir} or f_{oxio} assumes that the outflow CH_4 isotope signature represents all of the inflow CH_4 after oxidation. If a portion of the influent gas is entirely oxidized, its isotope signature is lost. To quantify this process a simple binary or two-path model is proposed that partitions inflow gas between partially oxidized flow (flow fraction P) and completely oxidized flow ($1 - P$, Figure 3). It is likely that there is actually a distribution of flow paths with varying

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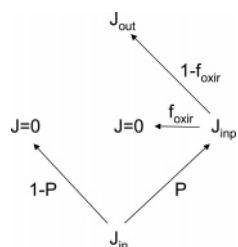


FIGURE 3. Binary closed-system model of the partitioning and oxidation of CH₄ in a biofilter. J_{in} is CH₄ inflow, P is the fraction that is exposed to partial oxidation, 1 - P is the fraction that is completely oxidized, J_{inp} = PJ_{in}, f_{oxir} is the fraction of CH₄ oxidized in the partially oxidized path and is determined from isotope fractionation (eq 2), and J_{out} is the outflow flux.

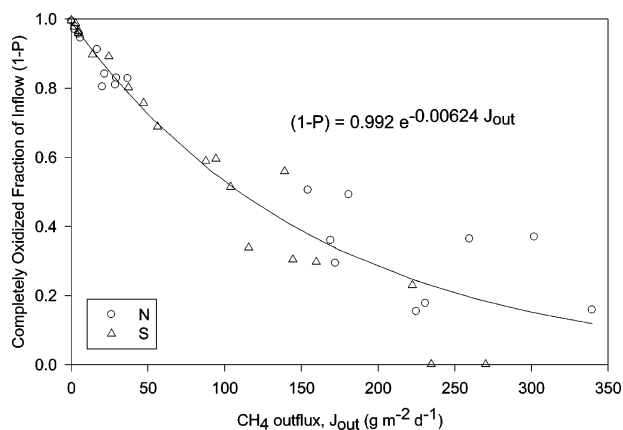


FIGURE 4. Part of the inflow that was completely oxidized (1 - P) versus outflux (J_{out}) for the compost biofilters. The parameters of the least-squares-fitted equation are 0.992 ± 0.0244 and -0.00624 ± 0.000421 (value ± asymptotic standard error, (24)), and the mean absolute error for the fitted curve is 0.0565.

276 residence times and reactivity, but a binary model provides
 277 a conceptual basis for the process involved. We assume that
 278 a fraction of the inflow is exposed to partial oxidation (J_{inp}):

$$J_{inp} = PJ_{in} \quad (6)$$

279 After oxidation of J_{inp} what is left (J_{out}) is emitted at the surface:

$$J_{out} = (1 - f_{oxir})J_{inp} \quad (7)$$

280 where f_{oxir} (eq 2) is the fraction oxidized in the partially
 281 oxidized path. The rest of the gas (1 - P) is completely
 282 oxidized before it is emitted at the surface. By combining eqs 1, 6,
 283 and 7:

$$P = \frac{1 - f_{oxm}}{1 - f_{oxir}} \quad (8)$$

284 For the binary model to be useful, an independent method
 285 of determining P is needed. The expression 1 - P may be
 286 thought of as the tortuous flow fraction that slowly seeps
 287 through small pores, resulting in complete oxidation. It might
 288 be expected that 1 - P would be less in faster flow conditions,
 289 due to a smaller proportion of the flow being carried in small
 290 pores. In fact 1 - P decreased exponentially with J_{out} for the
 291 compost biofilters (Figure 4) ranging from 99.1% at J_{out} =
 292 0.113 g m⁻² d⁻¹ to 11.9% at J_{out} = 340 g m⁻² d⁻¹. 1 - P also
 293 declined with increasing J_{out} for the water-spreading biofilters,
 294 but the trend was not well-defined due to 5 outlying points
 295 (Supporting Information, Figure S5). More research is needed
 296 to relate P to measurable properties such as pore-size
 297 distribution and volumetric water content. If P is known, eq

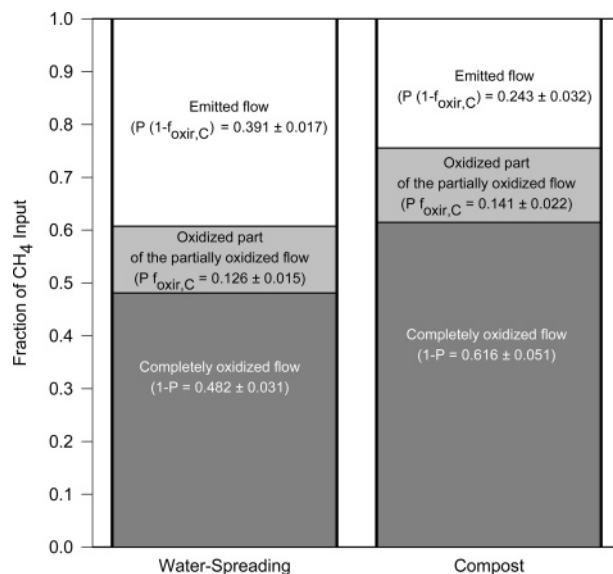


FIGURE 5. Division of input flux into partially oxidized (P) and completely oxidized (1 - P) components using C-isotopes for two biofilters. The partially oxidized component is further divided into emitted and oxidized parts, so that the binary closed-system fraction oxidized is the sum of the oxidized components (f_{oxib} = (1 - P) + (P f_{oxir})).

8 can be rearranged and the binary closed-system fraction oxidized (f_{oxib}) can be substituted for f_{oxm}: 298 299

$$f_{oxib} = 1 - P + P f_{oxir} \quad (9)$$

Flow Partitioning. The three-way partition of the input flux for each biofilter type, averaged over all carbon isotope measurements, is depicted in Figure 5. Part of the P flow was emitted to the atmosphere (P(1 - f_{oxir})) and part was oxidized before it escaped (P f_{oxir}). The rest of the input was completely oxidized in the “dead-end” flow (1 - P). 1 - P and f_{oxir,C} were compared in two-way ANOVAs (df = 3,75), where the individual biofilter and the type of biofilter were class variables. The average 1 - P for the compost biofilters (0.616) was greater than that for the water-spreading biofilters (0.482), possibly due to smaller pores in the compost, but the difference was not significant (F = 1.73, p = 0.1672). This lack of significance was likely due in part to the covariance of 1 - P with the wide range of J_{out} (Figure 4), resulting in a large variability around mean values for 1 - P. Average f_{oxir,C} for the compost biofilters (0.362) was significantly greater than that for the water-spreading biofilters (0.222, F = 20.16, p < 0.001).

The two model calculations of oxidation, f_{oxib} and f_{oxio}, were compared by using P and α_{trans} as fitting parameters (Figure 1). The average values of P (0.518 for water-spreading and 0.384 for compost biofilters) were used in eq 9 to derive f_{oxib} (Figure 1a and c). Individual values of α_{trans} were determined by replacing f_{oxio} with f_{oxm} in eq 4 and solving for α_{trans}. Average values for α_{trans} (1.0138 for water-spreading biofilters and 1.0094 for compost biofilters) were then used in eq 4 to derive f_{oxio,C} (Figure 1b and d). All fitted curves were closer to f_{oxm} than the curves with P = 1 or α_{trans} = 1. The fitted f_{oxio} curves have a variability similar to that of the f_{oxm} curves, although in some cases the trends are reversed (e.g., Figure 1b, days 30–45). In contrast, the variations in oxidation tend to be damped out in the f_{oxib} curves (Figure 1a and c). This is because the constant value of 1 - P in eq 9 sets a baseline for the fluctuations in f_{oxir}.

Biofilter effectiveness is usually assessed using f_{oxm}. The average f_{oxm} for the compost biofilters (0.757) was significantly greater (p = 0.001) than that of the water-spreading biofilters 334 335 336

(0.609). But the effectiveness of the biofilters became more similar with time, and Powelson et al. (20) showed that in the last 23 days of the experiment there was no significant difference in f_{oxm} ($p = 0.585$, water-spreading $f_{\text{oxm}} = 0.64$ and compost $f_{\text{oxm}} = 0.63$). During this 23-day period, however, compost $f_{\text{oxir,C}}$ (0.381) was still significantly greater than water-spreading $f_{\text{oxir,C}}$ (0.232, $p = 0.0011$). This greater fraction oxidized apparently acted on a larger proportion of gas (larger P), so that the final fraction oxidized was not statistically different. This may have been due to the drying of the compost resulting in larger gas-transport pores relative to the water-spreading biofilters.

A comparison of $f_{\text{oxio,C}}$ and $f_{\text{oxio,H}}$ (open system interpretation, eq 4) can indicate the importance of diffusion (as opposed to partitioning) in causing the discrepancy between f_{oxio} and f_{oxm} . The maximum value of α_{trans} for mass 16 (CH_4) relative to mass 17 ($^{13}\text{CH}_4$ and CH_3^2H) is 1.0195 (15). Also since their masses are the same, α_{trans} for $^{13}\text{CH}_4$ should be similar to α_{trans} for CH_3^2H (15). α_{trans} is similar in magnitude to α_{ox} for ^{13}C substituted CH_4 (1.0244) but much less than the value of α_{ox} for ^2H -substituted CH_4 (1.2370). The dominator in eq 4 will be considerably affected if $1 < \alpha_{\text{trans}} < 1.0195$ for C-isotopes but to a lesser extent for H-isotopes. Therefore, if the diffusion effect is neglected and α_{trans} is assumed to be 1, there will be a greater impact on the calculation of $f_{\text{oxio,C}}$ than for $f_{\text{oxio,H}}$. If the transport isotope effect was the culprit causing the isotope-determined fraction oxidized to be lower than the mass-balance determined values, then $f_{\text{oxio,H}} > f_{\text{oxio,C}}$. However, the results show the opposite (Supporting Information, Table S1). Therefore these data suggest that the pathway effect is what is governing the lower values in isotope-determined oxidation relative to the mass-balance oxidation. However, the samples where we determined $f_{\text{oxio,H}}$ were all experiments with high concentrations, due to the reduced sensitivity of the IRMS to H relative to C. Flux was high, and dominated by advection relative to diffusion. Consequently, these experimental conditions were less likely to be influenced by diffusive fractionation. So, while the experiment is indicative of the importance of the pathway model in explaining the reduced oxidation observed by isotopic analysis, it is not conclusive. More $\delta^2\text{H}$ and $\delta^{13}\text{C}$ measurements need to be done under conditions of greater relative importance of diffusion.

The binary pathway model explains the discrepancy between methane oxidation calculated from isotopes and measured by mass balance by considering part of the inflow to oxidize completely and not contribute to the outflow isotope ratio. Diffusive fractionation and open-system behavior were not considered in this calculation, however. It is likely that both complete oxidation of part of the flow and diffusion need to be considered to develop an advection-diffusion model that better describes the true situation.

Nomenclature

389		
390	f_{oxib}	Fraction of CH_4 oxidized based on isotopes in the binary closed-system model (eq 9)
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392	f_{oxio}	Fraction of CH_4 oxidized based on isotopes in the open-system model (eq 4)
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394	f_{oxir}	Fraction of CH_4 oxidized based on isotopes in the closed-system Rayleigh equation (eq 2)
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396	f_{oxm}	Fraction of CH_4 oxidized based on mass balance flux measurements (eq 1)
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398	J_{in}	Flux into the biofilter
399	J_{inp}	Flux in the partially oxidized path (eq 6)
400	J_{out}	Flux out of the biofilter

P	Fraction of flow in the partially oxidized path (eq 8)	401 402
R	Ratio of heavier to lighter isotopes	403
α_{ox}	Isotope fractionation factor due to oxidation (eq 5)	404 405
α_{trans}	Isotope fractionation factor due to transport	406
δ_{in}	Standardized difference between input R and standard R (eq 3)	407 408
δ_{out}	Standardized difference between output R and standard R (eq 3)	409 410

Acknowledgments

Financial support for this study was provided by the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, the National Science Foundation (Grant 0093677), and Waste Management, Inc. We thank John Schert and Gary Hater for support, Jose Morales for construction of the compost biofilter, and Claire Langford for running samples on the GCC-IRMS. Three reviewers aided our interpretation of the results.

Supporting Information Available

Incubation method, schematic of incubation flask, incubation results, $\delta^{13}\text{C}$ and $\delta^2\text{H}$ results, comparison of biofilter methane oxidation calculations, fraction of CH_4 oxidized calculated from isotopes, and flow partitioning. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review July 12, 2006. Revised manuscript received November 1, 2006. Accepted November 2, 2006.

ES061656G