Field Methane Oxidation Efficiency at Municipal Solid Waste Landfills
Located in the North of China

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Abstract. Municipal solid waste (MSW) landfills are one of main sources of anthropogenic methane emissions in China, and methane has been predicted to be the most significant greenhouse gas after 2030. In landfills, oxidation can take place naturally with methane migrating through the landfill cover. The value of fraction of methane oxidation recommended by the US EPA is 10%, which, however, is being challenged with more and more field measurement data from the Europe and the US. The characteristic of MSW in China is extremely different from that in the US, probably resulting in distinct differences in both methane generation and oxidation. The objective of this study was to determine the fraction of methane oxidized at MSW landfills in China and its spatial and temporal variations. Stable isotope technique was applied to determine the fraction of methane oxidized. The results showed that the fraction of methane oxidized where MSW was covered by soil ranged from 6.3% to 100% in Northeast China and 31% to 100% in North China. Methane oxidation could hardly occur in the operating surface. Besides, soil cover always had a high methane oxidation efficiency in summer. The fractional oxidation of methane in summer was more than 2 times than that in winter. All over the year, with the sampling depth decreasing, the fraction of methane oxidation of soil cover increased.

Introduction

Greenhouse effect is one of worldwide environmental issues nowadays. Greenhouse gases mainly includes CO₂, CH₄, N₂O, HFCS and so on. Among them, methane has the second largest radiative forcing of the long-lived greenhouse gases after CO₂ [1]. Over a time period of 100 years, the global warming potential for CH₄ is 25 compared with CO₂ [2]. The global atmospheric concentration of CH₄ has increased rapidly since Industrial Revolution. In addition, the current contribution of CH₄ to climate change forcing is 18% [1]. Thus controlling CH₄ emission will be an effective way to inhibit greenhouse effect.

Sources of atmospheric CH₄ include natural gas systems, enteric fermentation, rice production, manure management and landfills [3]. With methane accounting for about 50% (V), landfill gas (LFG) produced at municipal solid waste (MSW) landfills is one of the most important sources of greenhouse gases all over the world. In the US, landfills are the 3rd largest anthropogenic source of
CH₄ emissions, making up 16.2% of the total anthropogenic CH₄ emission [4]. In Europe, landfills are the 2nd largest anthropogenic source of CH₄ emissions, making up 22% of the total anthropogenic CH₄ emission [5]. Therefore, controlling landfill methane emissions is useful to reduce total methane emission. In landfills, methane produced by anaerobic digestion has three places to go——some are recovered by gas collection system, some are emitted to the atmosphere and others are oxidized. Oxidation can take place naturally when methane migrates through landfill cover, which has been well documented in lots of publications. The results has showed that fraction of methane oxidation can range from 12 to 100% in landfills[3,6-9]. As a consequence, methane oxidation is a significant way to reduce methane emission.

In China, landfill is the most important treatment for MSW, accounting for more than 80% of all disposal ways. However, there is very little information available about field methane oxidation at landfills in China. Stable isotope technique is useful to determine the fraction of methane oxidation [10-17]. The methane stable carbon isotope ratio (δ¹³C, ‰) is calculated by:

\[
\delta^{13}C = 1000 \left( \frac{R_{sam}}{R_{std}} - 1 \right)
\]  

(1)

where \( R_{sam} \) is the \(^{13}\)C/\(^{12}\)C ratio of the sample and \( R_{std} \) is the ratio for standard Vienna PeeDee Belemnite (0.01124)\(^{13}\).  

The following Eq. 2 is used for calculating the fraction of methane oxidation (fox) from \( \delta^{13}C \) values at different sampling depth.

\[
f_{ox,Z} = \frac{\delta_Z^{13}C - \delta_A^{13}C}{1000(\alpha_{ox} - \alpha_{trans})}
\]  

(2)

where \( \delta_A \) and \( \delta_Z \) are standard isotope ratios for the anoxic zone and sample depth Z or emitted methane. \( \alpha_{trans} \) will assumed to be 1. \( \alpha_{ox} \) is calculated by the Eq.3.

\[
\alpha_{ox} = \alpha_{ox,measured} - 0.00039(T - T_{measured})
\]  

(3)

Where \( \alpha_{ox} \) represents the fractionation factor at the temperature \( T \) (°C), and \( \alpha_{ox,measured} \) is the fractionation factor measured at \( T_{measured} \) (°C). Research has shown that the value of \( \alpha_{ox} \) is 1.022 at 25°C[18].  

The chamber isotope ratio emitted at the surface (\( \delta_0 \)) was determined from the initial and final samples:

\[
\delta_0 = \frac{\delta_F \varphi_F - \delta_I \varphi_I}{\varphi_F - \varphi_I}
\]  

(4)

where \( \delta_I \) and \( \delta_F \) are the initial and final carbon isotope ratios and \( \varphi_I \) and \( \varphi_F \) are the initial and final CH₄ volume fractions[15].

Methods and Materials

Methane oxidation was determined with the stable isotope (\(^{13}\)C) technique as a function of methane emission rate. Methane emission rate was determined with static chambers. Studies were conducted at three landfills in the north of China. Among them, one was located in Liaoning Province and we called it PJ landfill in this study. The other two were called ASW landfill and BSS landfill, respectively, located in Beijing. PJ landfill and BSS landfill had both HDPE cover and soil cover s depth was 30 – 100 cm. ASW landfill had only HDPE cover.
The chambers used in this study were constructed of steel. Its volume is 53 L and it can cover an area of 0.13m². Chambers were sealed to the ground. Methane samples were collected from chamber sequentially over a 45 minute period using 20 mL disposable syringes. Samples were analyzed on a gas chromatograph equipped with a FID. Methane flux was determined from concentration data (C in ug/mL) plotted versus elapsed time (t in hours). The CH₄ concentration within the chambers generally increased linearly, in which case dC/dt is the slope of the fit to the data. A non-zero flux was reported only if the there was 90% confidence (p < 0.1) in the correlation between CH₄ concentration and time, otherwise a zero-flux was reported[19]. Then we assumed methane oxidation fraction was 100%.

Methane oxidation was determined from the stable isotope approach. We used a probe to collect gas at different depth in landfills. The probes were hammered to the desired depth, ranging from 5 to 70 cm. The probes were separated horizontally by 5 to 10 cm. Before a sample was taken, existing gas was flushed from the probes. A 20 mL sample was taken with a syringe and injected into an evacuated vial. To chamber, stable isotopes for initial and final samples from each chamber were collected using 20 mL disposable syringes and immediately transferred to evacuated glass vials. Samples were only analyzed when the flux was positive to determine the carbon isotopic composition of residual CH₄ following oxidation as it passed through the soil beneath the chamber. The $^{13}$C of residual CH₄ was determined from the Eq.4.

Stable carbon isotopes values were measured by direct injection into GC-IRMS. Values are reported in the “δ” scale in ‰ relative to the standard, VPDB (Vienna Pee Dee Belemnite).

Results and Discussion

**The spatial variations of fraction of methane oxidation at MSW landfills in the north of China**

**Methane oxidation at the surface of different zones in the same landfill.** Landfills in China usually have three typical zones, and they are soil cover surface, operating surface, and waste unloading area (especially composed by old waste which had no enough time for landfilling), respectively. Anoxic zone methane $δ^{13}$C varied from -53.2‰ to -56.9‰ across the landfill, and there was no difference in anoxic zone at the three zones. This value was similar with that in the US [15].

<table>
<thead>
<tr>
<th>Zone type</th>
<th>soil cover surface</th>
<th>operating surface</th>
<th>waste unloading area</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number of samples</strong></td>
<td>19</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td><strong>Methane oxidation fraction [%]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>69.44%</td>
<td>10.68%</td>
<td>60.51%</td>
</tr>
<tr>
<td>Standard error</td>
<td>31.11%</td>
<td>14.86%</td>
<td>39.96%</td>
</tr>
<tr>
<td>Median</td>
<td>75.66%</td>
<td>0.00%</td>
<td>62.61%</td>
</tr>
<tr>
<td>Maximum</td>
<td>100.00%</td>
<td>30.31%</td>
<td>100.00%</td>
</tr>
<tr>
<td>Minimum</td>
<td>6.30%</td>
<td>0.00%</td>
<td>12.80%</td>
</tr>
<tr>
<td><strong>δ$^{13}$C [%]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>-40.985</td>
<td>-54.868</td>
<td>-47.095</td>
</tr>
<tr>
<td>Standard error</td>
<td>6.882</td>
<td>4.608</td>
<td>24.226</td>
</tr>
<tr>
<td>Median</td>
<td>-41.088</td>
<td>-55.439</td>
<td>-50.543</td>
</tr>
<tr>
<td>Maximum</td>
<td>-25.526</td>
<td>-48.510</td>
<td>-35.140</td>
</tr>
<tr>
<td>Minimum</td>
<td>-53.327</td>
<td>-63.460</td>
<td>-51.855</td>
</tr>
</tbody>
</table>
Table 1 showed the methane oxidation fraction ($f_{\text{ox}}$) of the three zones in PJ landfill. Nineteen oxidation fraction measurements were performed in the soil cover surface. The minimum measured methane oxidation fraction was 6.3% while the peak measured methane oxidation fraction was 100%. The mean methane oxidation fraction was 69.4% and the median value was 75.7%. Eight oxidation fraction measurements were performed in the operating surface. The minimum measured methane oxidation fraction was 0% while the peak measured methane oxidation fraction was 30.3%. The mean methane oxidation fraction was 10.7% and the median value was 0%. Eleven oxidation fraction measurements were performed in the surface of waste unloading area. The minimum measured methane oxidation fraction was 12.8% while the peak measured methane oxidation fraction was 100%. The mean methane oxidation fraction was 60.5% and the median value was 62.6%.

It was clear that methane oxidation hardly happened at operating surface. However, soil cover surface and old waste surface both had high methane oxidation fraction. Some researchers reported that soil cover and old waste were comfortable for the growth of methanotrophs [20].

**Methane oxidation at soil cover surface in different landfills located in the north of China.**

<table>
<thead>
<tr>
<th>Landfill location</th>
<th>Zone type</th>
<th>soil cover surface</th>
<th>operating surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panjing</td>
<td>Number of samples</td>
<td>19</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>69.44%</td>
<td>10.68%</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>31.11%</td>
<td>14.86%</td>
</tr>
<tr>
<td></td>
<td>Median</td>
<td>75.66%</td>
<td>0.00%</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>100.00%</td>
<td>30.31%</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>6.30%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Beijing</td>
<td>Number of samples</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>78.19%</td>
<td>0.00%</td>
</tr>
<tr>
<td></td>
<td>Standard error</td>
<td>26.70%</td>
<td>0.00%</td>
</tr>
<tr>
<td></td>
<td>Median</td>
<td>100.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>100.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>31.03%</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

Table 2 showed the fraction of methane oxidation in different landfills in the north of China. Samples representing Beijing’s landfills were taken from ASW landfill and BSS landfill. Methane oxidation fraction of soil cover in Beijing ranged from 31.0% to 100%, and the mean value was 78.2%. In PJ landfill, methane oxidation fraction of soil cover ranged from 6.3% to 100%, and the mean value was 69.4%. In general, methane oxidation fraction in soil cover was not quite similar in the two region and it had relationship with the soil cover’s character and depth, the climate, the landfill’s dimensions and operation condition, etc. Nevertheless, both in PJ landfill and those located in Beijing, methane oxidation almost did not happen in the operating surface.

**Methane oxidation at different depths of soil cover.** Fig.1 shows the fraction of methane oxidation at different depth in two landfills. The samples from Fig.1 were taken from April to May, in spring. The two landfill had similar trend of the methane oxidation behavior at different depth. With the sampling depth decreasing, the fraction of methane oxidation increased. Moreover, the fraction value at different depth of the two landfills were alike.
Methane oxidation at different seasons in the same landfill

The oxidation fraction value fluctuated in different months (Fig.2). In June, the oxidation fraction was 100%, reaching the maximum, while in November the value was 40.3% which was the minimum. Dividing the year into four seasons, as fig.3 showed, the sequence of methane oxidation fraction of different seasons from big to small is: summer > spring > autumn > winter.

Fig.2 Fraction of methane oxidation of soil cover surface at different months in PJ landfill
Fig. 3 Fraction of methane oxidation at different seasons in PJ landfill

Fig. 4 showed the fraction of methane oxidation at different depth in different seasons and samples were taken from PJ landfill. All over the year, with the sampling depth decreasing, the fraction of methane oxidation increased. In all sampling depth, the fraction of methane oxidation in summer was higher than others. The sequence of methane oxidation fraction at different depth from big to small is: summer > spring > autumn > winter.

Summer was always at high temperature while winter was opposite. And as we know, temperature has the most significant effect on methane oxidation reaction [21-23]. It can be concluded that temperature was main impact factor which lead to the difference of fox of soil cover at different seasons.
However, in operating surface, the methane oxidation fraction did not range a lot, whose fraction were nearly 0 (fig.5). Therefore, we can ignore the methane oxidation in operating surface.

Conclusions

This paper concluded that the three typical zones in one landfill had different methane oxidation behavior. Methane oxidation hardly happened at operating surface. However, soil cover surface and old waste surface both had high methane oxidation fraction, and the mean value were 69.4% and 60.5%, respectively. Methane oxidation fraction in soil cover was not quite similar in the different landfills even though they were all located in the north of China. The oxidation fraction value of soil cover surface fluctuated in different months, ranging from 40.3 - 100%. The sequence of methane oxidation fraction of different seasons from big to small is: summer > spring > autumn > winter. All over the year, with the sampling depth decreasing, the fraction of methane oxidation of soil cover increased.

Acknowledgments

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References


the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK and New York, NY, USA


