

DETERMINATION OF METHANE OXIDATION IN LANDFILL FUGITIVE EMISSIONS BY ^{13}C ISOTOPE MEASUREMENTS

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SUMMARY: Still today, the final destiny of a large part of the waste dumped is landfilling, which is an important source of methane. Quantifying the amount of methane that is oxidized when the landfill gas passes through the seal, it can provide valuable information when determining the total GHG potential emission of a landfill. In this work, methane oxidation has been determined for landfill gas samples taken on the surface of three Spanish landfills. For this, it has been determined the ^{13}C isotopic signal in methane by cavity ring-down spectroscopy (CRDS-WS). Previously, the preference of methanotrophic bacteria for ^{12}C isotope versus ^{13}C has been quantified using soil samples from the three landfills. The results obtained show a great variability, ranging from 0 to 70% of methane oxidized. This variability can be explained with the specific characteristics of each sample, suggesting a consistent methodology.

1. INTRODUCTION

In spite of the efforts made in recent years, in the development of alternative treatment for waste, in 2014 only in Spain there were 130 active landfills. According to (MAGRAMA 2014) they have received 11.96 Mt municipal waste, of which 7.13 Mt are refuse from other waste treatment plants.

The anaerobic digestion process of the organic matter contained in the waste is well reported. (Sadasivam and Reddy 2014) Thus, many studies discuss about the importance of landfills as methane sources and its great contribution to the anthropogenic global warming. According to (EPA 2012) landfills are the third largest source of anthropogenic methane emissions in the world. That, coupled with the high energy content of the landfill gas that is usually recovered by degassing systems, makes it of great interest to determine the amount of methane emitted through the landfill surface. These are called diffuse and fugitive emissions.

Several methods, based on modelling or methane measurements, have been developed to determine these emissions. In the methods based on the measurement of methane concentrations at the landfill surface, the methane concentration is mathematically related with surface emission in different ways. For example, those methods based on accumulation chambers are fairly simple mathematically but require a large number of measures to achieve significant results. Other methods such as tracer gas techniques, Eddy Covariance or differential absorption light detection and ranging (LiDAR) (Tregoures et al. 1999) are

mathematically more complex and require a very detailed study of the weather conditions. Although they can provide consistent results, the application of these methods is always considerably expensive.

The second group of methods are based in modelling biogas emissions considering different types of landfill and the qualities of the waste dumped. These methods have the advantage of not requiring constant monitoring of the concentration of methane in the landfill. However, they require a lot of information from the landfill that is not always accessible. Many models have been developed in recent years to predict methane emissions in landfills (Kamalan et al. 2011).

One of the parameters that some of these models take into account is the amount of methane that is oxidized when the biogas goes through the sealing of the landfill. The model for the calculation of methane emissions proposed by the Intergovernmental Panel on Climate Change (IPCC) is one of the most internationally extended. According to this, it is estimated that in a managed landfill 10% of the total methane emitted by the landfill is oxidized to carbon dioxide. (Pipatti and Svoldal 2006). Other models widely used as LandGEM do not take into account this oxidation (Alexander et al. 2005). Even so, some authors apply the oxidation factor proposed by the IPCC when estimating emissions using LandGEM (Scharff and Jacobs 2006).

Methane oxidation occurs when the biogas comes into contact with air. It is a biological process in which methanotrophic aerobic bacteria, degrades methane to give carbon dioxide. This process depends on many factors. For example, the material from which the sealing is made, temperature and humidity or the rate at which the biogas diffuses into the atmosphere. There are also several methods for determining how much methane is oxidized when the landfill gas passes through the sealing of the landfill. (Chanton et al. 2009)

The main objective of this study is to calibrate a method to quantify methane oxidation at three Spanish landfills. To measure oxidation, the preference of the bacteria for the $(\text{CH}_4)\text{-}^{12}\text{C}$ against the $(\text{CH}_4)\text{-}^{13}\text{C}$ has been used. This is quantified through the alpha parameter (α) that is determined in the laboratory using soil samples from each of the landfills.

$$\alpha = \frac{k_{12\text{C}}}{k_{13\text{C}}} \quad (1)$$

$k_{12\text{C}}$ and $k_{13\text{C}}$ are respectively the kinetic constants of the oxidation process from methane to carbon dioxide when the carbon of the methane is ^{12}C and ^{13}C isotopes. The parameter that will be measured to quantify the oxidation, is the isotopic signal of ^{13}C . The isotopic signal $\delta^{13}\text{C}$ express ^{13}C proportion in methane. It is defined as:

$$\delta^{13}\text{C} = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000 \quad (2)$$

Where R_{sample} is the $^{13}\text{C}/^{12}\text{C}$ proportion in each sample and R_{std} is the $^{13}\text{C}/^{12}\text{C}$ proportion in nature ($R_{\text{std}}=0.0112372$). $\delta^{13}\text{C}$ has been measured by cavity ring-down spectroscopy (CRDS-WS).

2. MATERIAL AND METHODS

2.1 Site description

The methodology developed has been applied in three Spanish landfills. Two of them are situated in the region of Madrid (A and B). The third is in the region of Cantabria (C), in the north

of the Iberian Peninsula. The main characteristics of these landfills are presented in table 1.

Table 1. Main characteristics of landfills A, B and C

Landfill	Surface (ha)	Meteorology*	Status	Cover	Degassing
A	110	Csa	Closed	Final ^a	Yes
B	85	Csa	In use	Intermediate ^b	Yes
C	50	Cfb	In use	Intermediate ^b	Yes

*The meteorology has been described according to Köppen-Geiger Climate Classification (Kottek et al. 2006). With this criterion, Csa corresponds to warm temperatures, with summers dry and hot. Climate type Cfb consists of warm temperature, fully humid with warm summer.

^a Final cover contains HDPE sheets.

^b Intermediate cover does not contain HDPE sheets.

2.2 Experimental design

The experimental part of this work has been developed in two steps as described in (Scharff et al. 2003):

- Laboratory calibration
- Determination of the oxidized methane fraction

2.2.1 Laboratory calibration

Before determining the methane fraction oxidised in each of the landfills, the preference of the methane oxidizing bacteria for ¹²C against ¹³C should be determined. This is quantified by the previously mentioned α parameter. This parameter relates the decrease in the methane concentration due to oxidation with the variation in the isotopic signal $\delta^{13}\text{C}$, that is, with the variation of the ¹³C/¹²C ratio. Equation (3) shows the mathematical relationship between these two variables:

$$\delta^{13}\text{C} = 1000 \left(\frac{1}{\alpha} - 1 \right) \cdot \ln \left(\frac{M}{M_0} \right) + \delta^{13}\text{C}_{t=0} \quad (3)$$

Where M and M₀ are methane concentrations in a given time or initial time respectively.

The α parameter has been calculated for each landfill, using soil samples from all of them. Soil samples collected at the landfills were air dried for 11 days, until constant humidity was reached. In this way the relative humidity of the three soil samples was below 5%. The relative humidity was calculated by weighing difference from a sample of about 10 g before and after drying in an oven at 105°C for 24 hours. Table 2 shows the relative humidity values of the soil samples before and after drying for the three landfills.

Table 2. Relative humidity values in soil samples from landfills before and after air drying.

Landfill	Relative Humidity (% p/p)	
	Before drying	After drying
A	13.3	2.4
B	16.1	3.5
C	3.6	0.9

In order to determine α 50 g of conditioned soil and 10 mL of distilled water are introduced in flasks like the one shown in figure 1:

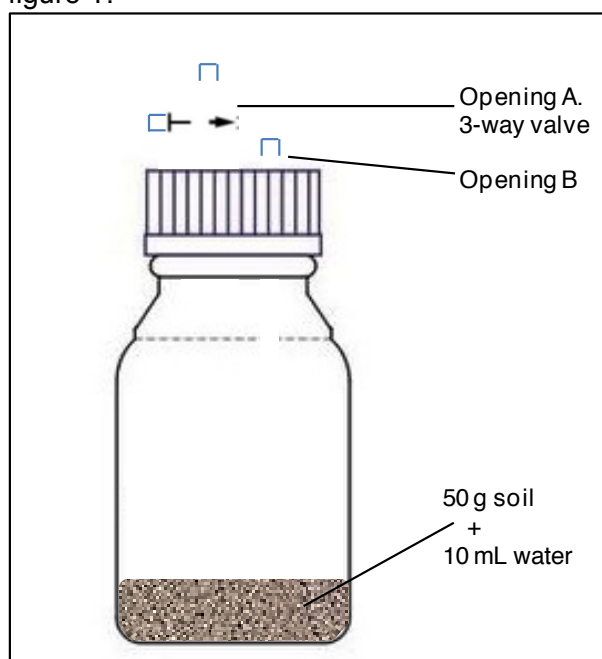


Figure 1. Flask assembly diagram for the study of the relationship between $\delta^{13}\text{C}$ and methane concentration.

Then, 5 mL of methane is introduced into the flasks with a gas syringe through the 3-way valve A, reaching an approximate methane concentration of 0.8%. This is the time $t=0$. After this, the flasks are closed and stored at 28°C until the analysis of each of them at different times.

At each time, methane concentration is first measured by gas chromatography in the corresponding flask. The analysis was carried out in a micro-GC Varian model CP-4900, equipped with a column CP740150 PPQ and using helium as carrier gas. The apparatus has a thermal conductivity detector. The initial methane concentration was determined accurately for 6 samples, obtaining an average value of 0.78% with a confidence interval of ± 0.1 to 95% confidence.

Once the concentration of methane is determined, the valve A of the flask is connected to a 1 L Tedlar bag and a stream of air is introduced with a pump into the bottle through port B until the bag is filled. The bags are equipped with lock valves that ensures the inertness and impermeability of air samples. In this process, the sample is diluted with ambient air from the laboratory. To determine the influence of this on the isotopic signal, laboratory air has been analyzed following the same protocol as the samples. A methane concentration of 4.85 ppm was detected in this ambient air with an isotopic signal of +24.53%. This concentration was very small compared to the measured concentrations on the flasks, so its influence on the process has been neglected.

The isotopic signal was determined using a laser-based analyzer (Picarro C2101-i) by cavity ring-down spectroscopy (CRDS-WS) (Crosson 2008) (Garcia-Anton et al. 2014). These analysis were carried out in the facilities of the Department of Geology of the National Museum of Natural Sciences of Madrid (MNCN-CSIC).

The $\delta^{13}\text{C}$ results were plotted versus $\ln(M/M_0)$. According to the equation 2, α value can be extracted from the slope of the resulting line. In figure 2 it can be seen the values obtained for each landfill. It is important to highlight the excellent correlation values obtained.

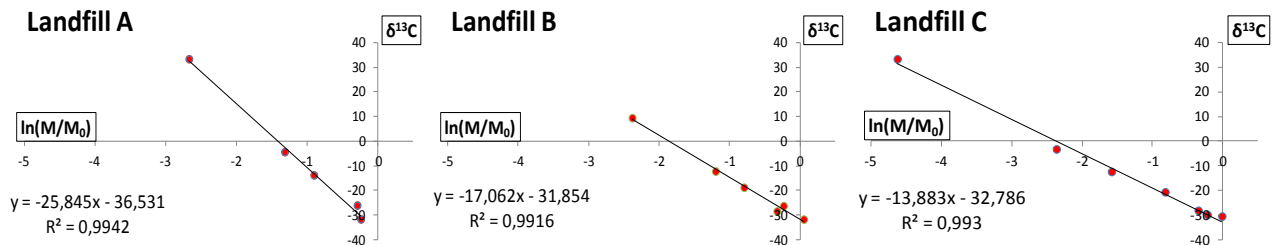


Figure 2. Representation of $\delta^{13}\text{C}$ versus $\ln(M/M_0)$ for the calculation of α from the slope. Results for α are shown in table 3.

Table 3. α values for landfills A, B and C

Landfill	A	B	C
α	1.026	1.017	1.014

2.2.2 Sampling and determination of the oxidized methane fraction

Once α parameter for each of the landfills is calculated, the amount of methane that has been oxidized in the samples taken at each landfill surface can be determined. Assuming that the biogas inside the landfill has not undergone aerobic oxidation, the isotopic signal on C ($\delta^{13}\text{C}$) of the samples taken outside were compared with that of the biogas generated inside the landfills. For this purpose, some landfill gas samples have been taken on the surface of the three landfills, as well as in the interior of the landfill. These samples were taken in Tedlar bags with lock system. To carry the gas to the bags the PMD Sensit PMD analyzer, which has an internal pump, was used. A probe has been attached to the analyzer to take the gas samples at ground level. In addition, the reading of the PMD during the sampling makes it possible to know the approximate concentration of methane in each sample. This information is useful in justifying the values of oxidized fraction obtained using Equation 4.

$$f_{ox} = \frac{\delta^{13}\text{C}_E - \delta^{13}\text{C}_A}{1000(\alpha - 1)} \quad (4)$$

Where $\delta^{13}\text{C}_E$ is referred to landfill gas samples taken at the surface while $\delta^{13}\text{C}_A$ refers to landfill gas samples taken of the degassing system.

3. RESULTS AND DISCUSSION

The method was applied to landfill gas samples taken in several points in the surface of the three landfills. The results obtained for the oxidized fraction are shown in Table 4.

Table 4. Isotopic signal (CH₄)-¹³C and oxidized fraction in several points of the three landfills.

Sample	Landfill	Date	$\delta^{13}C_E$ (‰)	f _{ox}	CH ₄ Concentration* (ppm)	Observations
1	A	27.10.2016	-58.55	No oxidation	150	Side and slope
2	A	27.10.2016	-60.79	No oxidation	75	Side and slope
3	A	27.10.2016	-63.08	No oxidation	15	Side and slope
4	A	27.10.2016	-63.48	No oxidation	25	Side and slope
5	A	27.10.2016	-54.72	0.14	100	Degassing well
6	A	27.10.2016	-64.20	No oxidation	350	Degassing well
7	B	11.11.2016	-50.86	0.41	100	Diffuse emission
8	B	11.11.2016	-60.35	No oxidation	35	Diffuse emission
9	B	11.11.2016	-54.88	0.18	50,000	Fugitive emission ^a
10	B	11.11.2016	-58.09	No oxidation	10	Diffuse emission
11	B	11.11.2016	-45.83	0.70	50	Side and slope
12	B	11.11.2016	-60.64	No oxidation	50,000	Side and slope
13	B	11.11.2016	-65.12	No oxidation	10	Side and slope
14	B	11.11.2016	-51.16	0.40	5	Atmospheric sample
15	C	15.12.2016	-55.69	0.13	10	Diffuse emission
16	C	15.12.2016	-58.93	No oxidation	80	Degassing well
17	C	15.12.2016	-56.51	0.07	80,000	Fugitive emission ^a
18	C	15.12.2016	-57.71	No oxidation	20	Side and slope
19	C	15.12.2016	-55.28	0.16	10	Diffuse emission

* Approximate value of methane concentration measured during sampling

^a Sample diffuses through a crack

The values for $\delta^{13}C_A$ for landfills A, B and C respectively were -58.56, -58.03 and -57.51. These have been calculated from samples of landfill gas taken from the degassing system. This values are within the range typical for terrestrial biogenic methane sources (Bergamaschi et al. 1998).

The $\delta^{13}C_E$ values obtained range from -65.12 to -45.83 (‰). These values are generally lower than those reported by (Scharff et al. 2003), which obtained an average oxidation value for the Braambergen landfill of 32.5%.

Landfill A is the only one of those studied with a final seal. On its top cover surface there are few diffuse emissions due to the high efficiency of its sealing. For this reason gas samples were taken at the sides and slopes of the landfill and in some degassing wells, where the seal is less efficient. These samples generally pass through the seal quickly and the oxidized fraction is expected to be small or negligible. An exception is sample 5 which has been taken in a well with a moderate methane concentration. It can be assumed that the sample diffuses into the well progressively and hence a high value of oxidized fraction was obtained.

In the case of landfill B several samples of diffuse emissions have been taken (samples 7, 8 and 10). Sample 14 can be considered a diffuse emission too as it was taken on the surface of

the landfill but not directly at ground level). For these samples values of the oxidation ratio ranging from 0 to 0.40 were found. This great variability can be due to different factors, for example, diffusion of air into the landfill in the sampled zone, which would increase the oxidation rate or a fast leakage of the gas through the landfill seal, which could decrease the oxidation rate in those cases.

Samples 9, 11, 12 and 13, were taken at sites where a rapid diffusion of the gas into the atmosphere could be expected, either sides and slopes or cracks with high methane concentrations. So that, the oxidation rate was expected to be lower than in the previous where the diffusion of methane through the seal is slower. Values for samples 12 and 13 are in agreement with this argumentation. Nevertheless, high values on oxidized fraction of samples 9 and 11 are striking. In the case of sample 11 a moderate concentration of methane is present, which may mean a slow diffusion of the gas towards the surface. Sample 9 corresponds to a surface leak associated with a big crack in the seal. The presence of the crack can point out to a large diffusion of air into the landfill. This could explain the high oxidation value found, compared to 12 and 13 samples.

Samples 15 and 19, from landfill C, correspond to diffuse emissions. In both cases oxidized fraction is above 0.1. These values could be due to a slow diffusion of landfill gas through the cover.

Samples 16 and 18 are associated with degassing well or slope leakage respectively. Unlike the previous ones and as might be expected, these samples have gone through the sealing rapidly without any measurable methane oxidation. In the case of sample 17, despite the high concentration, as in the case of sample 9, there is a crack associated with leakage. So that, although the high concentration could make us think of a zero oxidation, we can assume that there is a high diffusion of air to the interior which explains the oxidation value above 7 %.

4. CONCLUSIONS

The proposed method offers consistent results for samples taken. The results obtained can be related to the characteristics of the different samples. Despite this, there is great variability in the results of the oxidized fraction and it can be difficult to predict them due to the large number of factors involved in the oxidation process.

This variability in the results of oxidized fraction contrasts with the simplicity in determining this parameter in some models, such as the IPCC. While the model proposes a value of 10% for any managed landfill, our results reveal individual values up to 70%. According to (Chanton et al. 2009) the means for the fraction of methane oxidized on transit across the soil covers ranged from 22 to 55%. This fact suggests that determining this parameter accurately can be very relevant when determining the total emissions of methane in a landfill.

This method could be used to estimate the average oxidation across the entire surface of a specific landfill. For that it would be taken a great number of samples distributed in a way that would represent all the landfill surface. This would give an average value of oxidized fraction that would serve as input for the systematic use of a model of calculation of fugitive emissions in each landfill.

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