

Measurements of stable isotope ratios ($^{13}\text{CH}_4/^{12}\text{CH}_4$; $^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$) in landfill methane using a tunable diode laser absorption spectrometer

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Abstract. Variations in the isotopic composition ($\delta^{13}\text{C}$, δD) of methane produced within a landfill site near Mainz, Germany, were studied using a newly developed tunable diode laser absorption spectrometer (TDLAS) method. Additional data on the mixing ratios of CO_2 , O_2 , N_2 , CH_4 itself and $\delta^{13}\text{C}$ of the CO_2 in the landfill gas were also acquired. Samples taken from several branches of the landfill biogas collection system had methane isotopic compositions in the range $\delta^{13}\text{C} = -62.3$ to -55.3 ‰ VPDB ($n = 23$) and $\delta\text{D} = -327$ to -287 ‰ VSMOW ($n = 23$). Although the variability of the stable isotope ratios is small, several significant correlations were found between these and the other measured parameters, which provide insight into the microbiological processes occurring within the landfill. Several samples showed evidence of admixture of atmospheric air which occurs when the pumping rate in the collection branch exceeds the local methane production rate. A fraction of the atmospheric oxygen is consumed during the passage through the landfill and CO_2 is produced in addition to the CO_2 associated with methanogenesis. The consumption of oxygen is correlated with the $\delta^{13}\text{C}$ and δD of CH_4 and the $\delta^{13}\text{C}$ of CO_2 . The correlation is consistent with partial bacterial oxidation of CH_4 resulting in the progressive enrichment of the remaining CH_4 ($\alpha(\delta^{13}\text{C}) = 1.008 \pm 0.003$ and $\alpha(\delta\text{D}) = 1.044 \pm 0.020$) and in the formation of very depleted CO_2 . For samples showing no evidence of oxidation, there was a negative correlation between δD and $\delta^{13}\text{C}(\text{CH}_4)$ ($r = -0.86$, $n = 14$) and between $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{13}\text{C}(\text{CH}_4)$ ($r = -0.95$, $n = 14$), which we interpret as originating from slightly varying contributions from the two methanogenic pathways CO_2 reduction and acetate fermentation.

1. Introduction

Recent concern about the increased atmospheric CH_4 concentration which has more than doubled since preindustrial times [Etheridge *et al.*, 1992] centers on the contribution of CH_4 to global warming as well as on its central role in tropospheric and stratospheric chemistry [Lelieveld *et al.*, 1993; Cicerone and Oremland, 1988]. The determination of the stable isotope ratios $^{13}\text{C}/^{12}\text{C}$ and D/H of the methane emitted from different sources provides useful information about the sources and about the global methane cycle [Stevens and Engelkemeir, 1988; Wahlen, 1993]. Usually, the stable isotope ratios are expressed in the δ notation:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000,$$

where R_{sample} , R_{standard} are the $^{13}\text{C}/^{12}\text{C}$ (or D/H) ratios of the sample and a standard, respectively. The international standard for $^{13}\text{C}/^{12}\text{C}$ ratios is Vienna Pee Dee belemnite (VPDB), and for the D/H ratios Vienna Standard Mean Ocean Water (VSMOW) [Hut, 1987; Coplen, 1994]. Different methane formation processes are linked with different isotope fractionation with respect to the initial carbon and hydrogen pools used for the CH_4 generation, and the $\delta^{13}\text{C}$ - δD signatures of the resulting CH_4 are clearly distinguishable for the three principal methane production processes: (1) biogenic (bacterial) methane formation via acetate fermentation or CO_2 reduction, (2) thermogenic formation, and (3) incomplete combustion of biomass or fossil fuels [Whiticar *et al.*, 1986; Tyler, 1991; Wahlen, 1993].

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Among these processes, biogenic methanogenesis exhibits the strongest $\delta^{13}\text{C}$ fractionation compared to the initial organic matter ($\delta^{13}\text{C}$ values around -27‰ VPDB for C_3 plants) resulting in typical $\delta^{13}\text{C}(\text{CH}_4)$ values of -65 to -50‰ VPDB (acetate fermentation) and -80 to -60‰ VPDB (CO_2 reduction). Methane of thermogenic origin has $\delta^{13}\text{C} = -50$ to -25‰ VPDB, while CH_4 from biomass burning exhibits little or no fractionation compared to the organic matter resulting in $\delta^{13}\text{C}$ values around -27‰ (for C_3 plants). Differences in $\delta^{13}\text{C}$ of the organic matter are transferred to the $\delta^{13}\text{C}$ of the resulting CH_4 , as observed, for example, in CH_4 from ruminants fed with C_3 and C_4 plants ($\delta^{13}\text{C}$ of C_4 plants is about -13‰) [Rust, 1981; Levin *et al.*, 1993]. The range of δD values observed for biogenic CH_4 is between -400 and -160‰ VSMOW (with the more enriched values typical for CO_2 reduction and the more depleted typical for acetate fermentation), partly overlapping with the δD region of thermogenic CH_4 (-250 to -150‰ VSMOW), while the δD of CH_4 from biomass burning is clearly separated ($\delta\text{D} \approx -30\text{‰}$ VSMOW).

In a closed pool, the preferential removal of light isotopomers during biogenic methanogenesis is expected to result in a progressive isotopic enrichment of the remaining organic matter and thus of the generated CH_4 , an effect known as substrate depletion [Whiticar, 1990]. In addition, the isotopic composition of the CH_4 may undergo modification after formation by isotope fractionating processes, of which for most CH_4 sources the most important one is aerobic CH_4 oxidation by methanotrophic bacteria. Isotope fractionation factors associated with aerobic CH_4 oxidation have been determined to be in the range $\alpha(\delta^{13}\text{C}) = 1.013 - 1.025$ and $\alpha(\delta\text{D}) = 1.10 - 1.33$ in laboratory studies on methanotrophic cultures [Coleman *et al.*, 1981]. In the case of kinetic isotope effects, the fractionation factor is defined as ratio of rate constants of the two isotopomers considered, that is,

$$\alpha(\delta^{13}\text{C}) = \frac{k_{12\text{C}}}{k_{13\text{C}}} \quad \text{and} \quad \alpha(\delta\text{D}) = \frac{k_{\text{H}}}{k_{\text{D}}}$$

Thus, partial bacterial oxidation can distinctly shift the isotopic composition of the remaining CH_4 from its original signature (toward more enriched, i.e. more positive $\delta^{13}\text{C}$ and δD values).

Studies of the correlations between $\delta^{13}\text{C}$ and δD provide a powerful tool for differentiating between processes linked with the formation of CH_4 and secondary effects like CH_4 oxidation, and decrease the ambiguity in the interpretation of isolated $\delta^{13}\text{C}$ variation patterns. Thus CH_4 oxidation is characterized by positive $\delta^{13}\text{C}$ - δD correlations with a distinctly larger fractionation in δD compared to the fractionation in $\delta^{13}\text{C}$ ($\Delta\delta\text{D}/\Delta\delta^{13}\text{C} \approx 3 - 14$ [Coleman *et al.*, 1981; Burke *et al.*, 1988a; Whiticar, 1990]), while the effect of substrate depletion is linked with a slope of $\Delta\delta\text{D}/\Delta\delta^{13}\text{C} = 0 - 1$ [Whiticar, 1990]. Varying contributions of the

two biogenic pathways, acetate fermentation and CO_2 reduction, yield negative correlations between the two isotopes ($\Delta\delta\text{D}/\Delta\delta^{13}\text{C} < 0$). The $\delta\text{D}/\delta^{13}\text{C}$ correlations resulting from aerobic CH_4 oxidation and varying formation pathways have been observed in various marine and freshwater environments [Burke *et al.*, 1988a, b, 1992].

Despite increasing focus on isotope investigations of atmospheric methane sources, the isotope data available for many sources are still rather scarce. This in particular applies to sets of parallel δD and $\delta^{13}\text{C}$ measurements. One of the atmospheric methane sources, for which only a very few spot measurements of isotopic composition exist, are landfill sites. Despite their comparatively low estimated global CH_4 source strength of $20 - 70 \text{ Tg/yr}$ [Bingemer and Crutzen, 1987; Houghton *et al.*, 1992] corresponding to a contribution of $4 - 14\%$ of the total global CH_4 source strength, the special importance of landfill sites for the global CH_4 cycle arises from (1) their exclusively anthropogenic origin, (2) their expected increase in developing countries, and (3) the fact that CH_4 emissions from this source can be controlled by improved waste management practices.

In this paper we report $\delta^{13}\text{C}/\delta\text{D}$ investigations on a German landfill site. The study focusses on processes occurring within the landfill using samples which were taken from several branches of the landfill biogas collection system. It is important to note that these samples are not representative of the methane which, having passed through the incompletely sealed landfill cover, is released to the atmosphere, since the isotope ratios in that methane will probably be modified by oxidation occurring within the landfill cover. Nevertheless, our investigations of the biogas isotopic signatures provide insight into microbiological processes occurring within the landfill and are valuable for understanding the methane budget in landfills, which is determined by the generation of the biogas, its collection and loss processes by oxidation of CH_4 , and by the release into the atmosphere.

In order to determine the $\delta^{13}\text{C}$ and δD in CH_4 , we used a newly developed tunable diode laser absorption spectrometer (TDLAS), with which we determine the $^{13}\text{CH}_4/^{12}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$ ratios from the intensities of infrared absorption lines of the corresponding pairs of isotopomers [Bergamaschi *et al.*, 1994]. This optical method allows rapid direct measurements of the CH_4 samples without the need for the usual chemical conversion of CH_4 into CO_2 and H_2 . Hence the present study is also a demonstration of the applicability of this instrument for investigations of atmospheric CH_4 sources.

2. Experimental

2.1. Measurement Techniques

TDLAS measurements of $\delta^{13}\text{C}$ and δD in CH_4 . The TDLAS instrument has been described in detail

by [Bergamaschi *et al.*, 1994]. Briefly, the instrument is based on the difference of rovibrational transitions and the corresponding infrared spectra for the different CH_4 isotopomers. For $\delta^{13}\text{C}$ measurements we use a $^{13}\text{CH}_4/^{12}\text{CH}_4$ absorption line pair at $3007.145\text{ cm}^{-1}/3007.078\text{ cm}^{-1}$, for δD measurements a $^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$ line pair at $3042.345\text{ cm}^{-1}/3042.221\text{ cm}^{-1}$ or at $3044.289\text{ cm}^{-1}/3044.170\text{ cm}^{-1}$. A double heterostructure tunable Pb-salt diode laser is tuned over the spectral region of the respective absorption pairs. The main part of the laser beam is directed through a multipass reflection cell (White cell) with a maximum optical length of 213 m (base length 1.50 m), while a minor part of the beam traverses a 36 cm absorption cell containing a reference gas, whose isotopic composition has been determined by conventional isotope ratio mass spectrometry (IRMS) ($\delta^{13}\text{C} = -27.8\text{ ‰}$, $\delta\text{D} = -165\text{ ‰}$). Measurements are carried out at relative absorptions of 2 - 10 %, at total gas pressures of 30 - 40 mbar, and at room temperature. Using an automatic procedure, the White cell is alternately filled with the sample gases and the reference gas. The spectra of both optical channels are recorded simultaneously. Multiple linear regression procedures are carried out on-line for each set of spectra, comparing the $^{13}\text{CH}_4$ or $^{12}\text{CH}_3\text{D}$ absorptions and the $^{12}\text{CH}_4$ absorptions in the two channels. The $\delta^{13}\text{C}$ (or δD) value is obtained directly from the regression coefficients. For calibration to the VPDB / VSMOW scales additional working standard gases are used (CAL($\delta^{13}\text{C}$): $\delta^{13}\text{C} = 9.2\text{ ‰}$ VPDB; CAL(δD): $\delta\text{D} = 26\text{ ‰}$ VSMOW). The precision (1σ) of the TDLAS instrument is $\sigma(\delta^{13}\text{C}) = \pm 0.5\text{ ‰}$ and $\sigma(\delta\text{D}) = \pm 2.5\text{ ‰}$ for repeated measurements of the same sample. The overall accuracy has been determined in an intercomparison between TDLAS and IRMS for a variety of samples from different CH_4 sources (covering a range of $\delta^{13}\text{C} \approx -100$ to -20 ‰ VPDB and $\delta\text{D} \approx -330$ to -170 ‰ VSMOW; cf. [Bergamaschi *et al.*, 1994]) with a mean deviation of $\sigma(\delta^{13}\text{C}) = \pm 0.6\text{ ‰}$ and $\sigma(\delta\text{D}) = \pm 5\text{ ‰}$ and with a mean offset ($\delta_{\text{TDLAS}} - \delta_{\text{IRMS}}$) of $\Delta(\delta^{13}\text{C}) = -0.1 \pm 0.6\text{ ‰}$ and $\Delta(\delta\text{D}) = 4 \pm 3\text{ ‰}$ between the methods. We define the mean deviation $\sigma(\delta)$ as

$$\sigma(\delta) = \left[\frac{1}{n} \sum_{i=1}^n [\delta_{\text{IRMS}}(i) - \delta_{\text{TDLAS}}(i)]^2 \right]^{1/2}$$

In the present system the minimum mixing ratios required are 100 ppm CH_4 (sample size $4\text{ }\mu\text{mol CH}_4$) for direct $\delta^{13}\text{C}$ measurements and 2000 ppm CH_4 (sample size $80\text{ }\mu\text{mol CH}_4$) for direct δD measurements.

Supplementary measurements. $\delta^{13}\text{C}$ of CO_2 was determined using mass spectrometry (VG PRISM) after cryogenic extraction of CO_2 from the remaining sample gases (precision $\sigma(\delta^{13}\text{C}(\text{CO}_2)) = 0.1\text{ ‰}$). These mass spectrometer measurements were performed against a working standard gas, which was calibrated

against NBS19. The concentrations of O_2 , N_2 , CO_2 , and CH_4 were determined by means of a gas chromatograph (GC) equipped with a thermal conductivity detector. To compensate for the nonlinearity of the detector, a calibration was performed in the range of mixing ratios from 1 to 100 vol % for all four gases, using a dynamic mixture of pure O_2 , N_2 , CO_2 , and CH_4 . The precision of the GC measurements was 1 % (of the measured value), the accuracy about 2 %.

2.2. Site Description

The samples were taken during October 1992 at a landfill site near Mainz, Germany. This landfill extends over $150,000\text{ m}^2$ and is used for municipal solid wastes only. The landfilling started in 1965 and continues until the present. Three sections were used at various times as follows: (1) section 1 from 1965 to 1978, (2) section 2 from 1978 to 1986, and (3) section 3 from 1986 to 1991. All three sections are covered with a layer of clay or loess. The biogas produced within the landfill is pumped from a system of several vertical pipes laid within the waste and is used for electricity generation.

In this study the biogas samples were taken directly from various branches of the gas collection system. Samples are transferred into polyethylene-coated aluminium bags using a membrane pump.

3. Results and Discussion

3.1. Overview

A compilation of the $\delta^{13}\text{C}(\text{CH}_4)$, $\delta\text{D}(\text{CH}_4)$, and $\delta^{13}\text{C}(\text{CO}_2)$ data and the concentrations of CH_4 , CO_2 , O_2 , and N_2 is given in Table 1. The $\delta^{13}\text{C}$ values for CH_4 exhibit only a very small amount of variation ($\delta^{13}\text{C} = -62.3$ to -55.3 ‰), whereas the variation of $\delta^{13}\text{C}$ in CO_2 is distinctly larger ($\delta^{13}\text{C} = -8.6$ to 16.4 ‰). The δD values of CH_4 vary between -327 and -287 ‰ with a clear separation between samples from section 1 and 2 (1965-1986: $\delta\text{D} > -315\text{ ‰}$) and samples from section 3 (1986-1991: $\delta\text{D} < -315\text{ ‰}$) (Figure 1). The $\delta^{13}\text{C}$ value for sample 13 is anomalous, as is the ratio of CH_4/CO_2 (see below) and this point is not included further. The other data in Figure 1 indicate a clear relationship between the stable isotope ratios in CH_4 and consist of two groups, one with positive, one with negative correlation between $\delta^{13}\text{C}$ and δD .

3.2. Correlations of Isotopic Composition (CH_4 and CO_2) With CH_4/CO_2 Ratios and O_2 Consumption

Some of the samples listed in Table 1 exhibit very high mixing ratios of N_2 (up to 74 %) and O_2 (up to 20 %) caused by the admixture of atmospheric air in those parts of the biogas collection system where either the pumping rate exceeded the local biogas production rate or where leakages in the landfill cover allow the

Table 1. Compilation of Concentrations of CH₄, CO₂, O₂, N₂, and Isotopic Composition of CH₄ and CO₂.

Sample	CH ₄ , vol %	CO ₂ , vol %	CH ₄ / CO ₂	O ₂ , vol %	N ₂ , vol %	O ₂ cons/ CH ₄	δ ¹³ C (CH ₄), ‰	δD (CH ₄), ‰	δ ¹³ C (CO ₂), ‰	δ ¹³ C (CH ₄ +CO ₂), ‰
<i>Section 1 (1965-1978)</i>										
11	33.2	26.1	1.27	3.4	38.4	0.21	-61.6	-292.7	3.6	-32.9
12	31.2	27.2	1.15	1.0	41.5	0.32	-60.5	-298.5	4.3	-30.3
13	66.7	30.6	2.18	0.0	1.3	0.01	-55.3	-306.1	12.0	-34.2
14	21.8	14.6	1.50	12.9	51.6	0.04	-61.5	-298.9	14.7	-31.0
15	3.4	3.0	1.13	19.6	73.7	0.06	-57.5	-289.0		
16	28.5	23.5	1.21	2.3	47.7	0.37	-61.6	-295.6	2.4	-32.7
17	40.2	29.4	1.37	0.9	31.5	0.19	-61.3	-294.2	9.7	-31.3
<i>Section 2 (1978-1986)</i>										
18	36.3	23.4	1.55	8.9	33.5	0.00	-62.2	-301.4	16.3	-31.4
19	49.0	31.7	1.55	4.4	16.8	0.00	-61.6	-294.9	16.3	-31.0
20	28.0	17.5	1.60	12.0	44.1	-0.01	-61.0	-292.4	16.2	-31.4
21	60.3	37.3	1.62	0.6	2.6	0.00	-62.3	-296.9	16.4	-32.2
22	58.8	40.0	1.47	0.0	1.9	0.01	-61.2	-294.7	15.2	-30.3
23	58.4	38.2	1.53	0.4	4.1	0.01	-61.2	-292.5	14.9	-31.1
24	59.3	38.8	1.53	0.1	2.5	0.01	-60.8	-294.4	15.0	-30.8
25	22.2	24.2	0.92	0.9	54.5	0.62	-60.4	-286.9	-6.7	-32.4
26	37.2	28.8	1.29	1.0	34.4	0.22	-60.7	-293.6	2.7	-33.0
27	20.1	22.9	0.88	0.9	57.4	0.72	-59.5	-292.1	-8.6	-32.4
28	60.4	38.1	1.59	0.0	1.0	0.00	-61.0	-307.2	14.1	-31.9
<i>Section 3 (1986-1991)</i>										
29	55.1	41.6	1.32	0.4	2.9	0.01	-59.6	-322.8	11.2	-29.1
30	57.4	41.9	1.37	0.0	0.4	0.00	-58.3	-326.8	9.0	-29.9
31	56.4	43.1	1.31	0.0	0.5	0.00	-59.4	-322.8	9.8	-29.4
32	56.5	43.3	1.31	0.0	0.4	0.00	-60.1	-316.6	11.8	-28.9
33	56.1	43.3	1.30	0.0	0.4	0.00	-59.4	-316.5	10.2	-29.1

O₂cons is calculated according (1) and normalized to the CH₄ concentration. δ¹³C(CH₄+CO₂) is calculated according (8).

intrusion of atmospheric air. The O₂ from the atmosphere is partly consumed during the passage through the landfill, resulting in O₂/N₂ ratios lower than the atmospheric ratio of 20.95 % / 78.08 % = 0.268. The

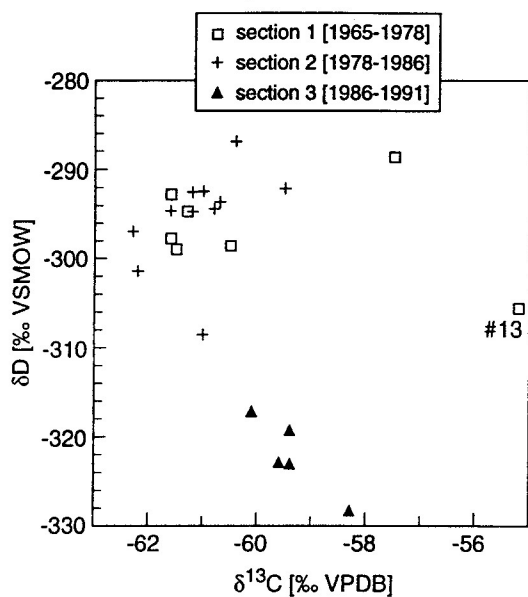
consumption of O₂ ([O₂]_{cons}) can be calculated from the measured mixing ratios [O₂]_f and [N₂]_f (f = final) assuming that N₂ is neither produced nor consumed within the waste:

$$[O_2]_{cons} = 0.268 [N_2]_f - [O_2]_f \quad (1)$$

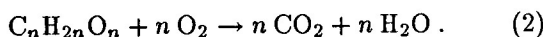
[O₂]_{cons} is normalized to the measured methane mixing ratios. Samples with negligible O₂ consumption ([O₂]_{cons}/[CH₄] < 0.05) have quite constant $r = CH_4/CO_2$ ratios (see Table 2). The CO₂ in these sample is attributed to CO₂ production associated with CH₄ formation under anaerobic conditions. Additional CO₂ which is formed in the presence of O₂ decreases the CH₄/CO₂ ratios of those samples exhibiting significant O₂ consumption. There are two possibilities, which could explain the partial consumption of O₂:

Table 2. Mean CH₄/CO₂ Ratios, δ¹³C(CH₄) and δ¹³C(CO₂) for Samples, which Are Not Affected by O₂ Consumption.

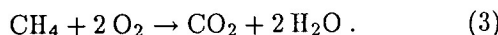
	CH ₄ /CO ₂ r _i	δ ¹³ C (CH ₄), ‰	δ ¹³ C (CO ₂), ‰
section 1 / 2	1.55 ± 0.04	-61.4 ± 0.5	15.5 ± 0.8
section 3	1.32 ± 0.03	-59.4 ± 0.6	10.4 ± 1.0

**Figure 1.** δD(CH₄)-δ¹³C(CH₄) diagram.

1. The availability of O_2 in some parts of the landfill allows local aerobic decomposition of organic matter leading to consumption of O_2 and production of CO_2 and H_2O according to



2. A fraction of CH_4 which was formed in the anaerobic parts of the landfill is oxidized by methanotrophic bacteria during the passage through the aerobic parts of the landfill resulting in the consumption of CH_4 and O_2 and production of CO_2 and H_2O :



Both possibilities will be discussed in the following subsections.

Hypothesis 1: Additional aerobic decomposition of organic matter. Under the first hypothesis the amount of additional CO_2 from aerobic decomposition can be evaluated from the measured mixing ratios $[CH_4]_f$ and $[CO_2]_f$ (i = initial; f = final):

$$[CO_2]_{\text{prod}} = [CO_2]_f - [CO_2]_i = [CO_2]_f - \frac{1}{r_i} [CH_4]_f, \quad (4)$$

where r_i is the mean ratio CH_4/CO_2 for samples showing no consumption of O_2 (Table 2). Figure 2a illustrates the calculated aerobic CO_2 production plotted against the calculated O_2 consumption ($[O_2]_{\text{cons}}$). A linear regression yields a slope of 0.64 ± 0.03 , while a slope of 1 is expected from (2), which corresponds to a deviation of $36 \pm 3\%$ of the observed slope compared to the expected one.

The admixture of CO_2 from aerobic decomposition of organic matter would lead to a strong shift in the observed $\delta^{13}C$ of the total CO_2 in the samples. While CO_2 originating from methanogenesis has very enriched $\delta^{13}C$ values of +10 to +16 ‰, the CO_2 produced by aerobic decomposition would be expected to have $\delta^{13}C$ values around -27 ‰ similar to the $\delta^{13}C$ of the organic matter itself. Figure 2b shows the measured $\delta^{13}C(CO_2)$ values plotted against the calculated fraction of aerobic CO_2 formation ($[CO_2]_{\text{prod}}/[CO_2]_f$). Since only the samples from section 1 and 2 exhibit significant O_2 consumption, the samples from section 3 are not plotted. The calculated mixing line describes the trend of the $\delta^{13}C(CO_2)$ reasonably well, though the data tend to lie slightly below this line.

Hypothesis 2: Partial bacterial oxidation of CH_4 . In the case of the second hypothesis the amount of CO_2 produced has to be calculated differently, since each CO_2 molecule produced corresponds to a CH_4 molecule consumed (neglecting partial utilization of CH_4 carbon for cell carbon of the bacteria and also neglecting small changes in the total gas volume due to condensation of the oxidation water)

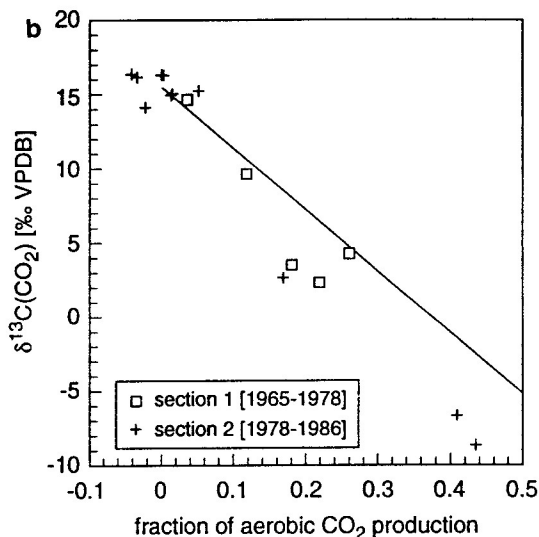
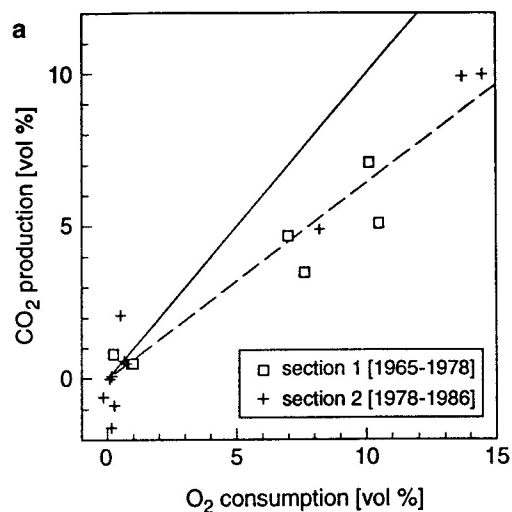


Figure 2. Hypothesis 1: (a) CO_2 production due to aerobic decomposition versus O_2 consumption calculated according (4) and (1). The dashed line represents the linear regression through the data with a slope of 0.64, while a slope of 1 is expected from (2) (solid line). (b) $\delta^{13}C(CO_2)$ versus calculated fraction of aerobic CO_2 production ($[CO_2]_{\text{prod}}/[CO_2]_f$). The solid line is the mixing line between CO_2 arising from methanogenesis and CO_2 from aerobic decomposition.

$$\begin{aligned} [CO_2]_{\text{prod}} &= [CO_2]_f - [CO_2]_i \\ &= [CO_2]_f - [CH_4]_i / r_i \\ &= [CO_2]_f - \frac{[CH_4]_f + [CO_2]_{\text{prod}}}{r_i} \\ \Rightarrow [CO_2]_{\text{prod}} &= \frac{[CO_2]_f - [CH_4]_f / r_i}{1 + 1/r_i} . \quad (5) \end{aligned}$$

$[CO_2]_{\text{prod}}$ calculated from (5) is plotted in Figure 3a against $[O_2]_{\text{cons}}$ calculated from (1). The regression yields a slope of 0.39 ± 0.02 , that is $22 \pm 4\%$ lower than a slope of 0.5 expected from (3). Thus the agreement is only slightly better than for hypothesis 1.

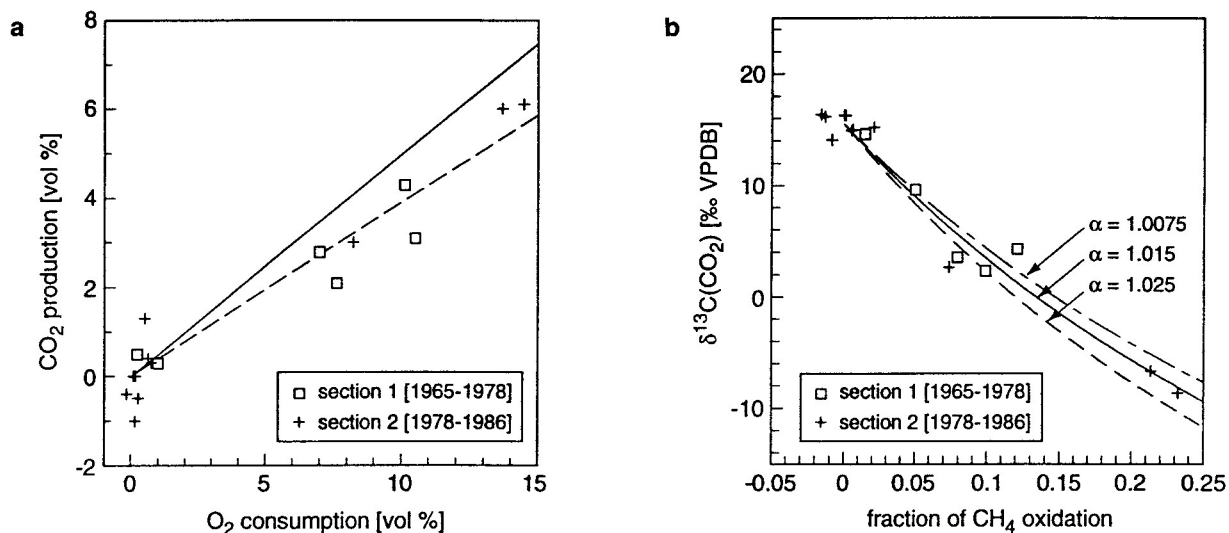


Figure 3. Hypothesis 2: (a) CO₂ production due to CH₄ oxidation versus O₂ consumption calculated according (5) and (1). The dashed line represents the linear regression through the data with a slope of 0.39, while a slope of 0.5 is expected from (3) (solid line). (b) δ¹³C(CO₂) versus calculated fraction of CH₄ oxidation (1-[CH₄]_f/[CH₄]_i). The curves represent the calculated course of δ¹³C(CO₂) for three different CH₄ oxidation fractionation factors α.

However, involvement of CH₄ oxidation gives a much better agreement with the observed δ¹³C variation in CO₂ than does hypothesis 1. The δ¹³C(CO₂) resulting from CH₄ oxidation can be calculated from mass balance, assuming, again, that incorporation of carbon into the bacteria is negligible:

$$\delta^{13}\text{C}(\text{CO}_2) = \frac{\delta^{13}\text{C}(\text{CH}_4)_i ([\text{CH}_4]_f + [\text{CO}_2]_f) - \delta^{13}\text{C}(\text{CH}_4)_f [\text{CH}_4]_f}{[\text{CO}_2]_f} \quad (6)$$

while the isotopic enrichment of the remaining CH₄ is described by the Rayleigh equation:

$$\delta^{13}\text{C}(\text{CH}_4)_f - \delta^{13}\text{C}(\text{CH}_4)_i = \left[\delta^{13}\text{C}(\text{CH}_4)_i + 1000 \right] \left[\frac{1}{\alpha} - 1 \right] \ln \frac{[\text{CH}_4]_f}{[\text{CH}_4]_i} \quad (7)$$

To model the mixing between CO₂ associated with CH₄ production and CO₂ from oxidation of CH₄, we again used only the data for sections 1 and 2 (see Table 2). Figure 3b shows the excellent agreement between the predicted change of δ¹³C(CO₂) and the data. Note that the predicted curves depend only weakly on the assumed fractionation factor for oxidation.

Further and strongest evidence for hypothesis 2 arises from the dependence of δ¹³C and δD in CH₄ from the calculated fraction of CH₄ oxidation which is shown in Figure 4a and 4b. The probabilities *P* that the calculated linear correlation coefficients *r* are exceeded by a random data set are 1.8 % and 3.2 %, respectively, and hence the significant increase of both δ¹³C and δD

with increasing calculated fractions of CH₄ oxidation is a strong indication for the actual occurrence of CH₄ oxidation. In the case of CO₂ production from aerobic decomposition, the δ¹³C and δD in CH₄ should be independent of the calculated "virtual" fraction of methane oxidation. The fractionation factors for oxidation determined from Figure 4a and 4b are α(δ¹³C) = 1.008 ± 0.003 and α(δD) = 1.044 ± 0.020.

3.3 Correlations Between Isotopes for Samples Not Affected by O₂ Consumption

Figure 5a shows the relationship between δ¹³C(CH₄) and δD for those samples which do not exhibit any significant O₂ consumption ([O₂]_{cons}/[CH₄] < 0.05). There is a clear negative correlation between δ¹³C(CH₄) and δD (*r* = -0.86; ΔδD/Δδ¹³C = -9.7 ± 1.7), in which the samples from section 3 lie in the region of more enriched δ¹³C and more depleted δD values. This correlation is a clear indication of a difference in the relative contribution of the methanogenic pathways, acetate fermentation, and CO₂ reduction, similar to that observed in natural environments [Burke *et al.*, 1988a, b]. According to this interpretation, the fraction of acetate fermentation is larger for the samples from section 3. Furthermore, there is a strong negative correlation between δ¹³C(CO₂) and δ¹³C(CH₄) for these samples (*r* = -0.95; Δδ¹³C(CO₂)/Δδ¹³C(CH₄) = -2.2 ± 0.2), as illustrated in Figure 5b, which might be a further confirmation for the given interpretation of a shift in the methanogenic pathways. Whiticar *et al.* [1986] have found more enriched δ¹³C(CO₂) and more depleted δ¹³C(CH₄) val-

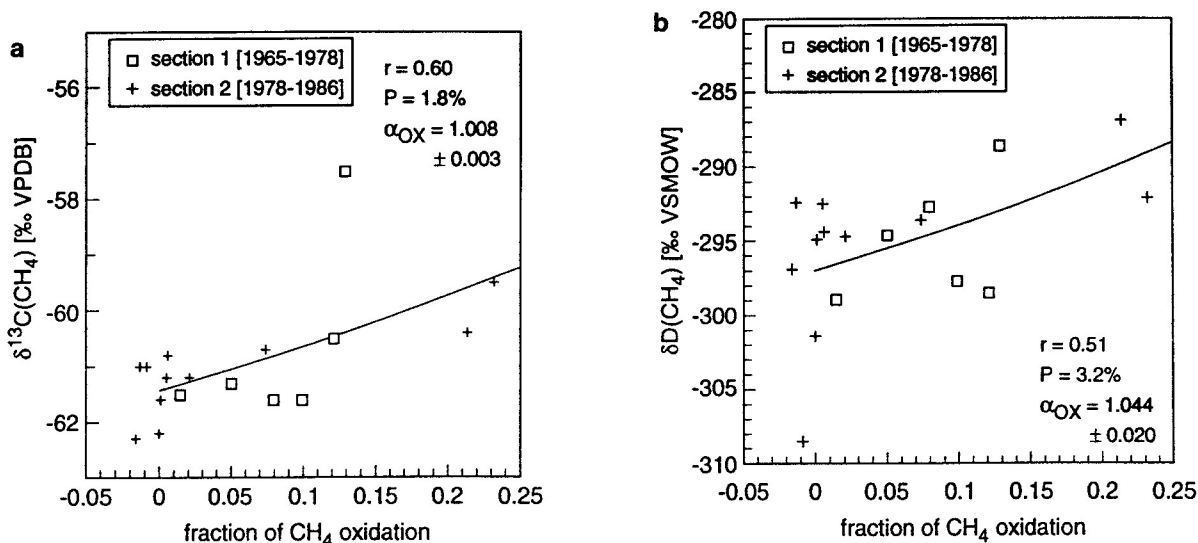


Figure 4. Isotopic enrichment of the remaining CH_4 as function of the calculated fraction of CH_4 oxidation ($1 - [\text{CH}_4]_f / [\text{CH}_4]_i$): (a) $\delta^{13}\text{C}(\text{CH}_4)$; (b) $\delta\text{D}(\text{CH}_4)$. r is the regression coefficient and P the corresponding probability for exceeding r in a random data set. $\alpha(\delta^{13}\text{C})$ and $\alpha(\delta\text{D})$ are the calculated isotope fractionation factors and the solid curves the corresponding courses of isotopic enrichment.

ues for samples from marine sediments (with mainly CO_2 reduction) if compared with samples from freshwater sediments (where acetate fermentation is the major pathway). One explanation for the small shift in the contribution of the two pathways in the landfill could be a change of substrates with ongoing degradation of the organic matter.

3.4. Mean $\delta^{13}\text{C}$ of Total Generated Biogas ($\text{CH}_4 + \text{CO}_2$)

In order to investigate a shift of the isotopic composition due to substrate depletion, the mean $\delta^{13}\text{C}(\text{CH}_4 + \text{CO}_2)$ content of the total generated biogas has to be considered. Neglecting minor contributions from non

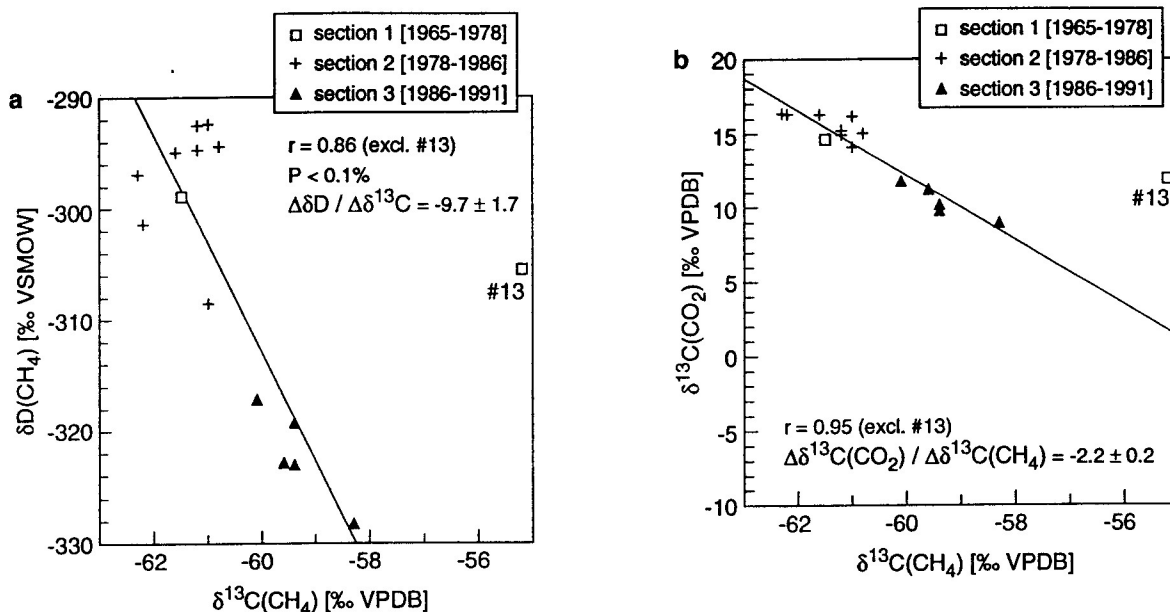


Figure 5. Correlations between isotopes for samples not affected by O_2 consumption. (a) $\delta\text{D}(\text{CH}_4)$ versus $\delta^{13}\text{C}(\text{CH}_4)$ and (b) $\delta^{13}\text{C}(\text{CO}_2)$ versus $\delta^{13}\text{C}(\text{CH}_4)$. The solid lines represent the calculated linear regressions.

methane hydrocarbons (NMHC), the mean $\delta^{13}\text{C}$ value is the average of the $\delta^{13}\text{C}$ values of CH_4 and CO_2 weighted with the corresponding mixing ratios:

$$\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2) = \frac{\delta^{13}\text{C}(\text{CO}_2)[\text{CO}_2]+\delta^{13}\text{C}(\text{CH}_4)[\text{CH}_4]}{[\text{CO}_2]+[\text{CH}_4]} \quad (8)$$

The calculated $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ values are listed in Table 1. Surprisingly, a decrease in $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ is apparent with increasing age of the wastes. From the substrate depletion effect an increase in $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ would be expected, because the preferential removal of light isotopomers should lead to a progressive isotopic enrichment of the remaining organic matter. Assuming that the observed trend in $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ is not due to a change of the composition of the wastes or / and their $\delta^{13}\text{C}$ content, then implies that the fractionation between the waste carbon and the resulting biogas ($\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$):

$$\alpha_{\text{biogas}} = \frac{\delta^{13}\text{C}(\text{organic matter}) + 1000}{\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2) + 1000} \quad (9)$$

is different in the different sections of the landfill or is changing in the course of the decomposition processes. This change of α_{biogas} could be due to the change of methanogenic pathways discussed in section 3.3 and would imply a greater fractionation from CO_2 reduction compared to acetate fermentation. The α_{biogas} values calculated from (9) are very low, ~ 1.002 for section 3 and ~ 1.005 for sections 1 and 2 of the landfill (assuming $\delta^{13}\text{C} = -27\text{‰}$ for the original organic matter). With these low α_{biogas} factors and assuming a Rayleigh process, a considerable turnover of the organic matter would be necessary to cause an effect of a few per mil in the observed $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$.

An alternative explanation for the observed shift of $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ could be the different timescales for the degradation of the various waste fractions. Reported decomposition times for food and garden wastes are in the range 1-5 years, for paper 5-20 years, and for the nonlignin fraction of wood 20-100 years [Rovers *et al.*, 1977]. Different $\delta^{13}\text{C}$ values of the carbon for these different waste components or different fractionation factors α_{biogas} for the different waste components might explain the observed trend of $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$.

4. Conclusions

The study presented here demonstrates the usefulness of parallel measurements of $\delta^{13}\text{C}$ and δD in CH_4 for the investigation of the interaction between CH_4 formation and CH_4 consumption. The application to landfill biogas was supported by additional measurements of $\delta^{13}\text{C}$ in CO_2 and the mixing ratios of O_2 , N_2 , CO_2 , and CH_4 . The main features which could be observed are as follows:

1. Admixture of atmospheric oxygen through the gas collection system leads to the formation of additional CO_2 beyond that produced in association with the methanogenesis and influences the $\delta^{13}\text{C}$ and δD of CH_4 as well as the $\delta^{13}\text{C}$ of the total CO_2 . The observed trends in the isotopic composition could be consistently explained with the occurrence of partial aerobic bacterial oxidation of CH_4 (hypothesis 2) resulting in the progressive enrichment of the remaining CH_4 and the formation of very depleted CO_2 ($\delta^{13}\text{C} \approx -60$ to -80‰). It is possible that aerobic decomposition of the organic matter also contributes to a part of the additional CO_2 (hypothesis 1), even though this effect alone could not explain the observed trends in $\delta^{13}\text{C}$ and δD in CH_4 .

2. Among the group of samples showing no significant CH_4 oxidation, a negative correlation is apparent between δD and $\delta^{13}\text{C}(\text{CH}_4)$ as well as between $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{13}\text{C}(\text{CH}_4)$. This effect is interpreted as being due to slightly varying contributions of the two methanogenic pathways, acetate fermentation and CO_2 reduction.

3. In contrast to an expected increase of the mean $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ of the generated biogas with increasing age of the wastes the opposite trend was observed. Apparently, the shift in $\delta^{13}\text{C}(\text{CH}_4+\text{CO}_2)$ that might have been expected to arise from substrate depletion was hidden by CH_4 formation related factors controlling the $\delta^{13}\text{C}$ fractionation between the organic matter and the resulting biogas or by differences in the $\delta^{13}\text{C}$ of different fractions of the waste.

It should be noted that despite the observed effects the overall variability of $\delta^{13}\text{C}$ and δD in CH_4 is very low. This also applies to the $\delta^{13}\text{C}$ in CO_2 for the group of samples showing no significant CH_4 oxidation. Factors responsible for these low variabilities are as follows:

1. The individual branches of the gas collection system pump the landfill gas from a volume with horizontal radius of ~ 50 m and vertical extent of > 10 m, resulting in an averaging of small-scale spatial variabilities in the composition of the organic matter and the conditions for methanogenesis.

2. The temperatures inside landfill (at depths > 2 m) have been found to be independent of ambient temperatures [Rettenberger, and Tabasaran, 1980]. Therefore a possible temperature dependence of fractionation factors associated with methanogenesis would be irrelevant.

While the CH_4 isotopic signatures of the landfill biogas sample discussed here are mainly controlled by CH_4 formation processes (with small contributions of oxidation processes within some parts of the landfill leading to shifts in $\delta^{13}\text{C}$ and δD) the CH_4 actually emitted into the atmosphere through the landfill cover may undergo substantial shifts both in $\delta^{13}\text{C}$ and δD due to oxidation processes within the landfill cover. $\delta^{13}\text{C}$ and δD measurements [Bergamaschi, 1993] in CH_4 both from the soil air of different landfill covers and from the emitted CH_4 showed distinctly larger $\delta^{13}\text{C}$ and δD variabilities (with a trend to more enriched $\delta^{13}\text{C}$ and δD val-

ues) than for the gas collection system samples. While the landfill biogas samples presented here exhibit the typical $\delta D/\delta^{13}C$ signature of biogenic methane sources dominated by acetate fermentation, CH_4 emitted from landfills into the atmosphere might represent a biogenic source of isotopically rather enriched CH_4 . This work has demonstrated the usefulness of our newly developed TDLAS technique for the study of stable isotope ratios in methane and for the elucidation of processes taking place within systems emitting CH_4 to the atmosphere.

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