ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Waste Management 28 (2008) 1535–1542

waste management

www.elsevier.com/locate/wasman

Modelling of stable isotope fractionation by methane oxidation and diffusion in landfill cover soils

Koenraad Mahieu [a,b,*], Alex De Visscher [c], Peter A. Vanrolleghem [b,d], Oswald Van Cleemput [a]

[a] Laboratory of Applied Physical Chemistry (ISOFYS), Ghent University, Coupure links 653, B-9000 Ghent, Belgium
[b] Department of Applied Mathematics, Biometrics and Process Control (BIOMATH), Ghent University, Coupure links 653, B-9000 Ghent, Belgium
[c] Department of Chemical and Petroleum Engineering, Schulich School of Engineering, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4
[d] Department of Civil Engineering (modelEAU), Université Laval, Pavillon Pouliot, Québec, Canada G1K 7P4

Accepted 11 June 2007
Available online 6 September 2007

Abstract

A technique to measure biological methane oxidation in landfill cover soils that is gaining increased interest is the measurement of stable isotope fractionation in the methane. Usually to quantify methane oxidation, only fractionation by oxidation is taken into account. Recently it was shown that neglecting the isotope fractionation by diffusion results in underestimation of the methane oxidation. In this study a simulation model was developed that describes gas transport and methane oxidation in landfill cover soils. The model distinguishes between $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$ explicitly, and includes isotope fractionation by diffusion and oxidation. To evaluate the model, the simulations were compared with column experiments from previous studies. The predicted concentration profiles and isotopic profiles match the measured ones very well, with a root mean square deviation (RMSD) of 1.7 vol% in the concentration and a RMSD of 0.8‰ in the $\delta^{13}C$ value, with $\delta^{13}C$ the relative ^{13}C abundance as compared to an international standard. Overall, the comparison shows that a model-based isotope approach for the determination of methane oxidation efficiencies is feasible and superior to existing isotope methods.

1. Introduction

Landfills are an important source of CH_4 since about 7% of CH_4 emissions to the atmosphere are estimated to originate from landfills (IPCC, 2001). The contribution of CH_4 to the climate change is estimated at 22% of the contribution of all greenhouse gases (Lelieveld et al., 1998).

In a landfill cover soil layer, part of the CH_4 is oxidized to CO_2. A promising method to quantify methane oxidation is by measuring isotope fractionation because it is a noninvasive technique. Bacteria oxidize the ^{12}C-isotope slightly faster than the ^{13}C-isotope. The result is an increase of the $^{13}C/^{12}C$ ratio of the remaining CH_4. This increase can be used to estimate CH_4 oxidation. The enrichment of ^{13}C in CH_4 is measured as isotopic abundance:

$$\delta^{13}C = \left(\frac{R}{R_{st}} - 1\right) \cdot 1000‰ \tag{1}$$

with R the isotope ratio $^{13}C/^{12}C$ of the sample and R_{st} the isotope ratio of the reference standard (VPDB for carbon).

When the isotope ratios are measured inside the waste mass where CH_4 is produced, and at the top of the landfill where it is emitted, the fraction of CH_4 oxidized can be calculated with the following equation (Monson and Hayes, 1980):

---

[*] Corresponding author. Address: Laboratory of Applied Physical Chemistry (ISOFYS), Ghent University, Coupure links 653, B-9000 Ghent, Belgium. Tel.: +32 9264 6001; fax: +32 9264 6242.
E-mail address: Koenraad.mahieu@lid.kviv.be (K. Mahieu).

0956-053X/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.wasman.2007.06.003

Nomenclature

a	specific biomass decay rate (s^{-1})
b	modified moldrup exponent
D_{ij}	binary diffusion coefficient mixture gases i and j ($m^2\ s^{-1}$)
D_{soil}	total dispersion coefficient
D_{mol}	molecular diffusion coefficient
D_{mech}	mechanical dispersion coefficient
F_{in}	CH_4 influx (mol $m^{-2}\ s^{-1}$)
f_{ox}	fraction CH_4 oxidized
K_m	half-saturation constants CH_4 (μl l^{-1})
K_{O_2}	half-saturation constants CH_4 (μl l^{-1})
M_i	molar mass ion i
N_i	flux of compound i (mol $m^{-2}\ s^{-1}$)
N_{tot}	total gas flux (mol $m^{-2}\ s^{-1}$)
Q	air flow rate ($m^3\ s^{-1}$)
r_i	reaction rate compound i (mol $kg^{-1}\ s^{-1}$)
R_{st}	isotope ratio of reference standard VPDB
v	interstitial gas velocity (m s^{-1})
V	headspace volume (m^3)
V_{max}	maximum oxidation rate (nmol CH_4 $kg_{soil\ DW^{-1}}$ s^{-1})
$V_{max,max}$	maximum V_{max} (nmol CH_4 $kg_{soil\ DW^{-1}}$ s^{-1})
x	CO_2 yield
y_i	mole fraction compound i
$y_{i,1}$	mole fraction at surface
$y_{i,b}$	mole fraction in atmosphere
α_{disp}	dispersivity (m)
α_{ox}	fractionation factor of CH_4 oxidation
α_{trans}	fractionation factor of CH_4 transport
$\delta^{13}C$	^{13}C-isotope abundance (‰)
$\delta^{13}C\_flux$	^{13}C-isotope abundance of the flux (‰)
δA	$\delta^{13}C$ of produced CH_4 (‰)
δE	$\delta^{13}C$ of emitted CH_4 (‰)
ε	air filled pore space
μ	net specific growth rate (s^{-1})
μ'_{max}	maximum gross specific growth rate (s^{-1})
Φ	total porosity
Ω	soil surface (m^2)

$$f_{ox} = \frac{\delta E - \delta A}{1000 \cdot (\alpha_{ox} - \alpha_{trans})} \quad (2)$$

with δE the isotopic abundance of the emitted CH_4, δA the isotopic abundance of the produced CH_4, α_{ox} the fractionation factor for CH_4 oxidation and α_{trans} the fractionation factor for CH_4 transport. This equation is used for field applications under the name “open system equation”. In a laboratory setup an alternative “closed system equation” is used, also called Rayleigh approach (Mahieu et al., 2006):

$$f_{ox} = 1 - \left(\frac{\delta E + 1000}{\delta A + 1000}\right)^{\frac{\alpha_{ox}}{1-\alpha_{ox}}} \quad (3)$$

Liptay et al. (1998) and Chanton et al. (1999) applied the isotope technique on several landfills in the Northeast United States, and found oxidation efficiencies in general agreement with the annual mean value of 10% reported by Czepiel et al. (1996). Chanton and Liptay (2000) estimated 20% oxidation for clay and mulch topsoil, but this was under a warmer climate than the studies of Czepiel et al. (1996) and Liptay et al. (1998). Much higher oxidation percentages, up to 80%, were also reported by Bergamaschi et al. (1998) who used ^{222}Rn activities. In these studies the fractionation factor for CH_4 transport is assumed to be equal to 1, which means that no fractionation due to transport is assumed. This is based on the assumption that CH_4 transport is dominated by advection, which is not an isotope-specific process (Liptay et al., 1998; Chanton and Liptay, 2000). However, De Visscher et al. (2004) demonstrated that next to advection, diffusion is also an important transport mechanism for CH_4 in landfill cover soils. They found that the fractionation factor due to transport, α_{trans}, can be as high as 1.014, due to the difference in molecular diffusion coefficients of CH_4 isotopes. The result of neglecting the fractionation by diffusion is an underestimation of CH_4 oxidation (De Visscher et al., 2004).

Unfortunately, there is no method to directly measure α_{trans}. So it is necessary to use a model-based approach. The goal of this paper is therefore to develop a model that can be used as a basis for this approach. This model will be calibrated with laboratory data.

Several models for describing mass transport and CH_4 oxidation in landfill cover soils have been proposed. Bogner et al. (1997) used collisions of CH_4 molecules to soil particles and biomass to describe diffusion and oxidation in a landfill cover soil. The model of Hilger et al. (1999) is based on the Stefan-Maxwell equations for gas flow and diffusion and a biofilm model with oxygen limitation for CH_4 oxidation. Stein et al. (2001) used Fick’s Law for diffusion instead of Stefan-Maxwell, but with concentration-dependent diffusion coefficients (Froment and Bischoff, 1990). A dual-substrate CH_4 oxidation model was used with CH_4 and O_2 limitation. Wilshusen et al. (2004) used this model to evaluate the effect of exopolymers on gas concentration profiles in passively aerated methane biofilters. A similar model was used by Perera et al. (2002) to calculate the source strength of a landfill.

De Visscher and Van Cleemput (2003) developed a model based on the Stefan-Maxwell equations and dual-substrate limitation for CH_4 oxidation. Their model also incorporates biomass growth.

The model presented here is an extension of the model developed by De Visscher and Van Cleemput (2003). It was extended by distinguishing explicitly between $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$. Fractionation of isotopes by biological oxidation and by molecular diffusion was accounted for, as well as mechanical dispersion, which has no fractionation effect. From dispersion measurements with a column filled with glass beads, Mahieu et al. (submitted for publication) concluded that mechanical dispersion is relevant also for the lower gas velocities that are encountered in landfills.

The model was tested with laboratory data of De Visscher et al. (2004), which is most representative to homogeneous covers like temporary covers, but there is no reason to assume that the model would be inapplicable to other types of cover soils.

2. Model development

2.1. Diffusion and oxidation model (De Visscher and Van Cleemput, 2003)

The main features of the model of De Visscher and Van Cleemput (2003) are summarized below.

The basis of the model is the following continuity equation:

$$\varepsilon \frac{\partial y_i}{\partial t}\frac{P}{RT} = \rho r_i - \frac{\partial N_i}{\partial z} \tag{4}$$

with y_i the mole fraction of component i, t the time (s), P the absolute pressure (Pa), R the ideal gas constant (8.314472 J mol^{-1} K^{-1}), T the absolute temperature (K), ε the air-filled pore space (–), z the depth (m) (0 = soil surface), ρ the dry bulk density of the soil (kg m^{-3}), r_i the reaction rate of compound i (mol kg^{-1} s^{-1}), and N_i the flux of compound i (mol m^{-2} s^{-1}, positive for downward flux).

The fluxes are calculated with the Stefan-Maxwell equations:

$$-\frac{P}{RT}\frac{\partial y_i}{\partial z} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{N_i y_j - N_j y_i}{D_{ij}} \tag{5}$$

with D_{ij} (m^2 s^{-1}) the binary diffusion coefficient of a mixture of gases i and j in a soil matrix.

Methane oxidation kinetics were described with the Michaelis-Menten equation with O_2 limitation:

$$r_{CH_4} = -\frac{V_{max} y_{CH_4}}{K_m + y_{CH_4}} \cdot \frac{y_{O_2}}{K_{O_2} + y_{O_2}} \tag{6}$$

with r_{CH_4} the reaction rate of CH_4 (nmol CH_4 $kg_{soil\ DW^{-1}}$ s^{-1}), V_{max} the maximum oxidation rate (nmol CH_4 $kg_{soil\ DW^{-1}}$ s^{-1}), K_m and K_{O_2} the half-saturation constants for CH_4 and O_2, respectively (μl l^{-1}).

Biomass growth is described by

$$\mu = \frac{\mu'_{max}\left(1 - \frac{V_{max}}{V_{max,max}}\right) y_{CH_4}}{K_m + y_{CH_4}} \cdot \frac{y_{O_2}}{K_{O_2} + y_{O_2}} - a \tag{7}$$

$$\frac{dV_{max}}{dt} = \mu V_{max} \tag{8}$$

with μ the net specific growth rate (s^{-1}), μ'_{max} the maximum gross specific growth rate (s^{-1}), $V_{max,max}$ the maximum value of V_{max} that would be obtained in the absence of decay, and a the specific biomass decay rate (s^{-1}).

The CH_4 flux from the anaerobic landfill to the cover soil is assumed to be known. In practice, this value will have to be determined by trial and error, using concentration profiles, isotope abundance profiles, and surface fluxes to test the accuracy of the value.

The concentration of CH_4 at the surface is a boundary condition and can be calculated with a mass balance for the mixed headspace:

$$\frac{dy_{i,1}}{dt} = \frac{1}{V}\left(\frac{RT}{P} Q y_{i,b} - N_i \Omega - y_{i,1}\left(\frac{RT}{P} Q - \Omega N_{tot}\right)\right) \tag{9}$$

with $y_{i,1}$ and $y_{i,b}$ the mole fraction of component i at the surface and in the atmosphere, respectively, Q the air flow rate above the soil column (m^3 s^{-1}), Ω the column cross-sectional area (m^2), V the headspace volume (m^3) and $N_{tot} = \sum_{i=1}^{4} N_i$ the total gas flux.

2.2. Extensions for fractionation by diffusion and oxidation

Fractionation by diffusion is accounted for by assigning different diffusion coefficients to the $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ isotopes. The influence of molar mass on diffusion coefficients in the gas phase is (Marrero and Mason, 1972):

$$D_{ij} \sim \frac{1}{\sqrt{\frac{M_i \cdot M_j}{M_i + M_j}}} \tag{10}$$

with M_i the molar mass of ion i and D_{ij} the binary diffusion coefficient of a mixture of gases i and j.

By using Eq. (10), the ratio between binary diffusion coefficients of different isotopes can be calculated. For example the binary diffusion coefficient of a mixture $^{13}CH_4$ and N_2, $D_{^{13}CH_4,N_2}$, can be calculated from its ^{12}C equivalent, $D_{^{12}CH_4,N_2}$:

$$\frac{D_{ij}}{D_{ij'}} = \sqrt{\frac{M_{j'}}{M_j} \cdot \frac{M_i + M_j}{M_{i'} + M_{j'}}} \Rightarrow \frac{D_{^{12}CH_4,N_2}}{D_{^{13}CH_4,N_2}} = 1.0193$$

The reaction rates for the $^{13}CH_4$ and $^{12}CH_4$ are calculated from the reaction rate of CH_4:

$$r_{^{13}CH_4} = \frac{1}{\alpha_{ox}} \cdot \frac{r_{CH_4} \cdot y_{^{13}CH_4}}{y_{CH_4}} \tag{11}$$

$$r_{^{12}CH_4} = r_{CH_4} - r_{^{13}CH_4} \tag{12}$$

Mechanical dispersion is added to the molecular diffusion to obtain the total dispersion D_{soil}:

$$D_{soil} = D_{mol} + D_{mech} \tag{13}$$

with D_{mol} the molecular diffusion coefficient in the soil calculated with a modified Moldrup et al. (2000) equation and D_{mech} the mechanical dispersion coefficient. Or

$$D_{\mathrm{soil,ij}} = \frac{\varepsilon^{1+b}}{\Phi} D_{\mathrm{ij}} + \alpha_{\mathrm{disp}} \cdot v \tag{14}$$

with ε the air filled porosity (–), Φ the total porosity (–), v the interstitial gas flow velocity ($\mathrm{m\,s^{-1}}$), b the modified moldrup exponent and α_{disp} the dispersivity (m) (not to be confused with any fractionation factor).

The model is run for a sufficient time to allow the system to reach steady state behavior. The results shown in this paper represent steady state conditions.

2.3. Experimental set-up and model calibration

The model was calibrated with the WEST modelling software (Hemmis NV, Kortrijk, Belgium) using data from a column experiment (De Visscher et al., 2004). A 60 cm high Plexiglas column (internal diameter: 14.1 cm) was filled up to 50 cm with fresh top soil from the Armhoede landfill (Lochem, The Netherlands). Soil properties are given by De Visscher et al. (2004). Every 10 cm a septum was installed through which samples can be taken with a syringe (Fig. 1). Pure CH_4 was sent to the column through a bottom inlet section. The CH_4 flow rate was 19.3 mol CH_4 $\mathrm{m^{-2}\,day^{-1}}$.

In a real landfill the produced gas is a mixture of CO_2 and CH_4, The use of pure CH_4 in the experiment has some advantages. The CH_4 concentration gradient will be larger, which means there will be more diffusion. As a result, fractionation by diffusion will be more clearly measurable.

The headspace above the column was flushed with air at a flow rate about 100 times higher than the incoming CH_4 flux. At several depths, sampling points were inserted to measure concentration and isotopic profiles. The samples were taken after an incubation period of 33 days. The moisture content profile was measured after breakup of the column.

The model was tested with simulations and calibrations. The simulations were based entirely on parameters determined independently, and indicate the predictive power of the model. The calibrations involved fitting of the model by adjusting parameters, and indicate the model's ability to describe the experimental data.

The simulations with the model were conducted to test whether it was possible to fit the concentrations and isotopic profiles with standard parameters. In the first simulation the fractionation by diffusion was not taken into account, while in a second simulation fractionation by diffusion was included.

The parameters used in the simulations are summarized in Table 1. For a detailed explanation of the parameters and the sensitivity of the model for these parameters, see De Visscher and Van Cleemput (2003). $V_{\mathrm{max,max}}$ was chosen as the maximum of the V_{max} profile measured in batch experiments conducted with soil from different depths. The fractionation factor α_{ox} was determined from batch experiments (De Visscher et al., 2004).

After this simulation a calibration was done to test whether better results could be obtained by varying $V_{\mathrm{max,max}}$, b, and the CO_2 yield (x), i.e., the number of moles of CO_2 produced per mole CH_4 oxidized (see also Section 3.2). Measured concentration profiles, V_{max} profile and CH_4 emission were used as input data for the calibration. Weights were assigned to these data to get an equal spreading of the sum of squares of the residuals over all variables.

In a second calibration the δ^{13}C profiles were also used as data, and mechanical dispersion was introduced with α_{disp} as an extra parameter to estimate.

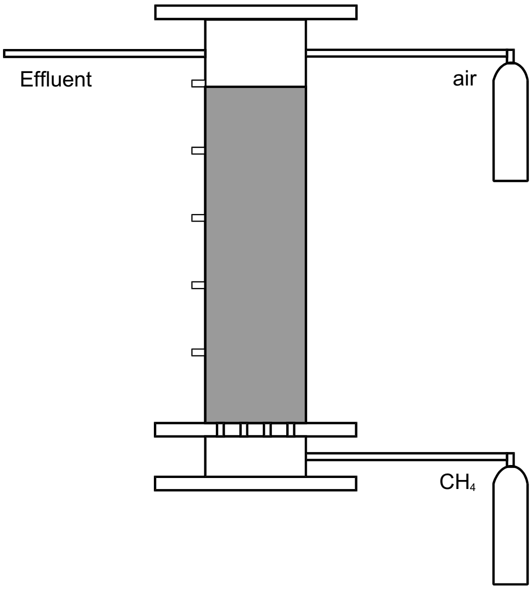

Fig. 1. Scheme of the experimental set-up.

Table 1
Parameters used for the simulation

Parameter	Value	Source
T	292.15 K	Measured
ρ	1012 $\mathrm{kg_{soil\ DW}\,m^{-3}}$	Measured
$V_{\mathrm{max,max}}$	2.4×10^{3} nmol CH_4 $\mathrm{kg_{soil\ DW^{-1}}\,s^{-1}}$	Measured (see 2.3)
K_{m}	5380 $\mathrm{\mu l\,l^{-1}}$	De Visscher and Van Cleemput (2003)
K_{O_2}	1.2%	De Visscher and Van Cleemput (2003)
μ'_{max}	2.2 $\mathrm{d^{-1}}$	De Visscher and Van Cleemput (2003)
Q	1.56×10^{-5} $\mathrm{m^3\,s^{-1}}$	Measured
Ω	0.0156 $\mathrm{m^2}$	Measured
F_{in}	0.000223 $\mathrm{mol\,m^{-2}\,s^{-1}}$	Measured
a	0.1 $\mathrm{d^{-1}}$	De Visscher and Van Cleemput (2003)
α_{ox}	1.0183	Measured (see 2.3)
ϕ	0.61	Measured
δA	−35.2‰	Measured

3. Results and discussion

3.1. Simulation

In Figs. 2 and 3, the results of the simulations are shown. The predicted concentration profiles (Fig. 2) are too steep, i.e., there is more dispersion than predicted by the model. The reason could be that mechanical dispersion was set equal to zero, as in most models. Alternatively, the molecular diffusion might be underestimated. Without fractionation by diffusion (Fig. 3), the isotopic abundance at the bottom starts at the same value as the incoming methane (−35.2‰) and from there the CH_4 enriches in ^{13}C as it is oxidized. When fractionation by diffusion is included in the model (Fig. 3), the simulated profile more closely follows the measured isotopic profile, although there is a slight underestimation in the top 20 cm of the soil column. The root mean square deviation (RMSD) of the concentrations is 8 vol%, while the RMSD of the $\delta^{13}C$ value is 1.8‰. It is clear that the profile calculated without fractionation by transport is entirely incorrect. The assumption that CH_4 transport does not fractionate cannot be made for this setup.

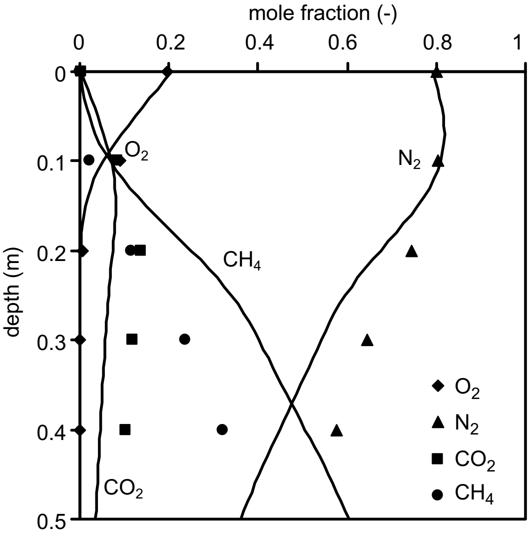

Fig. 2. Simulated concentration profiles (solid lines) and experimental values (dots).

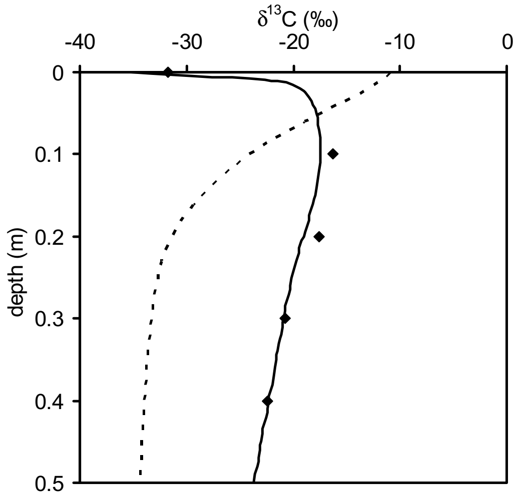

Fig. 3. Simulated $\delta^{13}C$ profile without fractionation by diffusion (dotted line) and with fractionation by diffusion (solid line) and experimental values of De Visscher et al. (2004) (dots). Data at 0 cm represent headspace.

At the start of the experiment the soil contained 22.3 g H_2O/100 g soil DW. After 33 days, moisture accumulation due to CH_4 oxidation was observed at 10 and 20 cm depth, and towards the bottom of the column. There was a slight depletion of the moisture content of the soil at the surface. The moisture profile was used in the model since changes in moisture content have an effect on the available air pores.

3.2. Calibration

The measured CO_2 concentration is higher than expected from the simulations. This is an indication that the assumed stoichiometry of the biological oxidation, 0.5 mole CO_2 formed per mole CH_4, is incorrect:

$$CH_4 + 1.5O_2 \Rightarrow 0.5CO_2 + 2H_2O + 0.5C_{org} \tag{15}$$

To deal with this, an extra parameter, x, was added to the model so the stoichiometry becomes the following:

$$CH_4 + (1+x)O_2 \Rightarrow xCO_2 + 2H_2O + (1-x)C_{org} \tag{16}$$

De Visscher and Van Cleemput (2003) found that the model is most sensitive to $V_{max,max}$. Therefore $V_{max,max}$ was also set as a parameter to be calibrated.

As indicated in the previous section, the simulation underestimated dispersion. For that reason, b was set as an adjustable parameter as well.

The concentration profiles and $\delta^{13}C$ profiles obtained after parameter estimation are given in Figs. 4 and 5. The parameters obtained from the calibration are given in Table 2, together with the corresponding values from the previous simulations.

The concentration profiles fit the measured ones much better. The model correctly describes the maximum in the N_2 concentration profile. This maximum occurs due to flow reversal, a phenomenon that was anticipated by De Visscher et al. (1999). Due to the stoichiometry of the reaction consuming gas, the total gas flow is downward in the top 10 cm. The RMSD of the concentration profiles is 1.6 vol%. The $\delta^{13}C$ profile, which fitted the experimental data well without calibration, changed because there is more diffusion (lower b in Eq. (14)). The RMSD of the $\delta^{13}C$ profile is now 2‰.

The parameters obtained from the calibration agree fairly well with independent literature values. $V_{max,max}$ is high in comparison with values of V_{max} measured in batch experiments. For example Stein et al. (2001) measured up to 540 nmol kg_{Soil} DW^{-1} s^{-1} and Kightley et al. (1995) measured up to 650 nmol kg_{Soil} DW^{-1} s^{-1}. Parameter b

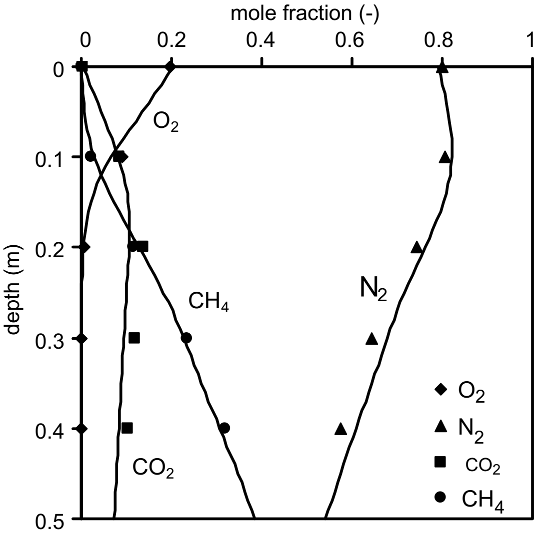

Fig. 4. Modeled concentration profiles (solid lines) after parameter estimation and experimental values (dots).

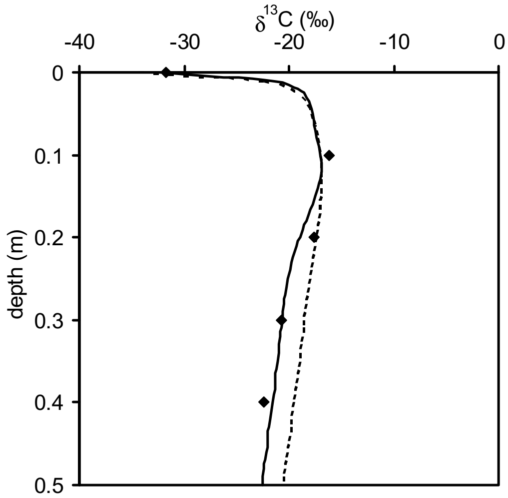

Fig. 5. Modeled δ^{13}C profile after parameter estimation with dispersion (solid line) and without dispersion (dotted line) and experimental values of De Visscher et al. (2004) (dots). Data at 0 cm represent headspace.

Table 2
Optimal parameters from calibration and corresponding values used for simulation

Parameter	Simulation	Calibration	Calibration with dispersion
$V_{\max,\max}$ (nmol CH_4 $\mathrm{kg_{soil}}$ DW^{-1} s^{-1})	2.4×10^3	2.54×10^3	2.67×10^3
α_{disp} (m)	0	0	0.052
b	1.5	1.007	1.098
x	0.5	0.711	0.75

from the modified equation of Moldrup et al. (2000) is also estimated. The estimated value is lower than the value of 1.5 obtained by Moldrup et al. (2000), indicating that diffusivities in soils used for the current study are higher than in the soils tested by Moldrup et al. (2000). This is probably due to small invertebrates burrowing in the soil, as observed in our column. The effect of these burrows is a decrease of the tortuosity of the air-filled pore space. Parameter x (stoichiometry) corresponds with the values used by Stein et al. (2001) and Hilger et al. (1999) (0.8) and Perera et al. (2002) (0.7). Overall, we conclude that the parameters obtained in the calibration are plausible and reflect the real properties of the system.

To reproduce the good fit for the isotope profile, a second calibration incorporating mechanical dispersion was executed. Mechanical dispersion does not fractionate, so it only has an effect on the concentration profiles. Molecular diffusion has virtually the same effect on the concentration profiles as mechanical dispersion but it has an effect on isotope ratio profiles, unlike mechanical dispersion. Therefore, it is also necessary to use the measured isotope profiles as input data, for the fitting procedure.

The results confirm that the concentration profiles do not change (RMSD = 1.7 vol%), but the isotope profile returns to the good fit which was obtained from simulations (Fig. 5). The RMSD is reduced to 0.8‰.

The optimal parameters for this estimation change slightly (Table 2); the added dispersion is compensated by a lower molecular diffusion (higher b).

Parameter α_{disp} is within the range derived from isotope data (0.001–0.07 m) obtained in a glass beads column (Mahieu et al., submitted for publication) and is slightly higher than values (0.0017–0.026 m) measured with pulse experiments (Popovicova and Brusseau, 1997; Ruiz et al., 1999; Garcia-Herruzo et al., 2000; Constanza-Robinson and Brusseau, 2002). This study confirms that early estimates (0.2–0.5 m) based on liquid phase dispersivities (Massmann and Farrier, 1992; Elberling et al., 1998) are overestimates.

The excellent fit of both concentration and isotopic profiles indicates that models will be a valuable tool to assist the in situ determination of CH_4 oxidation in landfill cover soils by means of isotope measurements.

It is interesting to investigate the ratio of isotope fluxes (δ^{13}C_flux) in the soil, as opposed to the ratio of isotope concentrations. Fluxes can only be measured at the in- and outlet of the column, but model calculations can be generated throughout the column. Unlike the concentration isotope ratio, the flux isotope ratio does not go through a maximum in the soil. This is indicated by the solid line in Fig. 6.

The model can be compared with the classical closed and open system equation (Eqs. (2) and (3)) by the δ^{13}C_flux profiles of the CH_4 flux calculated for the % oxidized CH_4 from the model. In Fig. 6 the δ^{13}C_flux profile of the CH_4 flux calculated with the open and closed system equation and the model is shown together with the measured flux isotope ratios of the incoming and outgoing CH_4. Below 20 cm depth the isotopic abundance is constant because there is no oxidation in this zone as there is not enough O_2. The result for the simulation without frac-

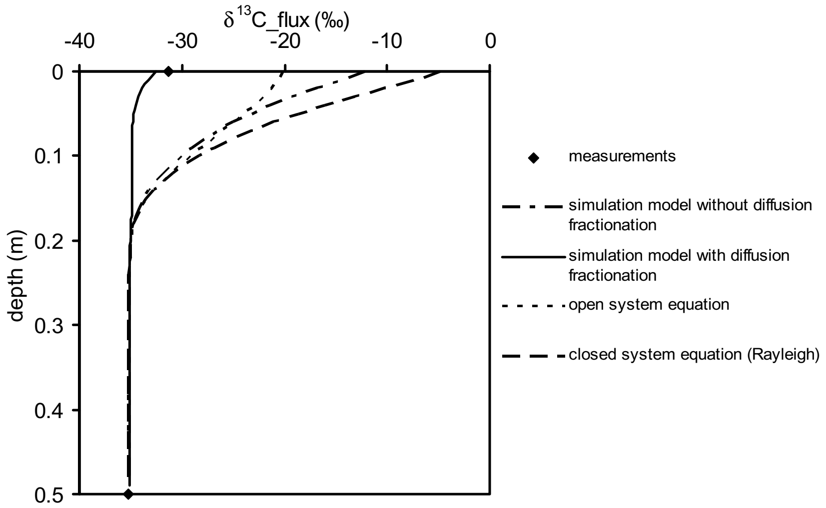

Fig. 6. $\delta^{13}C$ profile of the methane flux calculated with open and closed system equations compared with the measured in- and outflow and the simulation model.

tionation by diffusion is situated between the predicted profile with the closed and open system equation. When fractionation by diffusion is accounted for, the result is totally different; there is almost no net fractionation. This result is confirmed by the measurement, which also shows very little fractionation.

These results have an effect on the estimation of CH_4 oxidation from the difference between the $\delta^{13}C$ of the emitted CH_4 and the anoxic CH_4 (Eq. (2)). In this case only 20% oxidation would be estimated from the data using the open system equation while a mass balance yields more than 90% oxidation.

4. Conclusions

A model was developed that describes gas transport and CH_4 oxidation in landfill cover soils. The model distinguishes between $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$, and incorporates isotope fractionation by diffusion and CH_4 oxidation. Simulations with and without fractionation by transport show that fractionation by transport in this setup has a profound influence on the isotope profiles. After calibration of the model and introduction of a non-fractionating process, mechanical dispersion, there is an excellent agreement with measured concentrations and ^{13}C abundances in a laboratory setup.

Overall, the comparison shows that a model-based isotope approach for the determination of CH_4 oxidation efficiencies is feasible and is superior to existing isotope methods.

References

Bergamaschi, P., Lubina, C., Königstedt, R., Fischer, H., Veltkamp, A.C., Zwaagstra, O., 1998. Stable isotopic signatures ($\delta^{13}C$, δD) of methane from European landfill sites. Journal of Geophysical Research 103D, 8251–8265.

Bogner, J.E., Spokas, K.A., Burton, E.A., 1997. Kinetics of methane oxidation in a landfill cover soil: temporal variations, a whole – landfill oxidation experiment, and modeling of net CH_4 emissions. Environmental Science and Technology 31, 2504–2515.

Chanton, J., Liptay, K., 2000. Seasonal variation in methane oxidation in a landfill cover soil as determined by an in situ stable isotope technique. Global Biogeochemical Cycles 14, 51–60.

Chanton, J.P., Rutkowski, C.M., Mosher, B., 1999. Quantifying methane oxidation from landfills using stable isotope analysis of downwind plumes. Environmental Science and Technology 33, 3755–3760.

Constanza-Robinson, M.S., Brusseau, M.L., 2002. Gas phase advection and dispersion in unsaturated porous media. Water Resources Research 38 (4), 7/1–7/9, doi:10.1029/2001WR000895.

Czepiel, P.M., Mosher, B., Crill, P.M., Harriss, R.C., 1996. Quantifying the effect of oxidation on landfill methane emissions. Journal of Geophysical Research 101D, 16721–16729.

De Visscher, A., Van Cleemput, O., 2003. Simulation model for gas diffusion and methane oxidation in landfill cover soils. Waste Management 23, 581–591.

De Visscher, A., Thomas, D., Boeckx, P., Van Cleemput, O., 1999. Methane oxidation in simulated landfill cover soil environments. Environmental Science and Technology 33, 1854–1859.

De Visscher, A., De Pourcq, I., Chanton, J., 2004. Isotope fractionation effects by diffusion and methane oxidation in landfill cover soils. Journal of Geophysical Research 109, D18111, doi: 10.1029/2004JD004857.

Elberling, B., Larsen, F., Christensen, S., Postma, D., 1998. Gas transport in a confined unsaturated zone during atmospheric pressure cycles. Water Resources Research 34, 2855–2862.

Froment, G.F., Bischoff, K.B., 1990. Chemical Reactor Analysis and Design. J. Wiley and Sons, New York.

Garcia-Herruzo, F., Rodriguez-Marot, J.M., Garcia-Delgado, R.A., Gomez-Lahoz, C., Vereda-Alonso, C., 2000. Column study of the influence of air humidity on the retention of hydrocarbons on soil. Chemosphere 41, 1167–1172.

Hilger, H.A., Liehr, S.K., Barlaz, M.A., 1999. Exopolysaccharide control of methane oxidation in landfill cover soil. Journal of Environmental Engineering 125, 1113–1123.

IPCC, 2001. Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, United Kingdom, New York.

Kightley, D., Nedwell, D.B., Cooper, M., 1995. Capacity for methane oxidation in landfill cover soils measured in laboratory-scale soil microcosms. Applied and Environmental Microbiology 61, 592–601.

Lelieveld, J., Crutzen, P.J., Dentener, F.J., 1998. Changing concentration, lifetime and climate forcing of atmospheric methane. Tellus 50B, 128–150.

Liptay, K., Chanton, J., Czepiel, P., Mosher, P., 1998. Use of stable isotopes to determine methane oxidation in landfill cover soils. Journal of Geophysical Research 103, 8243–8250.

Mahieu, K., De Visscher, A., Vanrolleghem, P., Van Cleemput, O., 2006. Carbon and hydrogen isotope fractionation by microbial methane oxidation: improved determination. Waste Management 26, 389–398.

Mahieu, K., De Visscher, A., Vanrolleghem, P.A., Van Cleemput, O., submitted for publication. Gas dispersion in porous media: New measurement technique using stable isotopes. Journal of Contaminant Hydrology.

Marrero, T.R., Mason, E.A., 1972. Gaseous diffusion coefficients. Journal of Physical and Chemical Reference Data 1, 3–118.

Massmann, J., Farrier, D.F., 1992. Effects of atmospheric pressures on gas transport in the vadose zone. Water Resources Research 28, 777–791.

Moldrup, P., Olesen, T., Gamst, J., Schjonning, P., Yamaguchi, T., Rolston, D.E., 2000. Predicting the gas diffusion coefficient in repacked soil: water-induced linear reduction model. Soil Science Society of America Journal 64, 1588–1594.

Monson, K.D., Hayes, J.M., 1980. Biosynthetic control of the natural abundance of carbon 13 at specific positions within fatty acids in *Escherichia coli*. The Journal of Biological Chemistry 255, 11435–11441.

Perera, L.A.K., Achari, G.J., Hettiaratchi, P.A., 2002. Determination of source strength of landfill gas: a numerical modeling approach. Journal of Environmental Engineering 128, 461–471.

Popovicova, J., Brusseau, M.L., 1997. Dispersion and transport of gas-phase contaminants in dry porous media: effect of heterogeneity and gas velocity. Journal of Contaminant Hydrology 28, 157–169.

Ruiz, J., Bilbao, R., Murillo, M.B., 1999. Convective transport and removal of vapors of two volatile compounds in sand columns under different air humidity conditions. Environmental Science and Technology 33, 3774–3780.

Stein, V.B., Hettiaratchi, J.P.A., Achari, G., 2001. Numerical model for biological oxidation and migration of methane in soils. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management 5, 225–234.

Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A., Saint-Fort, R., 2004. Methane oxidation and formation of EPS in compost: effect of oxygen concentration. Environmental Pollution 129, 305–314.