Modelling methane oxidation in landfill cover soils using stable isotope ratios

Ir. Koenraad Mahieu

Promotors: Prof. dr. ir. A. De Visscher
             University of Calgary, Schulich School of Engineering
             Department of Chemical & Petroleum Engineering

             Prof. dr. ir. P.A. Vanrolleghem
             Ghent University
             Department of Applied Mathematics, Biometrics and
             Process Control
             Biomath

             Prof. dr. ir. O. Van Cleemput
             Ghent University
             Department of Applied Analytical and Physical Chemistry
             Laboratory of Applied Physical Chemistry (ISOFYS)

Dean: Prof. dr ir. H. Van Langenhove

Rector: Prof. dr. P. Van Cauwenberge

IR. KOENRAAD MAHIEU

MODELLING METHANE OXIDATION IN LANDFILL COVER SOILS
USING STABLE ISOTOPE RATIOS

Thesis submitted in fulfillment of the requirements
For the degree of Doctor (PhD) in Applied Biological Sciences

Dutch translation of the title:
Modelbouw van methaanoxidatie in stortafdekgronden door middel van stabiele isotopenverhoudingen

Cover image: Test field on the Leon county landfill (Florida)

Dankwoord

Een doctoraat mag dan nog een persoonlijk werk zijn zonder de steun van velen was het er waarschijnlijk nooit gekomen. In de eerste plaats bedank ik mijn promotoren Prof. Alex De Visscher Prof. Peter Vanrollegem en Prof. Oswald Van Cleemput. Ze waren altijd bereid te luisteren en het werk bij te sturen. In het begin waren Peter en vooral Alex nog heel dichtbij maar na hun emigratie naar Canada werd het een begeleiding van op een iets grotere afstand. Een tegenslag of een evolutie die erbij hoort wie zal het zeggen?

Dit werk is in grote mate gebaseerd op de problemen die ir. Ingrid Depourcq naar boven bracht tijdens haar ingenieursthesis. Het Bijzonder Onderzoeksfonds van de universiteit heeft dit project gedurende vier jaar gefinancierd, ziehier het resultaat.

De interesse in het verloop van het *landfill* of stortverhaal door de collega's van de *biodeg subgroup* heb ik steeds op prijs gesteld. De collega's van "isofys", "paint" en "biomath" zorgden dan weer steeds voor een goede sfeer.

In the beginning of 2006 I had the opportunity to go to Florida for a couple of months. I want to thank Prof. Jeff Chanton and Prof. Tarek Abichou from the Florida State , not only for their scientific contribution but also for their hospitality.

Uiteraard mogen mijn familie en vrienden hier niet ontbreken, allen hebben ze mij op hun eigen manier ondersteund, in het bijzonder mijn ouders waarbij ik altijd terecht kon.

Table of contents

Samenvatting

Methaanemissies op storten zijn een belangrijke bron van broeikasgassen. Storten zijn puntbronnen en kunnen in tegenstelling tot andere bronnen zoals rijstvelden en vee gemakkelijker onder controle gehouden worden. Biologische CH_4 oxidatie in de aërobe afdeklaag kan een goed alternatief zijn voor het verzamelen en verbranden van het gas, vooral voor oude storten waar grote investeringen niet meer mogelijk zijn. De bepaling van CH_4 oxidatie is echter niet gemakkelijk omdat emissies niet homogeen zijn en iedere verstoring van de afdeklaag het emissiepatroon verstoort. Via isotoopmetingen kan een schatting van het percentage CH_4 oxidatie gemaakt worden zonder de bodem te verstoren maar de huidige isotoopmethoden bevatten vereenvoudigingen met een grote onzekerheid als resultaat.

Om een goede schatting te bekomen is een accurate bepaling van de fractionatiefactor (α_{ox}) voor CH_4 oxidatie, of de voorkeur van de bacteriën voor lichtere isotopen, noodzakelijk. De berekening van α_{ox} is gebaseerd op onafhankelijke batch experimenten met grondstalen van een stortafdeklaag. Tot nu toe gebruikten de meeste studies vereenvoudigde versies van het Rayleigh model om de data te analyseren. In deze studie werden de meest voorkomende vereenvoudigingen, dit is de vereenvoudigde Rayleigh benadering en de Coleman methode, getest. Om dit mogelijk te maken werd het origineel model van Rayleigh beschreven in de meetbare variabelen CH_4 concentratie en isotoop abundanties en gefit aan resultaten van batch oxidatie experimenten met een gewogen niet-lineaire regressietechniek volgens de errors-in-variables methode. De resultaten van deze fitting werden als basis gebruikt om de resultaten van de twee vereenvoudigingen mee te vergelijken. De benadering van Coleman bleek aanvaardbaar voor C fractionatie maar toch niet aan te raden (fouten op $\alpha_{ox} - 1$ tot 5%) en onaanvaardbaar voor H fractionatie (fouten tot 20%). Het verschil tussen de Rayleigh benadering en het exact Rayleigh model is veel kleiner zowel voor C als voor H fractionatie (fouten op $\alpha_{ox} - 1$ kleiner dan 0.05%). Er is ook een klein verschil wanneer meetfouten in beide variabelen (CH_4 concentratie en isotoop abundantie) in rekening gebracht worden in plaats van te veronderstellen dat de onafhankelijk veranderlijke foutvrij is. Via theoretische berekeningen werden algemene criteria, niet beperkt tot CH_4, ^{13}C of D, vooropgesteld om de geldigheid van de Rayleigh benadering na te gaan bij gebruik van gelabelde producten.

Veelal wordt er verondersteld dat de CH_4 oxidatie zelf het enige fractionerende proces is in stortafdekgronden. Recent werd aangetoond dat het negeren van isotoopfractionatie door diffusie resulteert in een onderschatting van de CH_4 oxidatie. In deze studie werd een

simulatiemodel ontwikkeld dat gas transport en CH_4 oxidatie in stortafdekgronden beschrijft. Het model maakt expliciet onderscheid tussen $^{12}CH_4$, $^{13}CH_4$, en $^{12}CH_3D$ en houdt rekening met isotoopfractionatie door diffusie en oxidatie. Om het model te evalueren werden simulaties vergeleken met kolomexperimenten van vroegere studies. De voorspelde concentratieprofielen en isotoopprofielen komen goed overeen met de gemeten profielen. Simulaties met en zonder fractionatie door transportprocessen tonen aan dat fractionatie door diffusie in deze opstelling een grote invloed heeft op de isotoopprofielen. De diffusie verbergt als het ware de oxidatie en moet daarom in rekening gebracht worden bij de berekening van CH_4 oxidatie gebaseerd op isotopen. De klassieke isotoopmethode houdt hier geen rekening mee. Samengevat toont de vergelijking aan dat een modelgebaseerde benadering voor de bepaling van CH_4 oxidatie doenbaar is en beter dan de bestaande isotoopmethoden.

Dit onderzoek heeft de interesse gewekt in dispersie bij lage gassnelheden. In de modelevaluatie werd een significant dispersie effect gevonden in de stabiele isotoop profielen van CH_4 bij een labo simulatie van een stortafdekgrond. De huidige technieken om mechanische dispersie door gasstroming in poreuze media te bepalen vereisen verschillende experimenten en om een significant mechanische dispersie effect te zien zijn ze ook beperkt tot voldoende hoge gassnelheden. Het verschil tussen moleculaire diffusie en mechanische dispersie kan echter ook een grote invloed hebben op stabiele isotoop abundanties bij lage gassnelheden omdat moleculaire diffusie isotoopfractionatie veroorzaakt en mechanische dispersie niet. In deze studie werd een nieuwe methode ontwikkeld om dispersie van gas in poreuze media te bepalen met één enkel steady-state experiment. De bepaling was zelfs mogelijk bij lage gassnelheden. De dispersiviteit was constant rond 1 mm bij interstitiële gassnelheden van 10^{-4} tot 10^{-3} m s^{-1} maar steeg snel bij lagere snelheden tot maximaal 7 cm. Ook werd aangetoond dat de wet van Fick met constante diffusiecoëfficiënten niet geschikt is om deze data te analyseren en dat hiervoor de Stefan-Maxwell vergelijkingen gebruikt moeten worden.

Het hierboven beschreven CH_4 oxidatie en transport model werd ook getest op veldmetingen. Ook in een echte stortafdeklaag was het model in staat om de concentratie- en isotoopprofielen te beschrijven. Simulaties toonden aan dat de open systeem vergelijking die geen rekening houdt met fractionatie door diffusie een betere schatting van de CH_4 oxidatie zou moeten geven wanneer toegepast op δD metingen in plaats van op $\delta^{13}C$ omdat de fractionatiefactor voor oxidatie 10 keer groter is voor deuterium dan voor koolstof.

Hoewel de huidige isotoopmethode tekortkomingen heeft kan ze toch nog gebruikt worden als ruwe schatting met een onderschatting van het oxidatie percentage. Wanneer mogelijk zouden D isotopen gebruikt moeten worden en in dit geval wordt de fractionatiefactor best berekend met het Rayleigh model en niet de benadering van Coleman et al. (1981).

Summary

Methane emissions from landfills are an important source of greenhouse gases. Landfill emissions are point emissions and in contrast to other sources, such as rice fields and cattle, they can be controlled more easily. Biological CH_4 oxidation in the aerobic cover layer can be a good alternative for gas collection and recovery systems, especially for old landfills where large investments are not feasible. The quantification of CH_4 oxidation is not an easy task because the emissions are not homogeneous and any disturbance of the cover layer changes the emission. Isotope measurements enable to make an estimate of the CH_4 oxidation efficiency without disturbing the soil but current isotope methods contain simplifications that result in large uncertainties.

For good quantification an accurate determination of the isotope fractionation factor (α_{ox}) of CH_4 oxidation, or the preference of the bacteria for lighter isotopes, is required. The calculation of α_{ox} is based on independent batch experiments with soil samples from the landfill cover. Most studies so far used data analysis methods based on approximations of the Rayleigh model to determine α_{ox}. In this study, the two most common approximations were tested, the simplified Rayleigh approach and the Coleman method. To do this, the original model of Rayleigh was described in measurable variables, CH_4 concentration and isotopic abundances, and fitted to batch oxidation data by means of a weighted non-linear errors-in-variables regression technique. The results of this fit were used as a benchmark to which the results of the two conventional approximations were compared. The Coleman approximation was shown to be acceptable but not recommended for C fractionation (error on $\alpha_{ox} - 1$ up to 5%) and unacceptable for H fractionation (error up to 20%). The difference between the simplified Rayleigh approach and the exact Rayleigh model is much smaller for both C and H fractionation (error on $\alpha_{ox} - 1 < 0.05\%$). There is also a small difference when errors in both variables (CH_4 concentration and isotope abundance) are accounted for instead of assuming an error-free independent variable. By means of theoretical calculations general criteria, not limited to CH_4, ^{13}C, or D, were developed for the validity of the simplified Rayleigh approach when using labelled compounds.

It is usually assumed that the only fractionating process in landfill cover soils is the CH_4 oxidation itself. Recently it was shown that neglecting the isotope fractionation by diffusion results in underestimation of the CH_4 oxidation. In this study a simulation 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 $^{12}CH_3D$ 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. Simulations with and without fractionation by transport show that fractionation by diffusive transport in this setup has a profound influence on the isotope profiles. Diffusion hides the oxidation and must therefore be accounted for in the calculation of CH_4 oxidation based on isotopes. The classical isotope method does not account for that. Overall, the comparison shows that a model-based isotope approach for the determination of CH_4 oxidation efficiencies is feasible and superior to existing isotope methods.

This research has spurred interest in dispersion at low gas velocities. In the model evaluation a significant dispersion effect was found in the stable isotope profile of CH_4 in a landfill cover soil simulated in the lab. Current techniques to determine dispersivity of gas flow in porous media require multiple experiments and are restricted to flow velocities sufficiently high to observe significant mechanical dispersion effects. However, the difference between molecular diffusion and mechanical dispersion can have a significant influence on stable isotope signatures at low velocities as well because molecular diffusion leads to isotope fractionation, whereas mechanical dispersion does not. In this study a new method to determine the dispersivity of gas flow in porous media is developed using a single steady-state experiment. The determination is possible even at low gas velocity. The dispersivity was shown to be constant at approximately 1 mm at interstitial gas velocities of 10^{-4} to 10^{-3} m s^{-1} but increases rapidly at lower velocities, and can be as high as 7 cm. It was shown that Fick's law with constant diffusion coefficients is not adequate for analyzing these data and that the Stefan-Maxwell equations must be used.

The CH_4 oxidation and transport model was also tested on field data. Also in real landfill covers the model was able to fit the concentration profiles and isotopic profiles. Simulations indicate that the open system equation, which does not take into account diffusion fractionation, should give a better estimate for CH_4 oxidation when applied on δD measurements instead of $\delta^{13}C$ because the fractionation factor for oxidation is 10 times larger for deuterium than for carbon.

While current isotope method has shortcomings, it can still be used as a rough estimate with an underestimation of the oxidation percentage. If possible, D isotopes should be used and in

this case the fractionation factor should be calculated with the Rayleigh model and not the approximation by Coleman et al. (1981).

Chapter 1

Introduction

1.1 Greenhouse effect

1.1.1 Natural greenhouse effect

Trace gases present in atmosphere like H_2O, CO_2, CH_4, N_2O and O_3 absorb infrared radiation emitted from the earth surface while the incoming short wave radiation from the sun is almost completely left through. The result of this natural greenhouse effect is a surface temperature of 14°C. Without this effect the earth would have a surface temperature of -19°C (IPCC, 2001).

1.1.2 Enhanced greenhouse effect

Since the start of the industrial revolution the concentration of greenhouse gases in the atmosphere has increased rapidly. One way to quantify the effect of a greenhouse gas on global change is by its radiative forcing. Radiative forcing (W m^{-2}) is defined as the net change in available radiation energy for the earth-atmosphere (IPCC, 2001). From 1750 until now the radiative forcing has increased with 2.3W m^{-2} (IPCC, 2001). Another important characteristic of a greenhouse gas is the global warming potential (GWP), the relative radiative forcing of 1 kg greenhouse gas against 1 kg CO_2 integrated over time. The time basis is usually 100 years or the residence time of CO_2 (Lelieveld et al., 1998).

Methane has an atmospheric lifetime of 12 years (IPCC, 2001) and a GWP of 23 (IPCC 2001). While the total CH_4 emission on earth is much lower than the CO_2 emission, 20% of the total radiative forcing is caused by CH_4 (IPCC, 1996).

Methane is the most abundant greenhouse gas after CO_2 and water vapor. The CH_4 concentration has more than doubled since 1750 (Etheridge et al., 1992) due to an increase of population which resulted in higher CH_4 emissions from agriculture, waste disposal and fossil fuel use (Wuebbles and Hayhoe, 2002).

At the moment, the CH_4 concentration in the atmosphere is around 1.75 ppm. (Fig. 1.1). Recently stabilization of the CH_4 concentration was observed but it is unclear if equilibrium is reached or if it is just a temporary pause in the incline (Dlugokencky et al., 2003).
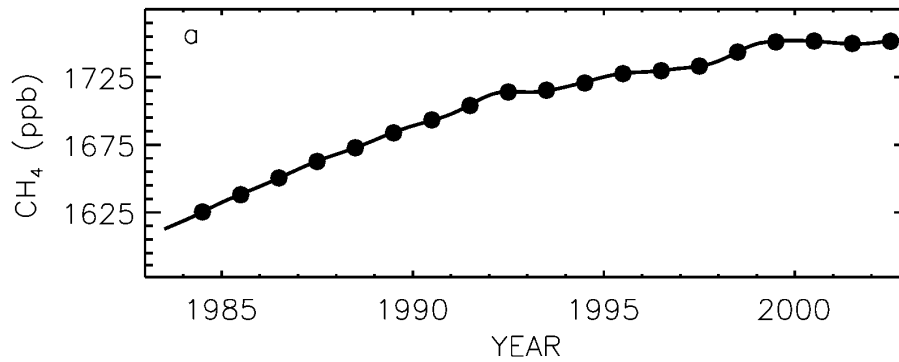
Fig. 1.1 Global mean CH$_4$ concentration in the atmosphere (Dlugokencky et al., 2003)

1.2 Kyoto protocol

With the growing concern about the enhanced greenhouse effect the Intergovernmental Panel on Climate Change (IPCC) was established in 1988. Their First Assessment report in 1990 confirmed that the human-induced climate change was a threat.

A United Nations Framework Convention on Climate Change (UNFCCC) was formed in 1992 with the objective "to achieve stabilization of atmospheric (human-induced) interference with the climate system …".The UNFCCC adopted the Kyoto Protocol in 1997 in Kyoto, Japan. Although 84 countries signed the Protocol and intended to ratify, the protocol only entered into force on 16 February 2006 when 55 countries ratified the protocol and these countries represented 55% of the greenhouse gas emissions.

In the commitment period 2008-2012 individual targets are set to a total cut of 5% from 1990 levels. Belgium has to reduce emissions with 7.5% (EEA, 2006). However if a linear path is calculated between the reference year and the targeted emissions, Belgium was not on track in 2004 (EEA, 2006) and an extra emission reduction of 0.9% is needed. This can only be obtained with additional measures.

1.3 Global warming effects of landfills

Methane is produced on all landfills where biologically degradable matter is placed. Seventeen % of the worldwide anthropogenic CH$_4$ emissions originate form landfills (Wuebbles and Hayhoe, 2002). The typical landfill gas consists of 60% CH$_4$ and 40% CO$_2$. Methane is a greenhouse gas but there can also be an explosion danger when the gas builds up. Because landfills are point sources of greenhouse gas it is more feasible to control these emissions than for example CH$_4$ emissions from cattle or rice fields which are also

responsible for respectively 23 % and 17% of the anthropogenic emissions (Wuebbles and Hayhoe, 2002).

1.4 Aim of this thesis

Methane emissions from landfills are an important source of greenhouse gases. Landfill emissions are point emissions and in contrast to other sources, such as rice fields and cattle, they can be controlled more easily. Biological CH_4 oxidation in the aerobic cover layer can be a good alternative for gas collection and recovery systems especially for old landfills where large investments are not feasible.

The quantification of CH_4 oxidation is not an easy task because the emissions are not homogeneous and any disturbance of the cover layer changes the emission. Isotope measurements enable to make an estimate of the CH_4 oxidation efficiency without disturbing the soil but current isotope methods contain simplifications that result in large uncertainties.

Modelling of the isotope specific processes in the cover layer can give more insight in which processes influence isotopes and can ultimately lead to a better quantification of CH_4 oxidation.

The aim of this thesis is to characterize isotope specific processes in landfill cover soils theoretically and experimentally, and to quantify them.

1.5 Outline of the thesis

After a short introduction in Chapter 1, a literature review is presented in Chapter 2. The processes and concepts used in the other Chapters are introduced ending with the isotope method as it is used today to measure CH_4 oxidation.

The current isotope method is consists of two parts: first the isotope fractionation factor (α_{ox}) for CH_4 oxidation, or the preference of the bacteria for lighter isotopes, is estimated from batch experiments with soil samples from the landfill cover and after that the CH_4 oxidation is measured with field isotope samples. Most studies so far used data analysis methods based on approximations of the Rayleigh model to determine α_{ox}. In Chapter 3, the two most common approximations were tested, the simplified Rayleigh approach and the Coleman method, to evaluate if these simplifications are justified and if not, if they can be avoided.

For the field measurements, it is usually assumed that the only fractionating process in landfill cover soils is the CH_4 oxidation itself. Recently it was shown that neglecting the isotope fractionation by diffusion, as in the current isotope method, results in underestimation of the CH_4 oxidation. In Chapter 4 a CH_4 transport and oxidation model is presented that incorporates the effects of both transport and oxidation on the CH_4 isotopes. This model is calibrated with data from a column experiment that represents a landfill cover soil layer.

In the model calibration with a column experiment in Chapter 4 a significant dispersion effect was found in the stable isotope profile of CH_4. With the current techniques, independent measurements of mechanical dispersion are restricted to high flow velocities because at low gas velocities mechanical dispersion is too low to be distinguished from diffusion. In Chapter 5 a new method with isotopes is developed to determine the dispersivity of gas flow in porous media. With this method it should be possible to distinguish diffusion from dispersion at low gas velocities because the transport processes have a different effect on isotopes: molecular diffusion leads to isotope fractionation, whereas mechanical dispersion does not fractionate isotopes.

In Chapter 6, the CH_4 oxidation and transport model of Chapter 4 was tested on field data from the Leon county landfill in Florida. In this evaluation D measurements are also used because the 10 times larger biological fractionation should give a better result.

Chapter 2

Literature review

2.1 Microbial methane oxidation, properties of methanotrophs

Microbial CH_4 oxidation is an important sink for CH_4 produced in anaerobic environments like rice fields, landfills but also for atmospheric CH_4.

The focus of this work is on landfill cover soils where CH_4 oxidizing bacteria oxidize the CH_4 produced in the underlying anaerobic part of the landfill.

The net reaction for microbial CH_4 oxidation can be described as:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
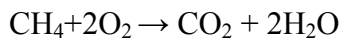
Figure 2.1 shows the pathway for the oxidation of CH_4 and the two possible pathways for the assimilation of formaldehyde.
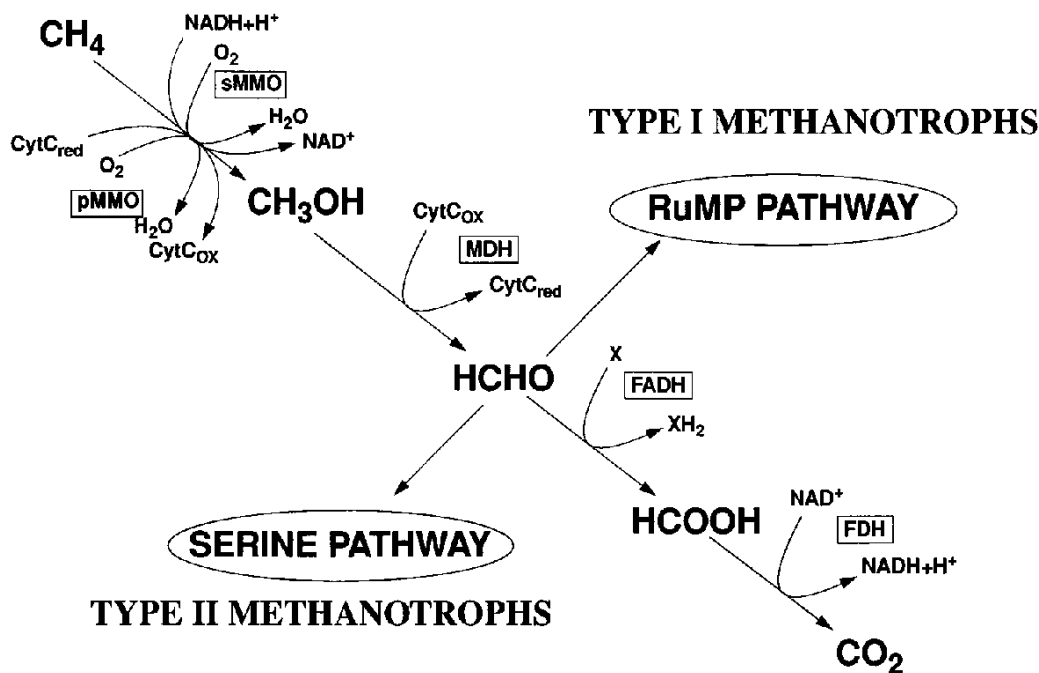
Fig. 2.1 Pathways for the oxidation of CH_4 (Hanson and Hanson, 1996)

Methane oxidizing bacteria can also be found in anaerobic environments but little is known about anaerobic CH_4 oxidation. A review of aerobic methanotrophic bacteria is given by Hanson and Hanson (1996).

Methanotrophs are a subset of the methylotrophs that are able to use one carbon compounds more reduced than formic acid. Methanotrophs can use CH_4 as the only carbon and energy source. The enzyme methane monooxygenase (MMO) catalyzes the conversion of CH_4 into

methanol but it is not substrate specific. Besides CH_4 methanotrophs can oxidize alkanes, alkenes, phenols, chlorinated hydrocarbons and aromatic hydrocarbons (Higgins et al., 1980).

The methanotrophs are Gram negative bacteria. Two types of methanotrophs can be distinguished (Bowman et al., 1993). Type I uses particulate MMO (pMMO) and formaldehyde is assimilated using the ribulose monophosphate pathway (RuMP). Most of type I methanotrophs cannot fix N_2. Type II methanotrops also use pMMO but in the absence of copper a soluble enzyme (sMMO) is used. They assimilate formaldehyde using the serine pathway and are able to fix N_2. Type I includes the genera *Methylomonas*, *Methylobacter* and *Methylomicrobium*. Type II includes *Methylosinus* and *Methylocystis*. Previously, a third type, type X, was distinguished, containing bacteria of the genus *Methylococcus* that can sometimes use the serine pathway next to the RuMp pathway. However, Bowman et al. (1993) suggested to form a family Methylococcaceae consisting of the genera of type I together with *Methylococcus*.

The RuMP pathway is more efficient than the serine pathway. For this reason type I methanotrophs tend to outgrow type II. But when there is a Cu or inorganic N limitation, type II methanotrophs grow faster (Graham et al., 1993).

In landfill cover soils the methanotrophic community can vary markedly. Mandernack et al. (2000) analyzed phospholipid fatty acids (PLFA) extracted from landfill cover soils from California and Washington and found type II methanotrophs. Wise et al. (1999) found both type I and type II. Borjesson (1997) found type I on a sewage sludge landfill cover, and type II on a mineral landfill cover. In methane-oxidizing biofilters, an environment similar to landfill cover soils, Gebert et al. (2004) found mainly type II. The reason for these differences is the influence of environmental factors which will be discussed later.

2.2 Processes and controls of methane oxidation in landfill cover soils

2.2.1 Gas transport in landfills

Gas transport in soils is mediated by several processes: flow (advection), molecular diffusion and mechanical dispersion. Molecular diffusion is caused by random movements of individual molecules whereas mechanical dispersion is a random effect caused by movements and different pathways of groups of molecules. Advective flow or bulk flow is the result of gradients in the total pressure.

Landfill gas transport is the result of a combination of these three mechanisms.

2.2.1.1 Advective transport

Darcy's law can be used to calculate the advective flow velocity u in a porous medium:

$$u = \frac{k}{\mu} \frac{\partial P}{\partial x}$$ (2.1)

with μ the gas-mixture viscosity (N s m^{-2}), k the intrinsic permeability (m^2) and P the total pressure (Pa). The advective flow velocity is the volumetric flow rate divided by the cross-sectional area, in other words the velocity the gas would have if the air-filled porosity of the porous medium was 1.

The advective flux of a component i is:

$$N_i = u \cdot C_i$$ (2.2)

with C_i the concentration of compound i (mol m^{-3}) and N_i the molar flux of compound i (mol m^{-2} s^{-1})

2.2.1.2 Free gas diffusion

For trace compounds in liquids and gases Fick's first law is used (Crank, 1967; Crank et al., 1981):

$$N_i = -D_i \frac{\partial C_i}{\partial z}$$ (2.3)

with D_i the diffusion coefficient of compound i (m^{-2} s^{-1}) and z the length coordinate (m).

The first law of Fick is only an approximation. A more accurate form is the set of Stefan-Maxwell equations (Jaynes and Rogowski, 1983):

$$-\frac{P}{R \cdot T} \frac{\partial y_i}{\partial z} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_i \cdot y_j - N_j \cdot y_i}{D_{ij,matr}}$$ (2.4)

with P total pressure (Pa)
R universal gas constant (8.314472 J mol^{-1} K^{-1})
T temperature (K)
y_i mole fraction of compound i
$D_{ij,matr}$ binary diffusion coefficient of compounds i and j (m^2 s^{-1})

This set of equations was originally derived by considering molecular dynamics in a multicomponent free gas mixture and includes advective flow and molecular diffusion. A review of binary diffusion coefficients of gases is given by Marrero and Mason (1972).

The Stefan-Maxwell equations reduce to the law of Fick with constant diffusion coefficients in three cases: diffusion of a trace concentration of gas in a mixture, equimolar counter-current diffusion in a binary gas mixture and diffusion in a ternary mixture where one gas is stagnant (Jaynes and Rogowski, 1983).

In a landfill soil cover the gas phase is a mixture of four gases (CH_4, O_2, CO_2, N_2) in large concentrations with a large production of CH_4 and CO_2. In this situation the conditions of Jaynes and Rogowski are not met. However some researchers use the law of Fick with adapted diffusion coefficients dependent on the mole fractions of the gases (Froment and Bischoff, 1990):

$$D_{i,m} = \frac{1 - y_i}{\sum_{\substack{j=1 \\ i \neq j}}^{m} \frac{y_i}{D_{ij}}}$$ (2.5)

with m a mixture of m gases, $D_{i,m}$ the diffusion coefficient of compound i in a mixture of m gases ($m^{-2}\,s^{-1}$) and z the length coordinate (m).

2.2.1.3 Diffusion in porous media

Diffusion in soils is similar to diffusion in air with a reduction in the diffusion coefficient. There are three reasons for the lower diffusivity in a porous medium. First the diffusion only takes place in a fraction of the soil, the air filled pore space ε. Second, diffusion does not occur along a straight line, i.e., the molecules have to follow the air-filled pore space (tortuosity). And last the cross-section of the pores is not uniform (constrictivity) and hinders diffusion, which leads to a lower diffusivity than expected from the average cross-section.

The reduction of the diffusion coefficient is quantified as the effective diffusion coefficient (Currie, 1960):

$$\frac{D_{soil}}{D_{air}} = \left(\frac{1}{l_e}\right)^2 f \cdot \varepsilon$$ (2.6)

with
D_{soil} the soil air diffusivity ($m^2\,s^{-1}$)
D_{air} the diffusivity in free air ($m^2\,s^{-1}$)
l the linear distance across the porous medium (m soil)
l_e the tortuous path length across the pore space (m air)
f the constrictivity (-)
ε the air-filled pore space (m^3 air m^{-3} soil)

Many researchers have tried to estimate the effective diffusivity in soils based on experiments.

One of the oldest models was presented by Penman (1940):

$$\frac{D_{soil}}{D_{air}} = 0.66 \cdot \varepsilon \tag{2.7}$$

The model of Millington and Quirk (1961) is the most used equation:

$$\frac{D_{soil}}{D_{air}} = \frac{\varepsilon^{10/3}}{\Phi^2} \tag{2.8}$$

with Φ the total porosity or the sum of the water and air filled porosity (m^3 m^{-3} soil).

Jin and Jury (1996) found that the overlooked Millington and Quirk (1960) equation gives accurate estimations, especially for disturbed soils.

$$\frac{D_{soil}}{D_{air}} = \frac{\varepsilon^2}{\Phi^{2/3}} \tag{2.9}$$

Moldrup (2000a) compared several models including the above described ones for disturbed soil under dry and wet conditions. Under dry conditions the Marshall (1959) equation performed best:

$$\frac{D_{soil}}{D_{air}} = \varepsilon^{3/2} \tag{2.10}$$

Under wet conditions the same model (Marshall, 1959) gives the best results when used with a water induced linear reduction factor:

$$\frac{D_{soil}}{D_{air}} = \frac{\varepsilon^{2.5}}{\Phi} \tag{2.11}$$

For undisturbed soils Moldrup (2000b) developed a procedure based on the soil water retention curve:

$$\frac{D_{soil}}{D_{air}} = \left(2\varepsilon_{100}^3 + 0.04\varepsilon_{100}\right)\left(\frac{\varepsilon}{\varepsilon_{100}}\right)^{2+3/b} \tag{2.12}$$

with ε_{100} the air filled pore space at -100 cm matric potential (m^3 air m^{-3} soil), and b the Campbell (1974) soil water retention parameter.

Both parameters must be estimated from the water retention curve.

2.2.1.4 Mechanical dispersion

It is usually assumed that mechanical dispersion, D_{mech} ($m^{-2}s^{-1}$), is proportional to the advective flow velocity:

$$D_{mech} = \alpha_{disp} \cdot v$$ (2.13)

With α_{disp} the dispersivity (m) and v the interstitial gas flow velocity ($m\ s^{-1}$) (i.e., the real average gas velocity in the pore space). This is a special one-dimensional case of dispersion. The general case involves both longitudinal and lateral dispersion. See for instance Mendoza and Frind (1990a) for the gas phase, and Engesgaard et al. (1996) for the liquid phase.

Mechanical dispersion is added to the molecular diffusion coefficient:

$$D_{matr} = D_{molec,matr} + D_{mech}$$ (2.14)

with D_{matr} the total dispersion coefficient ($m^2\ s^{-1}$), $D_{molec,matr}$ the molecular diffusion coefficient ($m^2\ s^{-1}$) and D_{mech} the mechanical dispersion coefficient ($m^2\ s^{-1}$)

Most of the literature on mechanical dispersion is in the liquid phase, in a saturated porous medium. Values of 0.01 to 100 m have been reported for α_{disp} in the liquid phase (Egboka et al., 1983). The value of α_{disp} increases with increasing scale (Gelhar et al., 1992). Dispersion is caused by a nonuniform velocity field. Two basic mechanisms drive dispersion in macroscopically homogeneous media. The first is kinematic: streamlines divide and rejoin at varying orientations, so they have varying lengths. The second is dynamic: due to varying resistances to flow in different pores, the velocity of the flow is variable. At sufficiently small scales molecular diffusion can be important to transfer the tracer particles out of slow or stagnant regions of the pore space, thus reducing the dispersion (Sahimi, 1993). When heterogeneities on a macro scale exist, but are not accounted for explicitly in the model, then dispersion will appear to be larger than it really is. An example is the effect of nonuniform flow. Gelhar et al. (1992) found that accounting for nonuniform flow effects in a realistic manner leads to lower estimates of α_{disp} from field measurement data. Mixing between layers of finer and coarser grained sand can also lead to increased apparent dispersion (Egboka et al., 1983).

Much less research has been devoted to dispersion in the gas phase of porous media. A fairly large range of values for α_{disp} can be found, from 0.0017 m (Garcia-Herruzo et al., 2000) to 0.5 m (Perera et al., 2002b). Early estimates of α_{disp} were at the higher end of this range. Massmann and Farrier (1992) and Elberling et al. (1998) used 0.2 m in their models, while

Mendoza and Frind (1990b) used 0.15 m. These high values where obtained by assuming that dispersivity in the air-filled pore space equals the dispersivity in the water-filled pore space at the same scale. However, these phases have very different properties. Diffusion coefficients in gas are 10^4 times higher than in water than in air (Scanlon et al., 2002). Heterogeneities on micro-scale are smoothened by diffusion more effectively in gas-filled pores, lowering the dispersion on macro-scale.

Recently, values of α_{disp} for the gas-filled pore space have been experimentally determined. The values are much lower than usually found in the water-filled pore space. Popovicova and Brusseau (1997), Ruiz et al. (1999), Garcia-Herruzo et al. (2000) and Constanza-Robinson and Brusseau (2002) found values ranging from 0.0017 to 0.026 m.

2.2.2 Methane oxidation kinetics

Microorganisms use enzyme reactions. As a consequence microbial kinetics is based on enzyme kinetics.

Enzyme kinetics can often be described by Michaelis-Menten kinetics:

$$r_s = \frac{V_{max}[S]}{K_s + [S]}$$

(2.15)

with
r_s the reaction rate
$[S]$ the substrate concentration
K_s an affinity constant
V_{max} the maximum reaction rate

Microbial growth kinetics was described by Monod (1958):

$$\mu = \mu_{max} \frac{[S]}{K_m + [S]}$$

(2.16)

with
μ the biomass specific growth rate
μ_{max} the maximum specific growth rate
K_s the affinity constant

This equation is consistent with the Michaelis-Menten equation (Panikov, 1995).

A deviation from Monod kinetics occurs when substrate is consumed for maintenance processes instead of growth (Pirt kinetics):

$$\mu = \mu'_{max} \frac{[S]}{K_m + [S]} - m \cdot Y_{max}$$

(2.17)

with

m the maintenance coefficient

Y_{max} the maximal or true biomass yield,

μ'_{max} the real maximum growth rate (never observed due to cell decay)

K_m values are given in nM because the biological oxidation occurs in the aqueous solution. In the case of CH_4 these values can be converted to the equivalent in the gas-phase by multiplying with 0.7 (around 25°C and 1 atm) to obtain ppm.

If the maximum biomass concentration that can be supported is responsible for limiting growth (rather than substrate limitation), a logistic equation for microbial growth or the Verhulst equation is obtained:

$$\mu[X] = \mu_{max}[X]\left(1 - \frac{[X]}{[X_{max}]}\right)$$

(2.18)

with $[X_{max}]$ the maximum biomass concentration

In a landfill cover layer the concentration of CH_4 is high (around 60%). The methanotrophic community will grow quickly and high CH_4 oxidation rates will be obtained. Atmospheric CH_4 oxidation is completely different from CH_4 oxidation in enriched environments. If the V_{max} and K_m of atmospheric CH_4 oxidizers were the same as for bacteria from enriched environments there would not be any atmospheric CH_4 oxidation at all (Roslev and King, 1994). This is because the atmospheric CH_4 concentration is too low to support CH_4 oxidizers from an enriched environment. Bacteria that oxidize atmospheric CH_4 have a high affinity (low K_m) and low maximum oxidation rate V_{max} (Bender and Conrad, 1992).

2.2.3 Influence of environmental factors on the processes occurring in landfill cover soils

2.2.3.1 Temperature

The temperature response of methanotrophs is typical for enzyme kinetics with both high and low temperature inactivation (Sharpe and De Michelle, 1977). The optimum temperature ranges from 22 to 38°C (De Visscher et al., 2007).

The temperature optimum for type I is lower than for than type II (Gebert et al., 2003). For this reason type I is more dominant at 10°C than at 20°C (Borjesson et al., 2004).

The diffusion coefficient increase is only 6-7% with a 10°C temperature increase. However oxygen transfer can limit CH_4 oxidation at high temperatures.

2.2.3.2 Moisture content

Moisture has a direct effect on methanotrophy but also influences CH_4 oxidation by a change in diffusion and advection.

The diffusion coefficient in the gas phase is 10^4 times larger than the diffusion coefficient in the liquid phase. As a result large scale diffusion like the vertical diffusion in landfill cover soils, only takes place in the gas phase.

When the moisture content increases, the gas-filled pore space becomes smaller. The hindered diffusion limits oxygen penetration. This effect is included in the empirical equations to calculate the effective diffusion coefficient of gases in soils.

The pore scale diffusion in the water layer around methanotrophic bacteria is also influenced by moisture content. With increasing moisture content the water layer becomes thicker and the CH_4 oxidation rate decreases. Usually this effect cannot be distinguished from physiological effects so they are treated simultaneously (De Visscher et al., 2007).

At low moisture contents the bacteria suffer from water stress with a lower oxidation rate as result.

Because of all these effects, the CH_4 oxidation rate versus moisture content goes through a maximum (De Visscher et al., 2007).

Moisture also has an effect on advective transport by a decrease in air permeability. However, in a landfill cover the gas produced in the anaerobic part of the landfill must escape so an increase in lateral transport or a pressure buildup will be the result or if there is a collection system present there will be more gas collected. An increased pressure restores the advective transport and in this case moisture has no effect on advective transport.

2.2.3.3 Inorganic nitrogen

The influence of nitrogen is complex and not yet fully understood because it can act as an inhibitor and as a nutrient and its influence is dependent of the form, concentration, pH, CH_4 concentration and type of methanotrophs.

At atmospheric CH_4 concentrations inorganic N is typically not the limiting substrate. NH_4^+ is a competitive inhibitor of CH_4 oxidation by the organisms. NO_2 is toxic but NO_3 causes only salt effects (Boeckx and Van Cleemput, 1996).

At high CH_4 concentrations the same inhibition as for low CH_4 concentrations occurs. However, N limitation can occur as well, and adding N can stimulate CH_4 oxidation (De Visscher et al., 1999; Bodelier and Laanbroek, 2004).

Also, the different types of methanotrophs react differently as type I methanotrophs need a source of inorganic N while type II are able to fix N_2. For this reason type I dominates in nutrient-rich environments (Borjesson et al., 1998).

2.2.3.4 Exopolymer formation

After a prolonged exposure to CH_4 the CH_4 oxidation declines due to production of exopolymers (EPS) (Hilger et al., 1999). This effect was only reported in lab experiments and never on a field scale but it is a concern for biofilters and other engineered systems for CH_4 oxidation in practical applications.

The methanotrophs produce EPS as a N-free carbon sink when they lack N i.e. in excess of carbon. The EPS causes pore clogging which creates a microaerophilic environment for the nitrogenase activity (Wilshusen et al., 2004). When the environment is already microaerophilic there is no excessive EPS formation.

2.3 Models for methane oxidation in landfill cover soils

Several models for describing mass transport and CH_4 oxidation in landfill cover soils have been proposed. A recent review was made by De Visscher and Spokas (in preparation).

These models can be divided in empirical models (Czepiel et al., 1996; Park et al., 2004) and process-based models (Hilger et al., 1999; Stein et al., 2001).

A special case is the collision model of Bogner et al. (1997), which balances computational efficiency with mechanistic realism. 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. Methane oxidation occurs when a gas molecule collides with bacteria and if there is enough oxygen.

2.3.1 Empirical models

Empirical equations are obtained by correlating measurement data and requires little information about fundamental processes influencing CH_4 oxidation. As a result extrapolation of empirical models beyond the range of experimental data used to develop the model should be avoided.

Czepiel et al. (1996) estimated the year-round average whole landfill CH_4 oxidation with an empirical model. From the CH_4 mixing ratio at 7.5 cm the mixing ratio gradient is estimated with an empirical equation, and with the mixing ratio gradient the mixing ratio profile is built. Microbial activities are calculated with another empirical equation from mixing ratios and the sum of the oxidation rates at all depths across the cover soil is the total CH_4 oxidation.

Park et al. (2004) developed empirical relations based on climatic data (soil temperature, moisture and ammonium content) to estimate CH_4 oxidation efficiencies of CH_4 biofilters.

2.3.2 Process-based models

Process-based models are more realistic than empirical models, but they are computationally intensive and require a large number of inputs. Gas transport, microbial oxidation and sometimes microbial growth are explicitly described.

The model of Hilger et al. (1999) is based on the Stefan-Maxwell equations (Eq. 2.4) 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 the Stefan-Maxwell equations, but with concentration-dependent diffusion coefficients (Eq. 2.5). A dual-substrate CH_4 oxidation model was used with CH_4 and O_2 limitation because deeper under the surface the oxygen concentration can be low enough to prevent CH_4 oxidation while at the surface the CH_4 concentration is usually close to atmospheric concentrations and too low to support a large CH_4 oxidation.

$$r_{CH_4} = -\frac{V_{max} \, y_{CH_4}}{K_m + y_{CH_4}} \cdot \frac{y_{O_2}}{K_{O_2} + y_{O_2}} \tag{2.19}$$

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 ($\mu l \, l^{-1}$).

A similar model was used by Perera et al. (2002a) to calculate the source strength of a landfill. These authors incorporated mechanical dispersion explicitly in their model.

De Visscher and Van Cleemput (2003) developed a model based on the Stefan-Maxwell equations (Eq. 2.4) and dual-substrate limitation for CH_4 oxidation. Their model also incorporates biomass growth (Section 4.3.1) while most other models use a constant V_{max} or a V_{max} profile measured on samples.

The differential equations are combined in a continuity equation or mass balance:

$$\varepsilon \frac{\partial y_i}{\partial t} \frac{P}{RT} = \rho r_i - \frac{\partial N_i}{\partial z} \tag{2.20}$$

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 (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 advective flow velocity of the total flux N appears explicitly in the law of Fick but is also needed to solve the Stefan Maxwell equations and can be calculated with the law of Darcy (Eq. 2.1). Usually the pressure gradient in a landfill cover is low and a constant pressure is sufficient (De Visscher and Van Cleemput; 2003).

The stoichiometry is another point of difference between CH_4 oxidation models. A general form is:

$$CH_4 + S_{O_2}O_2 \rightarrow S_{CO_2}CO_2$$
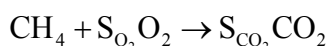
For the models described above the oxygen consumption yield, S_{O_2}, varies between 1.5 and 1.8 and the C_{O2} yield, S_{CO_2} between 0.5 and 0.8. The other products water, biomass and exopolymers are not in the gas phase and not considered by CH_4 oxidation models.

2.4 Measurement techniques for methane oxidation in landfill cover soils

Estimating the capability of a soil layer to oxidise CH_4 is not straightforward. One technique is to measure the difference between the CH_4 fluxes with and without cover layer (Boeckx et al., 1996). However, this technique disturbs the soil and can cause a bypass for the gas. Czepiel et al. (1996) combined field measurements, laboratory measurements and computer

modelling methods to estimate CH_4 oxidation in a landfill cover. This is a non intrusive method but it is unclear if the method is representative for other landfills and climates. Another method is integrating CH_4 oxidation rates of soil samples (Kjeldsen et al., 1997). Oonk and Boom (1995) used the mass balance technique to measure CH_4 oxidation in landfill cover soils. This technique involves measurements of both the CH_4 and CO_2 flux leaving the landfill cover soil. The ratio of these fluxes is calculated, and compared with the CH_4/CO_2 ratio occurring in the anaerobic zone of the landfill. Using the stoichiometry of CH_4 oxidation, the oxidation efficiency can be calculated from these ratios. The disadvantage of this method is that photosynthesis and soil respiration confound the measurements.

Qualitative methods are also used. Examples are counting the methanotrophic cells, measuring the N_2/O_2 ratio (Nozhevinikova et al., 1993; 2003) or using selective inhibitors for CH_4 oxidation such as difluoromethane (Kruger et al., 2001).

A promising method to quantify CH_4 oxidation is by measuring isotope fractionation. This method is explained in detail in Section 2.4.2. With isotopes the percentage oxidation can be calculated. To know the absolute amount that is oxidized, emission fluxes are measured. The measurement of emission fluxes is explained in Section 2.4.1.

2.4.1 Flux measurements

Chamber methods are the easiest way to measure the emission flux. The closed box method consists of a bottomless box pressed into the soil. The gas accumulates or is depleted in the box. The flux is calculated from the slope of the gas concentration versus time. The closed box method is the most sensitive, but an increased concentration can hinder diffusion (Granli and Bockman, 1994). This leads to an underestimation of the flux. There are methods to account for the accumulation, for example Hutchinson and Mosier (1981) and Powelson et al. (2006) but the accuracy of these models is unclear.

Another box method is the open box where an air stream is sent through the headspace. The flux is calculated from the difference between the concentration from the inflow and the outflow. In this method there is no accumulation but because the measurement is based on the difference between two concentrations, it is less sensitive.

More sophisticated methods to estimate the flux are the micrometeorological methods. One possibility is to use the vertical concentration gradient and the eddy diffusion coefficient to calculate the flux with the law of Fick (Eq. 2.3). Another method called eddy correlation

technique uses the correlation between the vertical component of the wind speed and the concentration. Tracers are also used for the estimation of the flux: the ratio of the emission rates is the same as the ratio of the concentrations. However, micrometeorological methods are less sensitive and only suited for large uniform areas.

2.4.2 Isotope technique

Bacteria oxidize CH_4 with ^{12}C slightly faster than CH_4 with ^{13}C (Barker and Fritz, 1981). 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 isotope abundance:

$$\delta^{13}C = \left(\frac{R}{R_{st}} - 1 \right) \cdot 1000 \text{ ‰} \tag{2.21}$$

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 abundances are measured at the waste, 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):

$$f_{ox} = \frac{\delta E - \delta A}{1000 \cdot \left(\alpha_{ox} - \alpha_{trans} \right)} \tag{2.22}$$

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 (ie., the preference for oxidizing $^{12}CH_4$ above $^{13}CH_4$) and α_{trans} the fractionation factor for CH_4 transport. δE is measured from the same samples as the emission flux while samples for δA are collected from vents or, if installed, from the gas extraction system.

Equation 2.22 was suggested by Blair et al. (1985) for open systems, and it is assumed that it is appropriate for landfill cover soils, where CH_4 can move freely to escape to the atmosphere, or to be oxidized by soil methanotrophs.

The fractionation factor, α_{ox}, is estimated by an independent incubation experiment with soil taken from the landfill cover. In this laboratory setup an alternative "closed system equation" is used, also called Rayleigh approach:

$$f_{ox} = 1 - \left(\frac{\delta E + 1000}{\delta A + 1000} \right)^{\frac{\alpha_{ox}}{1-\alpha_{ox}}} \qquad (2.23)$$

Table 2.1 presents some literature values of α_{ox} for landfill cover soils.

With this technique Liptay et al. (1998) measured 24 to 35% oxidation during the warm season on a landfill in New Hampshire and Chanton et al. (1999) found 0 to 23.6% during the whole year on the same lanfill. As these two studies have been conducted on the same landfills in Northeast United States as the study of Czepiel et al. (1996), they can be compared. The efficiencies found in the two isotope studies are in general agreement with the annual mean value of 10% reported by Czepiel et al. (1996), which was calculated from 20% oxidation during the flux measurement in summer and a temperature correction factor.

Chanton & Liptay (2000) estimated 20% oxidation for clay and mulch topsoil but this was under a warmer climate (Florida, US) than the studies of Czepiel et al. (1996) and Liptay et al. (1998). The oxidation efficiency was larger for mulch soil (26%) than for clay (14%) and there was a large difference between summer, with more than 40% oxidation, and winter with almost no oxidation.

Large seasonal variations from no oxidation in winter to nearly complete oxidation in the summer have also been reported for Swedish landfills (Börjesson et al., 2001).

Much higher oxidation percentages up to 80% were also reported for a Dutch and a German landfill (Bergamaschi et al., 1998), with a different technique based on ^{222}Rn activities.

Barlaz et al. (2004) used the isotope method to compare CH_4 oxidation efficiencies of soil and compost as landfill cover materials. The compost cover did better than the soil cover with an oxidation percentage of 55% and 21% respectively. The result on the compost cover was even an underestimation because a lot of places could not be measured with the isotope technique as there was no positive emission or even an atmospheric uptake of CH_4.

Table 2.1 α_{ox} values measured for landfill cover soils

α_{ox}	reference
1.022 ± 0.008	Liptay et al. (1998)
$1.025 - 1.049$	Chanton & Liptay (2000)
$1.023 - 1.038$	Börjesson et al. (2001)
1.008 ± 0.004	Bergamaschi et al. (1998)
1.018	De Visscher et al. (2004)

The isotope method has been used in other ecosystems as well. Ambus et al. (2002) used an isotope method to demonstrate that the occurrence of a threshold concentration for CH_4 oxidation from the atmosphere by soils is actually the result of CH_4 production. However, isotope data in many ecosystems like marches are much more difficult to interpret than in landfill cover soils, because CH_4 oxidation often occurs in isolated rhizospheric pockets where CH_4 oxidation is nearly complete, leaving no trace on the isotope signature of the emitted CH_4 (Happell et al., 1993).

Scharff et al. (2003) compared the mass balance method with the isotope method and could not find a significant difference. However, both methods had very large uncertainties so it remains unknown if the two methods lead to the same result. Christophersen et al. (2001) also compared oxidation percentages from CH_4 and CO_2 flux measurements with rough estimates with the isotope method in a study on lateral gas transport. They found an overestimation for the flux method but this could also be an underestimation of the isotope method.

2.5 Isotope fractionation effects in landfill cover soils

The measurement method described in Section 2.4.2 considers only fractionation by bacterial CH_4 oxidation. The method does not take into account the fractionation by gas transport by setting the fractionation factor for CH_4 transport, α_{trans}, equal to 1 in Eq. 2.22. However diffusion, which can be important in landfill cover soils, does fractionate isotopes as well. The difference between the diffusion coefficients of $^{12}CH_4$ and $^{13}CH_4$ is related to the molar mass of the isotopes (Marero and Mason, 1972):

$$D_{ij} \sim \frac{1}{\sqrt{\dfrac{M_i \cdot M_j}{M_i + M_j}}} \qquad (2.24)$$

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

The theoretical ratio $D_{molec}\ ^{12}CH_4,air / D_{molec}\ ^{13}CH_4,air$ calculated with this equation is 1.0195. This means that the fractionation by diffusion is in the same order of magnitude as the fractionation by oxidation (Table 2.1). De Visscher et al. (2004) estimated α_{trans} values as high as 1.014 from laboratory experiments.

The other transport mechanisms, mechanical dispersion and advection, do not fractionate. However mechanical dispersion has an effect on the total dispersion, which has an effect on the isotopic profile as well (Section 5.2).

Chapter 3

Carbon and hydrogen isotope fractionation by microbial methane oxidation: improved determination

Published in:

3.1 Abstract

Isotope fractionation is a promising tool for quantifying CH_4 oxidation in landfill cover soils. For good quantification an accurate determination of the isotope fractionation factor (α_{ox}) of CH_4 oxidation based on independent batch experiments with soil samples from the landfill cover is required. Most studies so far used data analysis methods based on approximations of the Rayleigh model to determine α_{ox}. In this study, the two most common approximations were tested, the simplified Rayleigh approach and the Coleman method. To do this, the original model of Rayleigh was described in measurable variables, CH_4 concentration and isotopic abundances, and fitted to batch oxidation data by means of a weighted non-linear errors-in-variables regression technique. The results of this fit were used as a benchmark to which the results of the two conventional approximations were compared. Three types of batch data were used: simulated data, data obtained from literature, and data obtained from new batch experiments conducted in our laboratory. The Coleman approximation was shown to be acceptable but not recommended for C fractionation (error on $\alpha_{ox} - 1$ up to 5%) and unacceptable for H fractionation (error up to 20%). The difference between the simplified Rayleigh approach and the exact Rayleigh model is much smaller for both C and H fractionation (error on $\alpha_{ox} - 1 < 0.05\%$). There is also a small difference when errors in both variables (CH_4 concentration and isotope abundance) are accounted for instead of assuming an error-free independent variable. By means of theoretical calculations general criteria, not limited to CH_4, ^{13}C, or D, were developed for the validity of the simplified Rayleigh approach when using labelled compounds.

3.2 Introduction

In the isotope method to evaluate CH_4 oxidation from isotope data, it is important that the fractionation factor is determined accurately by means of independent batch tests with soil samples from the cover soil. For the calculation of α_{ox} from such batch data, the Rayleigh (1896) equation applies. In most studies, α_{ox} is calculated by the simplified Rayleigh approach, which is based on the Rayleigh (1896) equation. For CH_4, the approximate method of Coleman et al. (1981), which is also based on the Rayleigh (1896) equation, has often been used to calculate α_{ox} based on batch oxidation experiments.

Hunkeler (2002) explained that the simplified Rayleigh approach is only applicable for studies at natural abundance level, which means that the Rayleigh approach can be used in batch studies for the determination of α_{ox} for CH_4 oxidation. Scott et al. (2004) compared different regression methods which use a linearized version of the simplified Rayleigh approach and concluded that there is no improvement in comparison with the classical linear regression for parameter estimation of α_{ox}. The errors associated with the method of Coleman (1981) have not been evaluated yet.

The aim of this paper is to test the accuracy of the method of Coleman et al. (1981) and the simplified Rayleigh approach by comparison with a benchmark method based on the original Rayleigh (1896) model. The methods were applied to simulated batch data, as well as on real data obtained from literature and obtained in our laboratory. We report the relative error of each method as ($\alpha_{ox} - 1$), because, following Eq. (2.22), an incorrect estimate of α_{ox} leads to a relative error on f_{ox} equal to the relative error on ($\alpha_{ox} - 1$).

3.3 Theoretical Background

For a closed system the model of Rayleigh (1896) can be used to describe the effect of CH_4 oxidation on the $^{13}C/^{12}C$ isotope ratio:

$$\frac{d\,^{13}C}{d\,^{12}C} = \frac{k_{13}}{k_{12}} \cdot \frac{^{13}C}{^{12}C}$$

(3.1)

with ^{12}C and ^{13}C the carbon isotope concentrations of the remaining CH_4 and k_{12} and k_{13} the oxidation rate constants of these isotopes; $d\,^{13}C$ and $d\,^{12}C$ refer to infinitesimal changes of ^{12}C and ^{13}C concentrations and should not be confused with $\delta^{13}C$.

The ratio $\dfrac{k_{12}}{k_{13}}$ is the fractionation factor α_{ox}. In some studies, α_{ox} is defined as the inverse, $\dfrac{k_{13}}{k_{12}}$ (King et al., 1989; Ambus et al., 2002). Rearranging Eq. 3.1 leads to:

$$\alpha_{ox} \frac{d\,^{13}C}{^{13}C} = \frac{d\,^{12}C}{^{12}C}$$

(3.2)

If α_{ox} is constant, both sides of the equation can be integrated from initial concentration $^{i}C_0$ (i = 12, 13) to final concentration ^{i}C:

$$\alpha_{ox} \ln\left(\frac{^{13}C}{^{13}C_0}\right) = \ln\left(\frac{^{12}C}{^{12}C_0}\right) \tag{3.3}$$

Taking the exponential of both sides, and rearranging, leads to:

$$\frac{^{13}C/^{12}C}{^{13}C_0/^{12}C_0} = \left(\frac{^{12}C}{^{12}C_0}\right)^{\frac{1-\alpha_{ox}}{\alpha_{ox}}} \tag{3.4}$$

with $^{12}C_0$ and $^{13}C_0$ the initial C isotope concentrations of the CH_4.

The isotope concentrations can be calculated from the δ value (Eq. 2.21) and by considering that the CH_4 concentration = total carbon concentration $C = {}^{12}C + {}^{13}C$:

$$^{12}C = \frac{CH_4}{1 + \dfrac{R_{st}.\delta^{13}C}{1000} + R_{st}}$$

$$^{13}C = \frac{CH_4 \cdot \left(\dfrac{\delta^{13}C}{1000} + 1\right)}{\dfrac{1}{R_{st}} + \dfrac{\delta^{13}C}{1000} + 1} \tag{3.5}$$

With Eq. 3.5 the ^{13}C and ^{12}C concentrations can be substituted in Eq. 3.4 to obtain measurable variables:

$$\frac{\delta^{13}C + 1000}{\delta^{13}C_0 + 1000} = \left(\frac{CH_4}{CH_{4,0}} \cdot \frac{1/R_{st} + \delta^{13}C_0/1000 + 1}{1/R_{st} + \delta^{13}C/1000 + 1}\right)^{\frac{1-\alpha_{ox}}{\alpha_{ox}}} \tag{3.6}$$

with $CH_{4,0}$ the initial CH_4 concentration. Because this equation is rigorously derived from Eq. 3.1 assuming constant α_{ox}, without approximations, this equation is referred to as the exact Rayleigh model.

The exact Rayleigh model can be simplified by approximating the ^{12}C concentration by the total CH_4 concentration because the natural ^{13}C concentrations are small (1.1%).

Combining Eq. 3.4 and Eq. 2.21 with $CH_4 \approx {}^{12}C$ gives:

$$\frac{\delta^{13}C + 1000}{\delta^{13}C_0 + 1000} = \left(\frac{CH_4}{CH_{4,0}}\right)^{\frac{1-\alpha_{ox}}{\alpha_{ox}}} \tag{3.7}$$

Equation 3.7 is best known as the Rayleigh approach (e.g. Liptay et al., 1998; Snover and Quay, 2000; De Visscher et al., 2004). In this paper it is referred to as the simplified Rayleigh approach to avoid confusion with the exact Rayleigh approach.

Coleman (1981) made further approximations. After rearranging the left-hand side of Eq. 3.7 and taking the logarithm, they approximated the left-hand side as follows:

$$\ln\left(1 + \frac{\delta^{13}C - \delta^{13}C_0}{\delta^{13}C_0 + 1000}\right) \approx \frac{\delta^{13}C - \delta^{13}C_0}{\delta^{13}C_0 + 1000} \tag{3.8}$$

because $\ln(1 + x) = x - \frac{x^2}{2} \ldots \approx x$ for a small x

This approximation was considered acceptable because the difference between the δ values during an experiment is small.

Equation 3.8 was further simplified because the initial abundance is small:

$$\frac{\delta^{13}C - \delta^{13}C_0}{\delta^{13}C_0 + 1000} \approx \frac{\delta^{13}C - \delta^{13}C_0}{1000} \tag{3.9}$$

This gives the equation of Coleman et al. (1981), which has been used by many researchers (e.g. Chanton and Liptay, 2000; Börjesson et al., 2001):

$$\frac{\delta^{13}C - \delta^{13}C_0}{1000} = \frac{1-\alpha_{ox}}{\alpha_{ox}} \ln\left(\frac{CH_4}{CH_{4,0}}\right) \tag{3.10}$$

Essentially the same technique was used by Miller et al. (2001) for methyl halides.

Methanotrophs also have a preference for H over D. Consequently two methods are available for the quantification of CH_4 oxidation: C and H isotope fractionation. The same derivations as above apply to the H fractionation.

Mariotti et al. (1981) developed an equation similar to Eq. 3.10 and used it for N fractionation.

The models used in the comparison are based on Eq. 3.6, 3.7 and 3.10. The equations were rearranged (Eq. 3.11 to 3.13) to always obtain $\ln(CH_4/CH_{4,0})$ on the left hand side.

Rayleigh model:

$$\ln\left(\frac{CH_4}{CH_{4,0}}\right) = \frac{\alpha_{ox}}{1-\alpha_{ox}}\ln\left(\frac{1000+\delta^{13}C}{1000+\delta^{13}C_0}\right) + \ln\left(\frac{1000+\delta^{13}C+{1000}/{R_{st}}}{1000+\delta^{13}C_0+{1000}/{R_{st}}}\right) \qquad (3.11)$$

Simplified Rayleigh model:

$$\ln\left(\frac{CH_4}{CH_{4,0}}\right) = \frac{\alpha_{ox}}{1-\alpha_{ox}}\ln\left(\frac{1000+\delta^{13}C}{1000+\delta^{13}C_0}\right) \qquad (3.12)$$

Coleman model:

$$\ln\left(\frac{CH_4}{CH_{4,0}}\right) = \frac{\alpha_{ox}}{1-\alpha_{ox}}\frac{\delta^{13}C-\delta^{13}C_0}{1000} \qquad (3.13)$$

From Eq. 3.11, α_{ox} can be obtained from experimental data only by nonlinear regression. This is the exact Rayleigh approach.

Plotting Eq. 3.12 with $\ln\left(1000+\delta^{13}C\right)$ on the X axis and $\ln(CH_4)$ on the Y axis yields a straight line with slope $\frac{\alpha_{ox}}{1-\alpha_{ox}}$ because the initial conditions $CH_{4,0}$ and $\delta^{13}C_0$ are constant.

Therefore, α_{ox} can be obtained by linear regression of experimental data in the same plot. This is the approximate Rayleigh approach.

Using Eq. 3.13, α_{ox} can also be obtained by linear regression of the data plotting $\delta^{13}C$ on the X axis and $\ln(CH_4)$ on the Y axis. This is the Coleman method. The Coleman method and the simplified Rayleigh approach can also be applied by interchanging the X and Y axes.

3.4 Materials and methods

3.4.1 Experiments

3.4.1.1 Experimental set-up

The fractionation factor α_{ox} was determined with a batch experiment. Soil samples were taken from the landfills Hooge Maey (Antwerp, Belgium) and Armhoede (Lochem, The Netherlands). 100 g soil taken from a landfill cover soil layer was put in a bottle of 215 ml. 24 hours before the experiment, 1 ml CH_4 was injected to activate the soil and the bottle was closed with a rubber stopper. Just before the experiment the bottle was opened for aeration. The bottle was closed again and 2 ml CH_4 was added. At regular time intervals, gas samples

were taken to measure $\delta^{13}C$ and the gas concentration. The CH_4 concentrations were measured with a Chrompack CP 9000 gas chromatograph with a FID detector. The isotopic abundances were measured with an isotope ratio mass spectrometer (IRMS) (Sercon model 2020).

Sampling frequency depended on the activity of the soil samples. For GC analysis it was typically 20 minutes. For IRMS analysis a sample was taken at the beginning of the experiment and when the CH_4 concentration was approximately half the concentration of the previous IRMS sample. In a typical experiment, about 20 samples (100 µl) were taken for GC analysis and 5 samples (varying volumes, to obtain 2 µl CH_4) were taken for IRMS analysis.

3.4.1.2 Measurement variance

It may be expected that errors on concentrations measured with a gas chromatograph are not constant over the measured range of concentrations but increase with increasing concentrations. To obtain an unbiased calibration of a model it is necessary to account for this effect.

Standards were prepared by injecting a known volume of pure CH_4 into empty 215 ml bottles. From these standards, samples were taken repeatedly, and injected into the GC. The number of samples taken from each bottle was limited so the variance created by depletion of CH_4 in the bottle was negligible compared to the measurement variance. In Fig. 3.1 the standard deviation of CH_4 concentration measurements together with the confidence interval is shown. The data shows that the measurement variability is roughly proportional with the concentration, with an average relative error of 1.7%. A parameter estimation with constant weights based on the logarithm of the concentration is consistent with a measurement error proportional to the concentration. From Fig. 3.1 it is evident that this is a justified assumption. It is concluded that Eq. 3.11-3.13 can be used without further transformations.
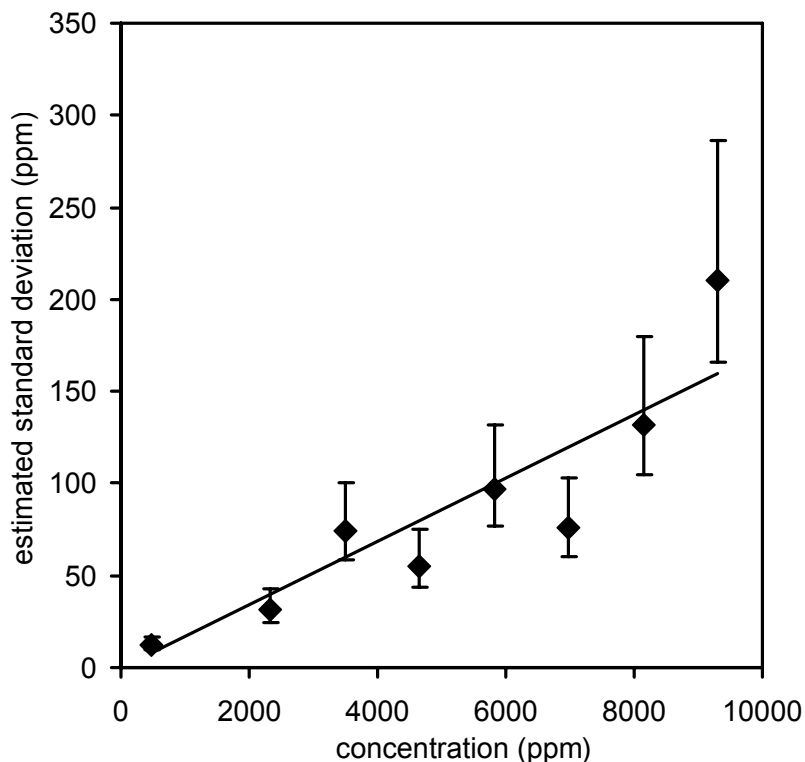
Fig. 3.1 Estimated standard deviation of concentration measurements at different CH_4 concentrations. Error bars are 95% confidence intervals

3.4.2 Literature data

Data from literature (Coleman et al., 1981; Snover and Quay, 2000) were also used to illustrate the differences between the models for hydrogen fractionation.

Snover and Quay (2000) measured the uptake of atmospheric CH_4 with static flux chambers on native grassland and forested arboretum in Washington State. Before the start of the experiment a sample of ambient air was taken for isotopic analysis. A second sample was taken when the CH_4 concentration dropped to 25-55% of the initial concentration in the chamber.

In the experiment of Coleman et al. (1981) bacteria were collected from different sources and incubated in flasks after addition of CH_4 (18 to 30%). Periodically samples where taken to measure the CH_4 concentration and isotopic composition.

3.4.3 Parameter estimation

From the experiments the fractionation factor could be calculated with the above mentioned models (Eq 3.11, 3.12, 3.13) because they were all closed systems. In the experiments of

Snover and Quay (2000) there was also fractionation by diffusion through the soil. In that case the calculated fractionation factor was a combination of bacterial fractionation and fractionation by diffusion. The data of Coleman et al. (1981) and our data refer to bacterial fractionation, because these experiments were incubations in flasks where diffusion plays a minor role.

Parameters (e.g. α_{ox}) are estimated by minimisation of a function, the objective function, J. In the case of an unweighted regression (simple linear regression in the case of Eq. 3.12-3.13, simple nonlinear regression in the case of Eq. 3.11) the objective function is the sum of squares of the residuals:

$$J(\alpha_{ox}) = \sum_{k=1}^{N} \left(Y_k - \hat{Y}_k(\alpha_{ox}) \right)^2 \tag{3.14}$$

with Y the measured value of the dependent variable and $\hat{Y}$ its calculated value for the kth measurement.

With this objective function it is assumed that the independent variable (e.g. $\delta^{13}C$ in Eq. 3.11-3.13) is free of error.

However, both variables used in the models, CH_4 concentration and the $\delta^{13}C$ value, are measured and not error-free. This is a so called errors-in-variables problem: both variables have a measurement error. According to Dochain and Vanrolleghem (2001) the objective function to be minimised in this case is:

$$J(\alpha_{ox}) = \sum_{k=1}^{N} \varepsilon_k^T(\alpha_{ox}) V_k^{-1} \varepsilon_k(\alpha_{ox}) \tag{3.15}$$

with V_k the measurement error covariance matrix and ε_k the residual vector:

$$\varepsilon_k(\alpha_{ox}) = \begin{bmatrix} Y_k - \hat{Y}_k(\alpha_{ox}) \\ X_k - \hat{X}_k(\alpha_{ox}) \end{bmatrix} \tag{3.16}$$

with X_k the independent, and Y_k the dependent variable of the kth measurement.

Here the measurement error covariance matrix can be simplified because there is no correlation between the measurement error of $\delta^{13}C$ and the measurement error of the CH_4 concentration.

$$V_k^{-1} = \begin{bmatrix} \dfrac{1}{\sigma_Y^2} & 0 \\ 0 & \dfrac{1}{\sigma_X^2} \end{bmatrix} \tag{3.17}$$

with $\sigma_Y{}^2$ and $\sigma_X{}^2$ the measurement variance of the variables.

Hence the objective function becomes:

$$J(\alpha_{ox}) = \sum_{k=1}^{N} \frac{1}{\sigma_Y^2}\left(Y_k - \hat{Y}_k(\alpha_{ox})\right)^2 + \sum_{k=1}^{N} \frac{1}{\sigma_X^2}\left(X_k - \hat{X}_k(\alpha_{ox})\right)^2 \qquad (3.18)$$

For the estimation of the fractionation factor with the errors-in-variables method, knowledge about the measurement errors is needed. With our setup the measurement errors are:

$\sigma_{\delta^{13}C} = 0.6\text{‰}$ and $\sigma_{CH_4} = 0.017\,CH_4$

with CH_4 the CH_4 concentration.

The measurement error of the IRMS is a safe number determined from different studies in the past with $^{13}CH_4$ gas samples.

3.4.4 Determination of parameter estimation error

The parameters defining the $100 \cdot (1-a)\%$ confidence region (e.g. a=0.05 for the 95% confidence region) are found where the objective function equals the critical value (Dochain and Vanrolleghem, 2001):

$$J_{crit} = J_{opt} \cdot \left(1 + \frac{p}{N_{data} - p} F_{a;p,N_{data}-p}\right) \qquad (3.19)$$

With J_{crit} the critical value and J_{opt} the minimum value of the objective function, p the number of parameters (2 in the present case), N_{data} the number of data points and $F_{a;p,N_{data}-p}$ the value of the F distribution with p and N_{data}-p degrees of freedom and a confidence level a.

3.4.5 Parameter estimation on simulated data

With the exact model of Rayleigh CH_4 concentrations and isotopic abundances were generated for different values of α_{ox}. Each simulated data set consisted of 5 samples points. Each sample had half the CH_4 concentration of the previous sample to reflect the experiments (Section 3.4.1.1). With these virtual experimental data, α_{ox} was estimated again with the approximated models. An ordinary least squares estimation could be used here because there is no measurement error in the simulations. The parameter estimations were performed for typical values of α_{ox} for C and H fractionation in landfill cover soils.

The error of each method is reported as percentage: $\left(\dfrac{\alpha_{approx} - \alpha_{true}}{\alpha_{true} - 1} \cdot 100 \right)\%$. In fractionation studies the deviation of α_{ox} from 1 is of importance because the CH_4 oxidation efficiency as calculated from isotope data (Eq. 2.22) is inversely proportional to $(\alpha_{ox}-\alpha_{trans}) \approx (\alpha_{ox}-1)$. Therefore $(\alpha_{ox}-1)$ was used to compare the three models.

3.5. Results and discussion

3.5.1. Theoretical differences between the models

3.5.1.1 Simplified Rayleigh approach

Figures 3.2 show the difference between the true α_{ox} and the calculated α_{ox}. The differences remain small (< 0.05%) for both C and H fractionation, which confirms the finding of Hunkeler (2002) that the simplified Rayleigh approach can be used at natural abundance level. The difference increases with increasing values of α_{ox}, $\delta^{13}C_0$ or δD_0. This is because the fractionation is more pronounced when α_{ox} increases.

3.5.1.2 Coleman Model

Again, a parameter estimation can be performed on virtual data generated by the exact model. The results are shown in Fig. 3.3. The difference decreases as α_{ox} or $\delta^{13}C_0$ increases. In the case of C fractionation the error can be up to 5% (Fig. 3.3 top). In the case of H fractionation the differences are larger and under some conditions exceed 20% (Fig. 3.3 bottom). This can be explained by the more negative δD_0 for H. For some combinations of α_{ox} and δD_0 the error vanishes (Fig. 3.3 bottom).
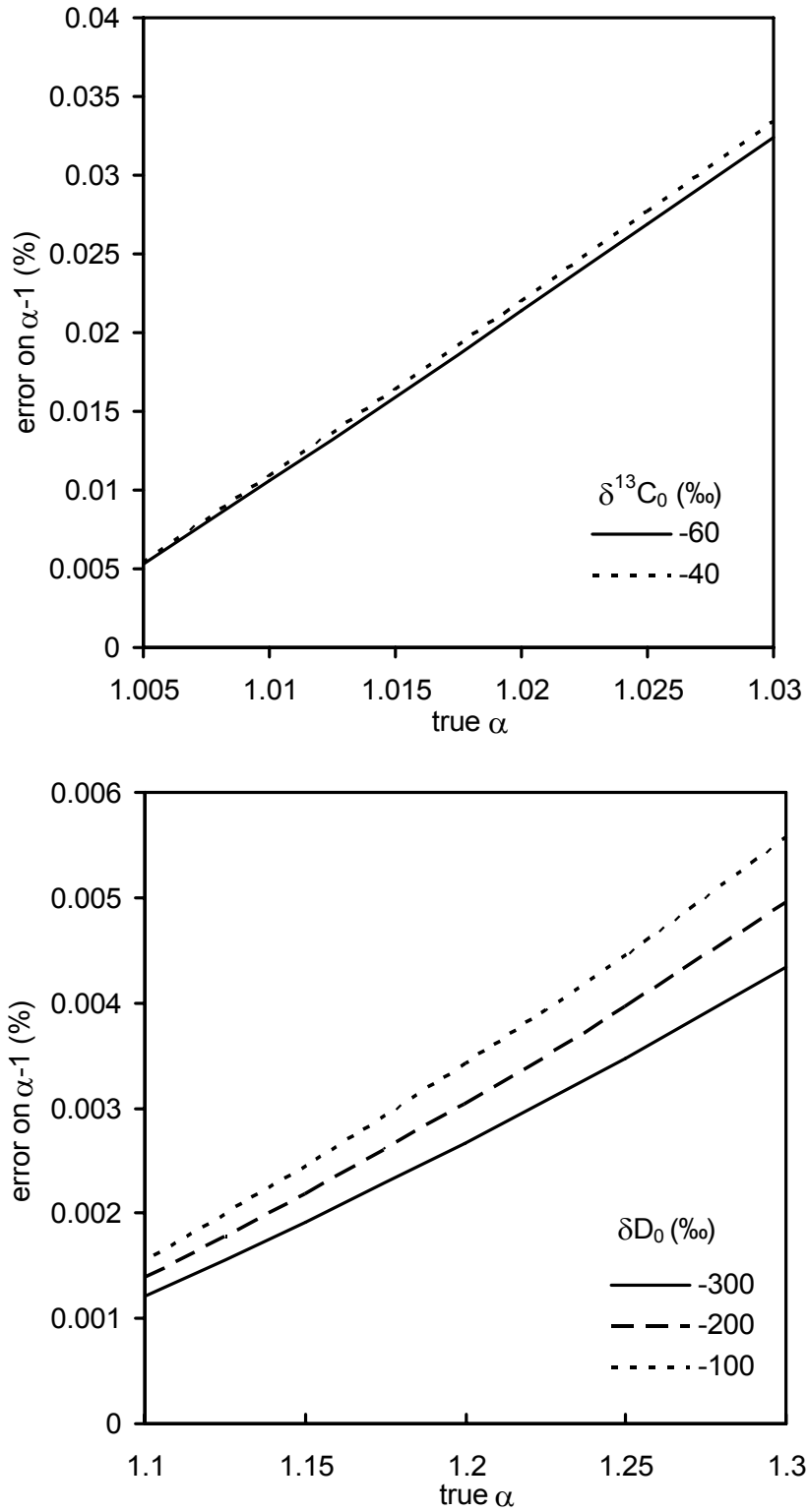
Fig. 3.2 Influence of the approximation of the Rayleigh model on the parameter estimation of α_{ox} for C fractionation (top) and H fractionation (bottom)
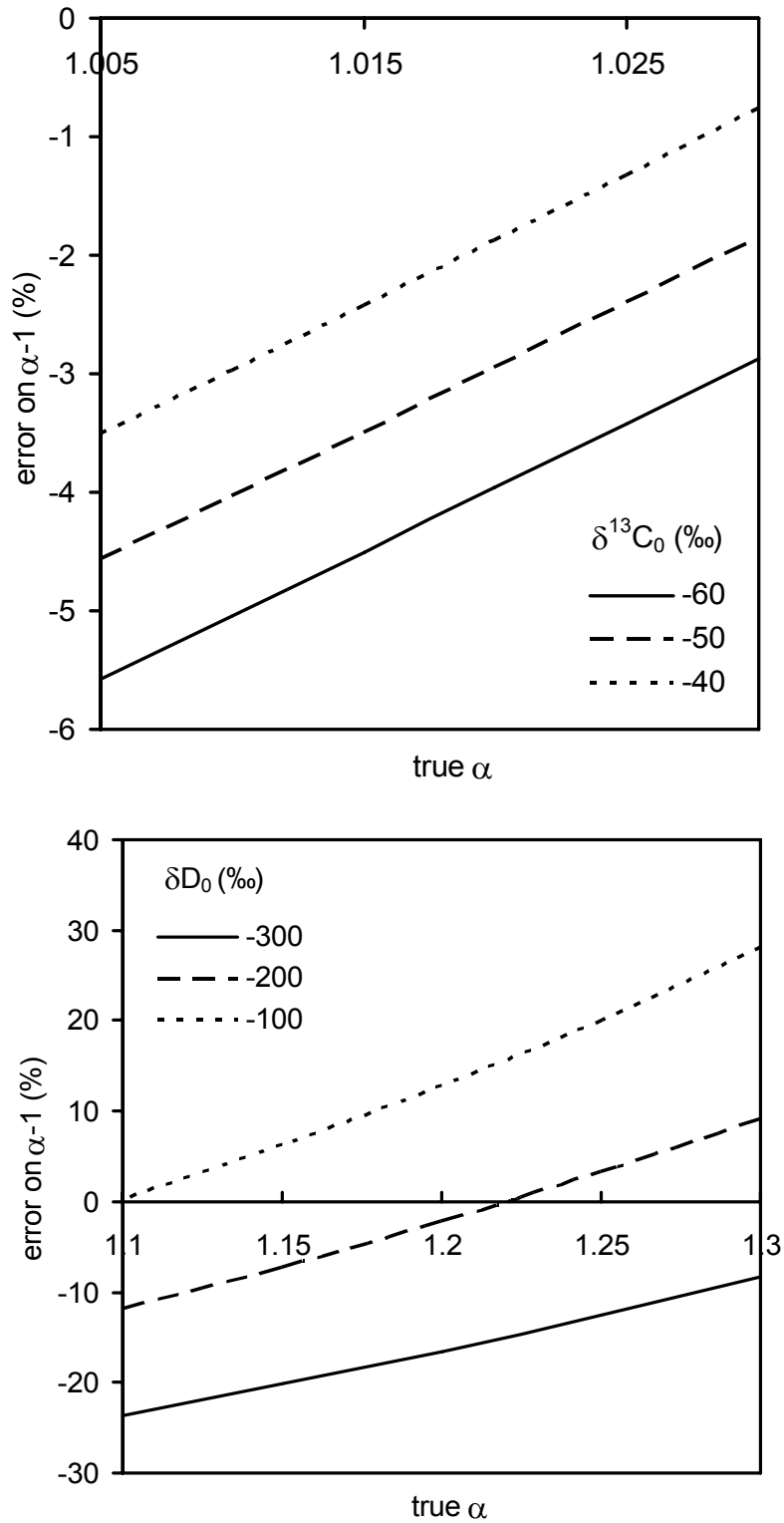
Fig. 3.3 Influence of the approximations in the model of Coleman et al. (1981) on the parameter estimation of α_{ox} for C fractionation (top) and H fractionation (bottom)

3.5.2. Illustrative parameter estimations

Using data from actual batch experiments some parameter estimations were performed with the different approximated models described above.

In Table 3.1 and 3.2 the results of parameter estimations for experiments with soil of the landfill of Armhoede and Hooge Maey is shown. To check if it was necessary to apply the errors-in-variables method the fractionation factor was estimated with an errors-in-variables method and also with a simple linear regression where all error is attributed to either $\delta^{13}C$ or CH_4.

The errors made by approximating the CH_4 concentration by the ^{12}C concentration are smaller than 0.05%. This justifies the use of the simplified Rayleigh approach. However, Hunkeler (2002) concluded that this approximation can only be used for isotopes at natural abundance level and not for studies with labelled compounds.

The approximation of Coleman et al. (1981) results in errors of up to 3%. For both experiments the α_{ox} for C fractionation calculated with the model of Coleman et al. (1981) lies within the confidence interval of the α_{ox} calculated with the model of Rayleigh, but α_{ox} is systematically underestimated. Consequently, systematic use of the Coleman model can potentially lead to a systematic overestimation of CH_4 oxidation in landfill cover soils.

Mariotti et al. (1981) compared the same approximation of Coleman et al. (1981) with the simplified Rayleigh approach, but for N fractionation. In the study of Mariotti et al. (1981) the differences between the models where of the same magnitude as for C fractionation in this study but the confidence interval was larger.

Table 3.1 Calculated $\alpha_{ox,C}$ values, 95% confidence interval half-width and difference between $\alpha_{ox} - 1$ values calculated with different models for data from Hooge Maey

dependent variable	Rayleigh	Simplified Rayleigh	Coleman	Difference (%)[a] Simplified Rayleigh	Coleman
$\delta^{13}C$	1.01731 ± 0.00052	1.01731 ± 0.00064	1.01709 ± 0.00057	0.040	-1.3
$lnCH_4$	1.01732 ± 0.00052	1.01733 ± 0.00064	1.01710 ± 0.00057	0.020	-1.3
Both variables	1.01731 ± 0.00051	1.01732 ± 0.00051	1.01709 ± 0.00046	0.020	-1.3

(a) difference between approximated models and Rayleigh model (% on $\alpha_{ox} - 1$)

Table 3.2 Calculated $\alpha_{ox,C}$ values, 95% confidence interval half-width and difference between $\alpha_{ox} - 1$ values calculated with different models for data from Lochem

dependent variable	Rayleigh	Simplified Rayleigh	Coleman	Difference (%)[a] Simplified Rayleigh	Coleman
$\delta^{13}C$	1.0189 ± 0.0018	1.0189 ± 0.0020	1.0184 ± 0.0019	0.023	-3.0
$lnCH_4$	1.0190 ± 0.0020	1.0190 ± 0.0020	1.0184 ± 0.0019	0.021	-3.0
Both variables	1.0189 ± 0.0019	1.0189 ± 0.0019	1.0184 ± 0.0018	0.020	-3.0

(a) difference between approximated models and Rayleigh model (% on $\alpha_{ox} - 1$)

In this study the experiments consisted of 5 samples at most. If more samples are taken or more experiments in the same conditions are carried out, the confidence interval will be smaller and as a result, the differences between the models will become more statistically significant.

The result of the errors-in-variables method approaches the result obtained when it is assumed that all error is in the $\delta^{13}C$ measurements. This could be expected because the errors on the $\delta^{13}C$ measurements relative to the range observed in an experiment are larger than the errors in the CH_4 concentration. For example for Hooge Maey:

$$\frac{\sigma_{\delta^{13}C}}{\left(\delta^{13}C_0, \delta^{13}C_t\right)} = \frac{0.6‰}{45‰} = 0.013$$

$$\frac{\sigma_{\ln CH_4}}{\left(\ln CH_{4,0}, \ln CH_{4,T}\right)} = \frac{\frac{1}{CH_4}\sigma_{CH_4}}{2.7} = 0.006$$

The numerators of the latter equation are based on the assumption that the errors are sufficiently small to apply differential calculus: $d(\ln CH_4) = d(CH_4)/CH_4$. Based on analysis of simulated data, Scott et al. (2004) do not recommend the errors-in-variables method. However, the analysis of Scott et al. (2004) corresponds to making assumptions on the values of $\sigma_{\delta^{13}C}$ and σ_{CH_4} (e.g. $\sigma_{\delta^{13}C} = \sigma_{CH_4}$ or $\sigma_{\delta^{13}C}^2/\sigma_{CH_4}^2 = \sum\left(\delta^{13}C - \overline{\delta^{13}C}\right)^2 / \sum\left(CH_4 - \overline{CH_4}\right)^2$), whereas our analysis is based on independent measurements of $\sigma_{\delta^{13}C}$ and σ_{CH_4}. When independent measurements of $\sigma_{\delta^{13}C}$ and σ_{CH_4} are available, the errors-in-variables method is the preferred method.

For the dataset of Hooge Maey and Lochem the difference between the fractionation factor when all error is associated with $\delta^{13}C$ and the assumption that all error is in ln CH_4 is small (<0.1% based on $\alpha_{ox} - 1$) but larger than the difference between the simplified Rayleigh approach and the exact Rayleigh equation. In this case it is better to apply an errors-in-variables method or to assign all error to the $\delta^{13}C$ measurements even if only the simplified Rayleigh approach is used.

The fractionation factors of two datasets with δD measurements from Coleman et al. (1981) and Snover and Quay (2000) were also recalculated. The measurement errors of the dataset of Coleman et al. (1981) were unknown so the errors in variables method could not be applied to these data. In Table 3.3 and 3.4 only the two simple regression methods are shown. From the data of Snover and Quay (2000) α_{ox} must be calculated analytically because only two isotope measurements were performed (Table 3.5). Snover and Quay (2000) repeated the experiments several times so the fractionation factors in Table 3.5 are mean values.

The approximation of Coleman et al. (1981) gives larger errors for H fractionation than for C fractionation, which is consistent with the simulation experiments. The differences between the approximation of Coleman et al. (1981) and the exact Rayleigh model are up to 15% (Table 3.3 to 3.5) which is unacceptable for a good quantification of isotope fractionation. Again the fractionation factor calculated with the simplified Rayleigh approach is close to the one calculated with the original Rayleigh model.

For the experiments of Coleman et al. (1981) and Snover and Quay (2000), the difference between assuming all error in ln CH_4 or in the $\delta^{13}C$ measurements is small like in parameter estimates for Hooge Maey and Lochem (Table 3.1 and 3.2).

Note that the confidence interval for the dataset of Coleman with culture A at 26 °C is very large (Table 3.4). In this experiment only three points were plotted in the graphs of Coleman et al. (1981), which is not sufficient to accurately estimate the error of α_{ox}.

The consequences of the errors in the approximations for the quantification of CH_4 oxidation can be calculated with Eq. 2.22. If $\alpha_{trans} = 1$ the relative error in the estimated CH_4 oxidation percentage will be the same as the relative difference given in Table 3.1 and 3.2.

However, if $\alpha_{trans} = 1.01$, which is realistic following De Visscher et al. (2004), the relevant error is the relative error of $\alpha_{ox} - 1.01$, which will be more than two times the relative error of

$\alpha_{ox} - 1$ when C fractionation is used for the determination. So even for C fractionation the Coleman model can lead to unacceptable inaccuracies in the determination of α_{ox}.

One could argue that even an error of 20% on CH_4 oxidation estimates is acceptable, given the fact that the natural variability of landfill gas fluxes and CH_4 oxidation is usually greater than 20%. However, the errors reported here are systematic. Unlike the random variation encountered in ecosystem gas exchange measurements, systematic errors due to incorrect data analysis do not diminish by averaging large numbers of measurements.

Table 3.3 Calculated $\alpha_{ox,C}$ values and 95% confidence interval half-width with different models for data from Coleman (1981)

| | | | | | Difference (%)[a] | |
sample	dependent variable	Rayleigh	Simplified Rayleigh	Coleman	Simplified Rayleigh	Coleman
A 26°C	$\delta^{13}C$	1.0243 ± 0.0012	1.0243 ± 0.0014	1.0239 ± 0.0014	0.053	-1.4
	$\ln CH_4$	1.0243 ± 0.0013	1.0243 ± 0.0014	1.0240 ± 0.0014	0.027	-1.4
B 11.5 °C	$\delta^{13}C$	1.01322 ± 0.00033	1.01322 ± 0.00053	1.01283 ± 0.00054	0.022	-3.0
	$\ln CH_4$	1.01323 ± 0.00034	1.01323 ± 0.00053	1.01284 ± 0.00054	0.014	-2.9

(a) difference between approximated models and Rayleigh model (% on $\alpha_{ox} - 1$)

Table 3.4 Calculated $\alpha_{ox,D}$ values and 95% confidence interval half-width with different models for data from Coleman (1981)

| | | | | | Difference (%)[a] | |
sample	dependent variable	Rayleigh	Simplified Rayleigh	Coleman	Simplified Rayleigh	Coleman
A 26°C	δD	1.33 ± 0.18	1.33 ± 0.18	1.281 ± 0.033	0.38	-15
	$\ln CH_4$	1.33 ± 0.44	1.33 ± 0.18	1.281 ± 0.033	0.0045	-15
B 11.5 °C	δD	1.1404 ± 0.0074	1.141 ± 0.012	1.1230 ± 0.0075	0.40	-12
	$\ln CH_4$	1.1413 ± 0.0087	1.141 ± 0.012	1.1232 ± 0.0075	0.0018	-13
B 26 °C	δD	1.305 ± 0.019	1.307 ± 0.025	1.2687 ± 0.0063	0.77	-12
	$\ln CH_4$	1.308 ± 0.022	1.308 ± 0.025	1.2687 ± 0.0063	0.0041	-13

(a) difference between approximated models and Rayleigh model (% on $\alpha_{ox} - 1$)

Table 3.5 Calculated $\alpha_{ox,C}$ and $\alpha_{ox,D}$ values and 95% confidence interval half-width with different models for data from Snover and Quay (2000)

sample		Rayleigh	Simplified Rayleigh	Coleman	Difference (%)[a] Simplified Rayleigh	Coleman
WSU site 1	$\alpha_{ox,C}$	1.0162 ± 0.0040	1.0162 ± 0.0040	1.0155 ± 0.0038	0.017	-4.4
	$\alpha_{ox,D}$	1.088 ± 0.010	1.088 ± 0.010	1.0807 ± 0.0080	0.0013	-7.8
WSU site 2	$\alpha_{ox,C}$	1.0174 ± 0.0046	1.0174 ± 0.0046	1.0167 ± 0.0044	0.019	-4.3
	$\alpha_{ox,D}$	1.125 ± 0.013	1.125 ± 0.013	1.117 ± 0.015	0.018	-6.3
ARB	$\alpha_{ox,C}$	1.01786 ± 0.00019	1.01786 ± 0.00019	1.01709 ± 0.00014	0.019	-4.3
	$\alpha_{ox,D}$	1.069 ± 0.010	1.069 ± 0.010	1.064 ± 0.010	0.0010	-7.7

(a) difference between approximated models and Rayleigh model (% on $\alpha ox - 1$)

3.5.3 The validity of the simplified Rayleigh approach

In all examples discussed so far the simplified Rayleigh approach turned out to be a valid method for α_{ox} determination. It would be useful to test the range of validity of this approach when labelled compounds (CH_4 or others). A set of simulations similar to the ones discussed in Section 3.4.5 was performed with varying values of R_{st}, α_{ox}, δI_0 (I = isotope) and the concentration range of the degrading compound in the batch experiment. For each simulation α_{ox} was calculated with the simplified Rayleigh approach, and compared with the set value. Two general observations were made. First, the concentration range had a limited influence on the error on α_{ox}. The error increased with increasing concentration range (i.e., with decreasing final concentration). All further calculations were based on a final concentration of 1/16 of the initial concentration, consistent with the approach in Section 3.4. As most experiments described in literature used a more narrow concentration span, we consider this to be a worst-case scenario. Second, it was observed that the error on α_{ox} was independent of R_{st} if the initial heavy isotope fraction, F% (expressed as % of total compound) was kept constant. The maximum value of F% to obtain a set error of ε% (expressed as % of $\alpha_{ox} - 1$) was determined. Figure 3.4 shows the maximum allowable value of F% as a function of $\alpha_{ox} - 1$, to stay within a set value of ε %.

The range of validity of the simplified Rayleigh approach is strongly dependent on α_{ox}. In strongly fractionating systems even a limited amount of labelled compound can lead to errors of 1% or more, whereas the simplified Rayleigh approach is always valid in weakly

fractionating systems. As a rule, the error expressed as % of ($\alpha_{ox} - 1$) never exceeds 100($\alpha_{ox} - 1$). In Fig. 3.4 it can be observed that a change of ε% leads to a vertical displacement of the curve. From this the following empirical relationship for the calculation of F% was developed:

$$\ln(F\%) = \ln(\varepsilon\%) - 0.756337 - 1.4352 \ln(\alpha_{ox} - 1) - 0.084315 (\ln(\alpha_{ox} - 1))^2 - 0.00542 (\ln(\alpha_{ox} - 1))^3 \quad (3.20)$$

Using Eq. 3.20 the necessity to use the exact Raleigh approach can be determined for any given batch system based on any given isotope.
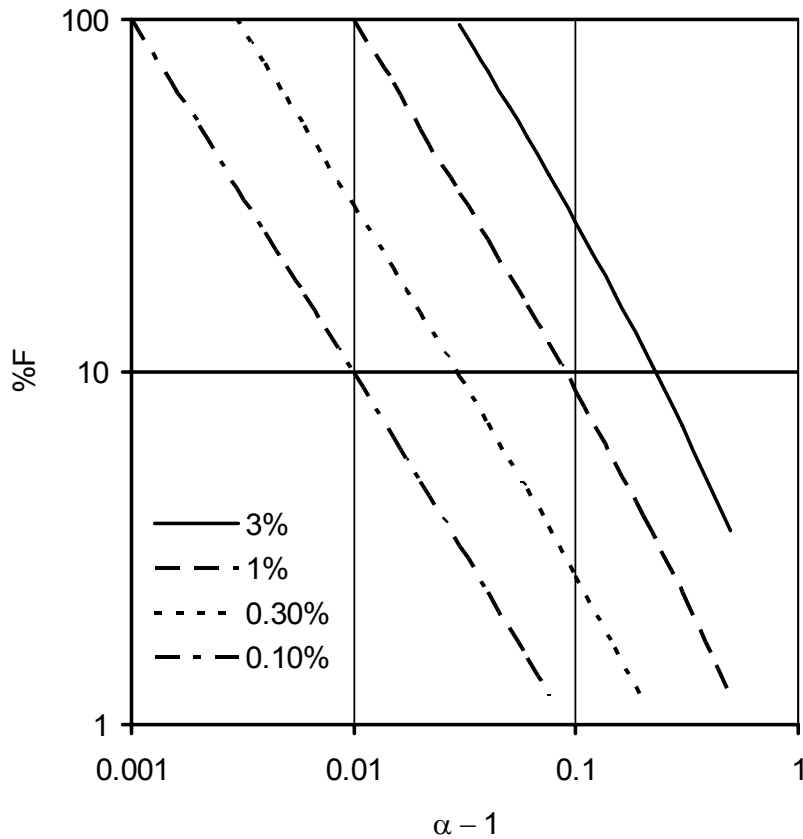
Fig. 3.4 Maximum allowable initial heavy isotope percentage (%F) in a labelled batch fractionation experiment versus $\alpha_{ox} - 1$ for different values of the allowable error (expressed as % of $\alpha_{ox} - 1$)

3.6. Conclusions

In this study the original model of Rayleigh for determining the fractionation factor α_{ox} of CH_4 oxidation was compared with the two most common approximations, the simplified Rayleigh approach and the Coleman method.

The differences caused by the simplified Rayleigh approach are small (< 0.05 % for C, < 0.006% for H), so this approach can be considered valid when the experiment is performed with unlabelled CH_4. However, the further simplifications made by Coleman et al. (1981) lead to large errors, especially for H fractionation (up to 5% for C, up to 20% for H).

Simulation results (Fig. 3.2 and 3.3) were confirmed with experimental data (Tables 3.1 to 3.4).

When errors are assigned to both variables, the difference with the assumption that all error is in the CH_4 concentration is small (< 0.1%) but can be larger than the error made by the simplified Rayleigh approach.

The advantage of the equation of Coleman et al. (1981) and the simplified Rayleigh approach is that α_{ox} can be estimated by simple linear regression. However, nowadays it is perfectly feasible to use non-linear parameter estimation. In the case of labelled systems, this is especially important when the fractionation is strong. In contrast, the simplified Rayleigh approach is always valid when fractionation is weak.

Chapter 4

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

Submitted:

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O., 2006. Modelling of stable isotope fractionation by methane oxidation and diffusion in landfill cover soils.

4.1 Abstract

A technique to measure biological CH_4 oxidation in landfill cover soils that is gaining interest is the measurement of stable isotope fractionation in the CH_4. To quantify CH_4 oxidation, it is usually assumed that the only fractionating process in this system is the CH_4 oxidation itself. Recently it was shown that neglecting the isotope fractionation by diffusion results in underestimation of the CH_4 oxidation. In this study a simulation 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 $^{12}CH_3D$ 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. Overall, the comparison shows that a model-based isotope approach for the determination of CH_4 oxidation efficiencies is feasible and superior to existing isotope methods.

4.2 Introduction

In studies measuring CH_4 oxidation with the isotope method (Section 2.4.2), 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. The fractionation factor due to transport, α_{trans}, can be as high as 1.014 (De Visscher et al., 2004), 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 chapter is therefore to develop a model that can be used as a basis for this approach. This model will be calibrated with laboratory data.

The model presented here is an extension of the model developed by De Visscher and Van Cleemput (2003). This model 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. Chapter 5 shows that mechanical dispersion is relevant also for the lower gas velocities which are encountered in landfills. This conclusion is obtained from dispersion measurements with a column filled with glass beads.

4.3 Model development

4.3.1 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.

Basis of the model is the following continuity equation:

$$\varepsilon \frac{\partial y_i}{\partial t} \frac{P}{RT} = \rho r_i - \frac{\partial N_i}{\partial z} \tag{4.1}$$

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:

$$-\frac{P}{RT} \frac{\partial y_i}{\partial z} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_i y_j - N_j y_i}{D_{ij}} \tag{4.2}$$

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 was described with the Michaelis-Menten equation with O_2 limitation:

$$r_{CH_4} = -\frac{V_{max} y_{CH_4}}{K_m + y_{CH_4}} \frac{y_{O_2}}{K_{O_2} + y_{O_2}} \tag{4.3}$$

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 converted to mole fractions.

Biomass growth is described by:

$$\mu = \frac{\mu'_{max}\left(1 - \frac{V_{max}}{V_{max,max}}\right)y_{CH_4}}{K_m + y_{CH_4}} \frac{y_{O_2}}{K_{O_2} + y_{O_2}} - a \tag{4.4}$$

$$\frac{dV_{max}}{dt} = \mu\, V_{max} \tag{4.5}$$

with μ the 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 estimated by calibration of the model with other measured data.

The concentration of CH$_4$ at the surface is a boundary condition and can be calculated with a mass balance for the mixed headspace:

$$\frac{dy_{i,l}}{dt} = \frac{1}{V}\left(\frac{RT}{P}Qy_{i,b} - N_i\Omega - y_{i,l}\left(\frac{RT}{P}Q - \Omega N_{tot}\right)\right) \tag{4.6}$$

with $y_{i,l}$ 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), 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 (mol m^{-2} s^{-1}).

4.3.2 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 binary diffusion coefficients of mixtures with $^{13}CH_4$ were calculated from the binary diffusion coefficient of $^{12}CH_4$ mixtures with Eq. 2.24.

For example $D_{^{13}CH_4,N_2}$ can be calculated from $D_{^{12}CH_4,N_2}$:

$$\frac{D_{ij}}{D_{ij'}} = \sqrt{\frac{M_{j'}}{M_j} \cdot \frac{M_i + M_j}{M_{i'} + M_{j'}}} \implies \frac{D_{^{12}CH_4,N_2}}{D_{^{13}CH_4,N_2}} = 1.0193 \tag{4.7}$$

The reaction rates for the $^{13}CH_4$ and $^{12}CH_4$ are calculated from the reaction rate of CH$_4$:

$$r_{^{13}CH_4} = \frac{1}{\alpha_{ox}} \cdot \frac{r_{CH_4} \cdot y_{^{13}CH_4}}{y_{CH_4}} \tag{4.8}$$

$$r_{^{12}CH_4} = r_{CH_4} - r_{^{13}CH_4} \tag{4.9}$$

Mechanical dispersion is added to the molecular diffusion:

$$D_{soil} = D_{mol} + D_{mech} \tag{4.10}$$

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

$$D_{soil,ij} = \frac{\varepsilon^{1+b}}{\Phi} D_{mol,gas,ij} + \alpha_{disp} \cdot v \tag{4.11}$$

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

4.3.3 Experimental set-up and model calibration

The model was calibrated with the modelling and simulation software WEST (Hemmis, 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. 4.1). Pure CH$_4$ was sent to the column through a bottom inlet section. The CH$_4$ flow rate was 19.3 mol CH$_4$ 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 if it was possible to fit the concentrations and isotopic profiles with standard parameters. The parameters used in the simulations are summarized in Table 4.1. In the first simulation the fractionation by diffusion was not taken into account while in a second simulation fractionation by diffusion was included.
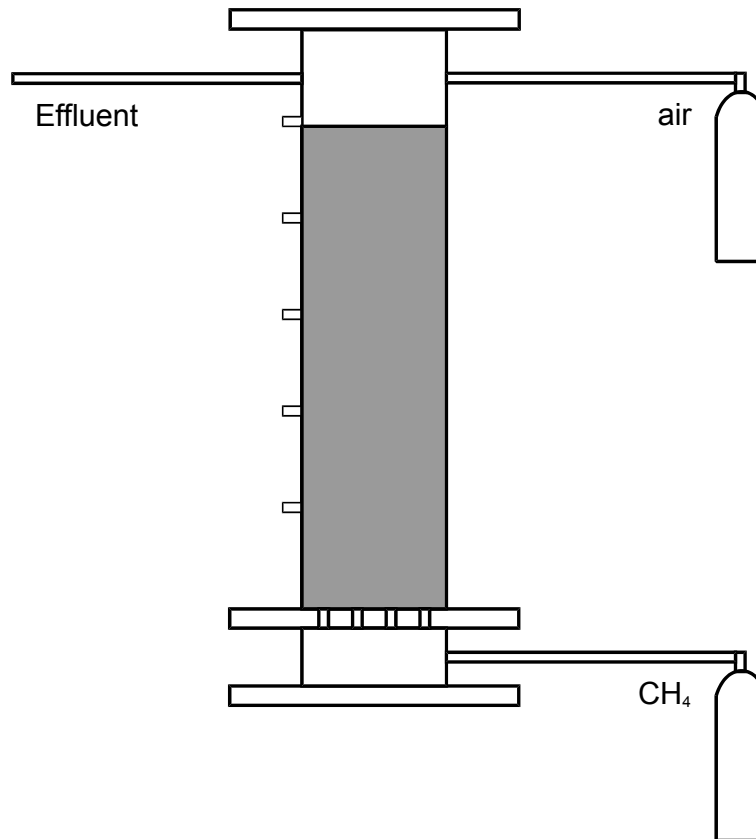
Fig. 4.1 Scheme of the experimental set-up

For a detailed explanation of the parameters, see De Visscher and Van Cleemput (2003). $V_{max,max}$ 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 independent batch experiments (De Visscher et al., 2004).

After this simulation a calibration was done to test if better results could be obtained by varying $V_{max,max}$, b, and the CO_2 yield (x). 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 $\delta^{13}C$ profiles were also used as data and mechanical dispersion is introduced with α_{disp} as an extra parameter to estimate.

Table 4.1 Parameters used for the simulation

Parameter	Value	Source
T	292.15 K	measured
ρ	1012 $kg_{soil\ DW}$ m^{-3}	measured
$V_{max,max}$	2.4×10^3 nmol CH_4 $kg_{soil\ DW}^{-1}$ s^{-1}	measured
K_m	5380 µl l^{-1}	De Visscher and Van Cleemput (2003)
K_{O2}	1.2 %	De Visscher and Van Cleemput (2003)
µ'max	2.2 d^{-1}	De Visscher and Van Cleemput (2003)
Q	1.56×10^{-5} m^3 s^{-1}	measured
Ω	0.0156 m^2	measured
F_{in}	0.000223 mol m^{-2} s^{-1}	measured
A	0.1 d^{-1}	De Visscher and Van Cleemput (2003)
α_{ox}	1.0183	measured
Φ	0.61	measured
δ_{in}	-35.2 ‰	measured

4.4 Results and discussion

4.4.1 Simulation

In Fig. 4.2 and 4.3 the results of the simulations are shown. The predicted concentration profiles (Fig. 4.2) are too steep i.e. there appears to be more dispersion than predicted by the model. The reason could be the fact that mechanical dispersion was set equal to zero, as with most models. Alternatively, the molecular diffusion might be underestimated. Without fractionation by diffusion (Fig. 4.3) the isotopic abundance at the bottom starts at the same value as the incoming CH_4 (-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. 4.3), the simulated profile follows the measured isotopic profile more closely, although there is a slight underestimation in the first 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.
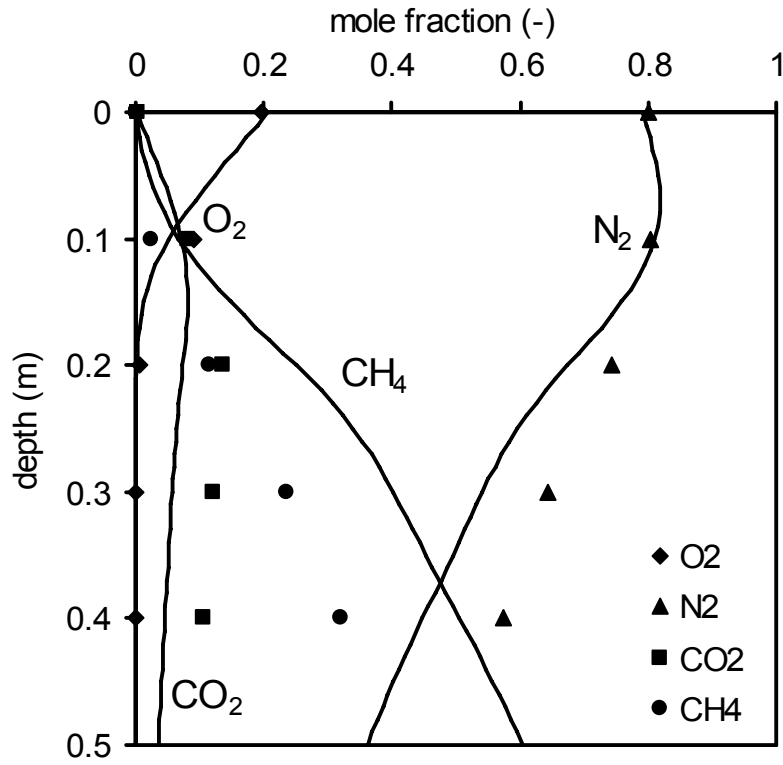
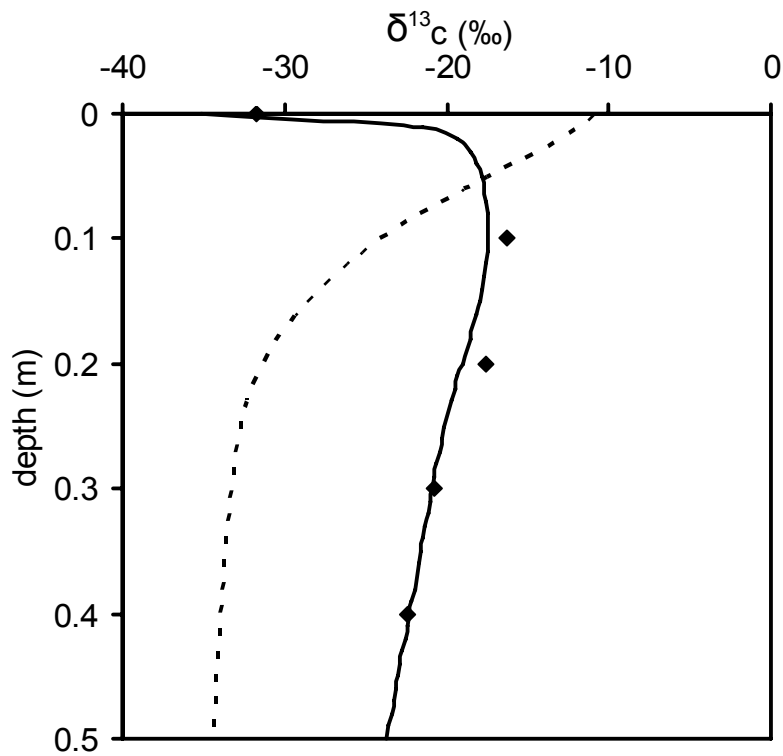Fig. 4.2 Simulated concentration profiles (solid lines) and experimental values (dots)

Fig. 4.3 Simulated $\delta^{13}C$ profile without fractionation by diffusion (dotted line) and with fractionation by diffusion (solid line) and experimental values (dots)

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.

4.4.2 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 moles CO_2 formed per mole CH_4, is incorrect. To deal with this, an extra parameter, x, was added to the model so the stoichiometry becomes the following:

$$CH_4 + (1+x)O_2 \Rightarrow xCO_2 + 2H_2O + (1-x)C_{org} \qquad (4.12)$$
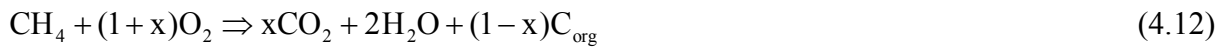
De Visscher and Van Cleemput (2003) found that the model is very sensitive to $V_{max,max}$. Therefore $V_{max,max}$ was also set as a parameter to calibrate.

As indicated in the previous section, the simulation underestimated dispersion. For that reason, b (Eq. 4.11) was set as an adjustable parameter as well.

The concentration profiles and $\delta^{13}C$ profiles obtained after parameter estimation are given in Fig. 4.4 and Fig. 4.5. The parameters obtained from the calibration are given in Table 4.2, 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 (2 + x moles used for x moles produced), 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. 4.11). The RMSD of the $\delta^{13}C$ profile is 2 ‰.

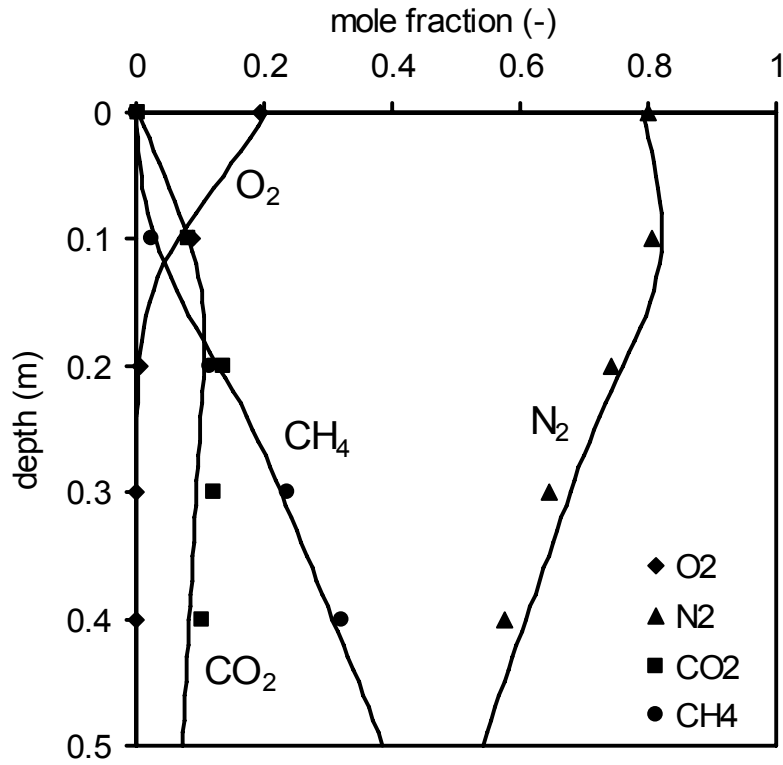Fig. 4.4 Modeled concentration profiles (solid lines) after parameter estimation and experimental values (dots)
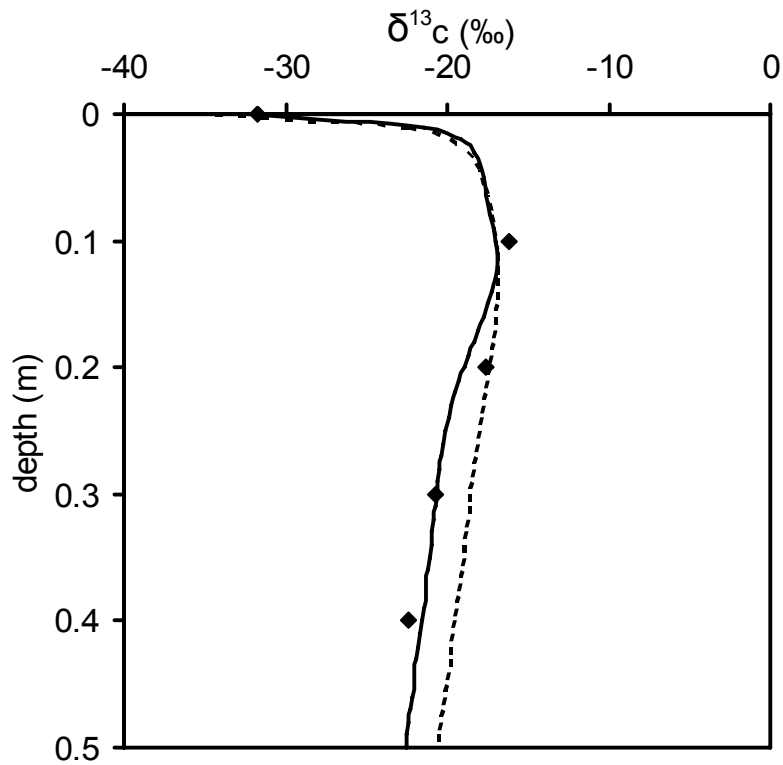

Fig. 4.5 Modeled $\delta^{13}C$ profile after parameter estimation with dispersion (solid line) and without dispersion (dotted line) and experimental values (dots)

Table 4.2 Optimal parameters from calibration and corresponding values used for simulation

Parameter	Simulation	Calibration	Calibration with dispersion
$V_{max,max}$ (nmol CH_4 $kg_{soil\ DW}^{-1}$ 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

The parameters obtained in 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 from the modified equation of Moldrup et al. (2000a) is also estimated. The optimum value is lower than the value of 1.5 obtained by Moldrup et al. (2000a) indicating that diffusivities in soils used for the current study are higher than in the soils tested by Moldrup et al. (2000a). 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. (2002a) (0.7). Overall we conclude that the parameters obtained in the calibration are plausible and reflect the real properties of the system.

4.4.3 Model with dispersion

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. For fitting it is also necessary to use the measured isotope profiles as input data.

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. 4.5). The RMSD is reduced to 0.8 ‰.

The parameter values obtained in this estimation are slightly different (Table 4.2): the added dispersion is compensated by a lower diffusion (higher b).

Parameter α_{disp} is slightly higher than values (0.0017-0.026m) measured with pulse experiments (Popovicova & Brusseau (1997), Ruiz et al. (1999), Garcia-Herruzo et al. (2000) and Constanza-Robinson & Brusseau (2002)). This study confirms that early estimates (0.2-

0.5 m) based on liquid phase dispersivities (Massmann & 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 isotope ratio of the CH_4 flux in the soil, as opposed to the isotope ratio of the CH_4 concentration present at a certain place. 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. 4.6.

The model can be compared with the classical closed and open system equation (Eq. 2.22 and 2.23) where the oxidation percentage is calculated from the difference between the $\delta^{13}C$ of the emitted CH_4 and the $\delta^{13}C$ of the produced CH_4. The $\delta^{13}C$ profiles are calculated from the % oxidized CH_4 predicted by the model with both equations and compared to the simulated $\delta^{13}C$ profile of the CH_4 flux. In Fig. 4.6 the $\delta^{13}C$ 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 abundance 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 fractionation by diffusion is situated between the predicted profile with the closed and open system equation. With diffusion the result is totally different, there is almost no 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. 4.2). In this case only 20% oxidation would be measured with the open system equation while a mass balance yields more than 90% oxidation. So, diffusion hides the fractionation due to oxidation.
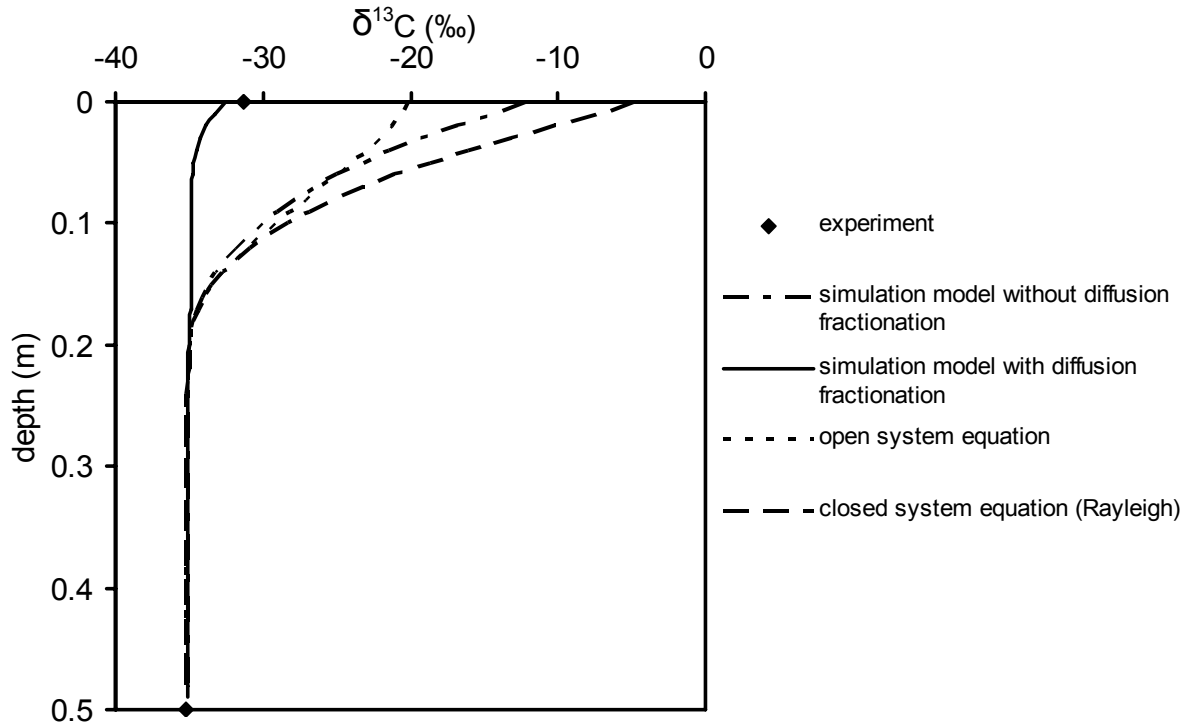
Fig. 4.6 $\delta^{13}C$ profile of the CH_4 flux calculated with open and closed system equations compared with the measured in- and outflow and the simulation model

4.5 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 diffusive and dispersive transport in this setup has a profound influence on the isotope profiles. Diffusion hides the oxidation and must therefore be accounted for in the calculation of CH_4 oxidation based on isotopes. The classical isotope method does not account for that. 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.

Chapter 5

Gas dispersion in porous media: New measurement technique using stable isotopes

Submitted:

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O., 2006. Gas dispersion in porous media: New measurement technique using stable isotopes.

5.1 Abstract

Current techniques to determine dispersivity of gas flow in porous media require multiple experiments and are restricted to flow velocities sufficiently high to observe significant mechanical dispersion effects. However, the difference between molecular diffusion and mechanical dispersion can have a significant influence on stable isotope signatures at low velocities as well because molecular diffusion leads to isotope fractionation, whereas mechanical dispersion does not. In this study a new method to determine the dispersivity of gas flow in porous media is developed using a single steady-state experiment. The determination is possible even at low gas velocity. The dispersivity was shown to be constant at approximately 1 mm at interstitial gas velocities of 10^{-4} to 10^{-3} m s^{-1} but increases rapidly at lower velocities, and can be as high as 7 cm. It was shown that Fick's law with constant diffusion coefficients is not adequate for analyzing these data and that the Stefan-Maxwell equations must be used.

5.2 Introduction

In traditional studies measuring dispersivity, α_{disp}, in the gas phase (Section 2.2.1), dispersion was measured with a pulse experiment. For different flow velocities the total dispersion, which is defined as the sum of the molecular diffusion and the mechanical dispersion, was plotted versus interstitial velocity. The intercept of the graph gave the molecular diffusion and the slope gave the dispersivity α_{disp}. However, for low velocities it is difficult to estimate α_{disp} for gases because the change of the total dispersion is too small to be quantified.

Recent research on the transport and microbial oxidation of CH_4 in landfill cover soils has spurred interest in dispersion at low gas velocities. It is not yet clear to what extent mechanical dispersion influences CH_4 mass transfer, but in Chapter 4 a significant dispersion effect was found in the stable isotope profile of CH_4 in a landfill cover soil simulated in the lab.

Diffusion fractionates isotopes, whereas mechanical dispersion does not. For low gas velocities, where mechanical dispersion does not change the concentration profiles but does lead to a significantly different isotopic profile, it is crucial to make the distinction between these two processes. For this reason the aim of this chapter is to develop a method to estimate α_{disp} at low gas velocities based on isotopic profiles.

5.3 Materials and methods

5.3.1 Experimental set-up

A column experiment was set up as shown in Fig. 5.1. A 60 cm high column (internal diameter: 14.1 cm) was filled up to 50 cm with glass beads (diameter 2-3 mm, bed porosity: 0.356). Every 10 cm a septum was installed through which samples could be taken with a syringe. The sample ports are made of Plexiglas tubes inserted into the column mantle, and sealed with rubber septa. A layer of plasticine was used to cover the connection between the tubes and the column to ensure an air tight seal. The column was tested for leaks with a bubble solution and a mass balance over the column.

Two different set-ups were tested (Fig. 5.1). In the first one the bottom of the column was connected to an air bottle for low gas velocities (20-50 ml/min) or an air pump for higher gas velocities. The headspace was flushed with CH_4 from a gas bottle. In the second set-up CH_4 entered the bottom of the column and the headspace was flushed with air from a pump. The experiments were conducted at 22°C and atmospheric pressure.
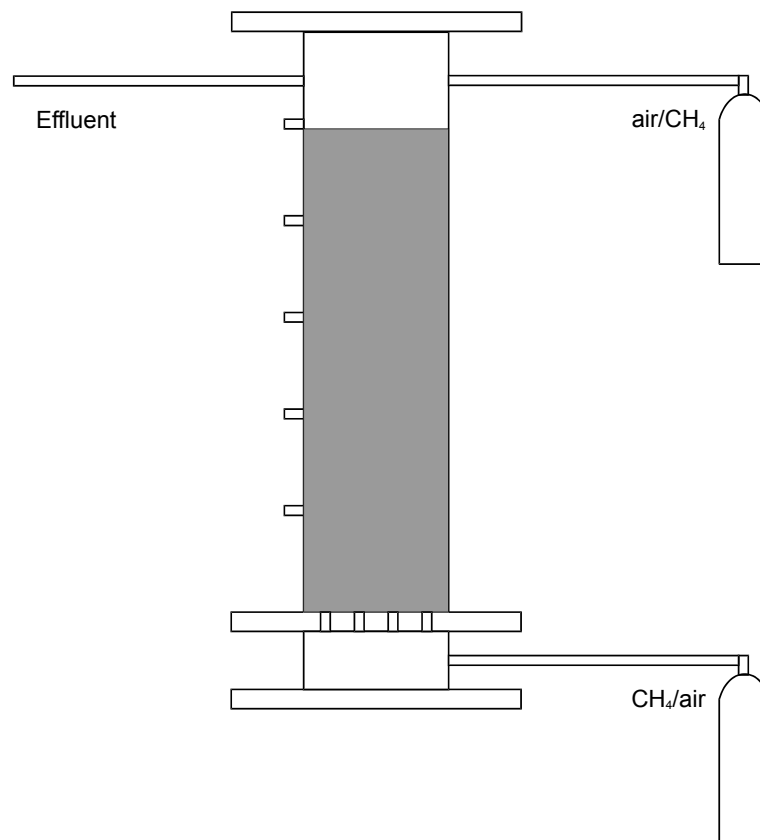

Fig. 5.1 Schematic overview of the experimental set-up

Different flow rates were tested: 20, 50, 100, 200 and 300 ml min^{-1} air in the first set-up and 5, 10 and 20 ml min^{-1} CH_4 in the second set-up. The flow above the column was fixed at 600 ml min^{-1} in the first set-up and 200 ml min^{-1} in the second set-up. Flow rates were measured with a soap film flow meter.

The Reynolds number was calculated with the formula (Reddi and Inyang, 2000):

$$Re = \frac{v \rho d}{\mu} \tag{5.1}$$

with μ the dynamic viscosity (1.8×10^{-5} Pa s for air), d the particle diameter (m) and ρ the density (kg/m^3).

The Reynolds number for the lowest velocity in the column was 2×10^{-3} (5 ml min^{-1}) and for the highest (300 ml min^{-1}) 1.5×10^{-1}. Thus all flows were laminar (Re<1).

Methane concentrations were measured by a Chrompack CP 9000 gas chromatograph with a FID detector. Isotope abundance was measured with an ANCA-TGII isotope ratio mass spectrometer.

Isotope abundance is expressed as $\delta^{13}C$, which is defined as:

$$\delta^{13}C = \left(\frac{R}{R_{st}} - 1 \right) 1000‰ \tag{5.2}$$

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). The $\delta^{13}C$ value of the incoming CH_4 is -42 ‰.

5.3.2 Data analysis

5.3.2.1 Diffusion and Dispersion

Before embarking on the data analysis a number of concepts need to be introduced quantitatively.

Molecular diffusion in a porous matrix is always lower than the molecular diffusion in free air, $D_{molec,air}$. The relationship is given by:

$$D_{molec,matr} = \frac{\varepsilon}{\mu} D_{molec,air} \tag{5.3}$$

with ε the air-filled porosity (-) and μ the tortuosity (-). This implicitly assumes that mass transfer in porous media follows the same laws as mass transfer in free air. It has been argued

that this is the case if Knudsen diffusion can be ignored, which is usually the case (De Visscher and Van Cleemput, 2003).

The total dispersion coefficient in a given matrix, D_{matr}, is the sum of the molecular diffusion coefficient in that matrix, $D_{molec,matr}$, and the mechanical dispersion coefficient, D_{mech}: (Eq. 2.14). Mechanical dispersion is usually assumed to be proportional to the advective flow velocity (Eq. 2.13). With Eq. 2.13, 2.14 and 5.3 the total dispersion can be described as:

$$D_{matr} = \frac{\varepsilon \cdot D_{molec,air}}{\mu} + \alpha_{disp} \cdot v \tag{5.4}$$

5.3.2.2 Fick's Law

Mass transfer can be described by a diffusion-and-advection equation. Using Fick's law for diffusion, this leads to the following equation for the flux, N_i (mol m^{-2} s^{-1}) of gas component i:

$$N_i = \frac{p}{R \cdot T} \left(-D_{i,matr} \frac{\partial y_i}{\partial z} + u \cdot y_i \right) \tag{5.5}$$

with $D_{i,matr}$ (m^2 s^{-1}) the dispersion coefficient of gases i in air within a matrix
       y_i the mole fraction of gas component i (-)
       u the superficial velocity (m s^{-1}) (= $\varepsilon \cdot v$, or the empty bed gas velocity)
       p the absolute pressure (Pa)
       T the absolute temperature (K)
       z the vertical distance along the column (m) (0 = packing surface)
       R the ideal gas constant (8.314472 J mol^{-1} K^{-1})

The first term between brackets is the diffusive mass transfer, as described by Fick's law (Eq. 2.3). The second term describes advective mass transfer (Eq. 2.2).

Fick's law was developed to describe molecular diffusion of a binary gas mixture. Since dispersion acts as an enhancement of the molecular diffusion, Fick's law can describe dispersion as well. Fick's law is applicable to multi-component gas mixtures in the cases: (1) diffusion of a trace component, and (2) diffusion in a ternary mixture where one gas is stagnant (Jaynes and Rogowski, 1983) as mentioned in Section 2.2.1. These authors overlooked a third case: diffusion in a mixture of components, each having the same diffusion coefficient. The latter case leads to the conclusion that Fick's law is always valid when mechanical dispersion dominates gas transfer. Fick's law performs poorer as conditions deviate more from the three cases mentioned above.

For CH$_4$ the value of $D_{molec,air}$ can be calculated with an equation of Marrero and Mason (1972) which can be rewritten as:

$$D_{molec,CH_4,air} = \frac{A \cdot T^s}{p} \tag{5.6}$$

with A (1.03×10^{-9} atm m² s^{-1} K^{-s}) and s (1.747) empirical constants derived by Marrero and Mason (1972) by fitting the equation to experimental data . In Eq. (5.6) p is the absolute pressure given in atm.

At 22°C and 1 atm the value of $D_{molec, CH4, air}$ is 2.13×10^{-5} m² s^{-1}. We assumed that this is the value for $^{12}CH_4$, as $^{12}CH_4$ is almost 99% of the total CH_4 concentration. Marrero and Mason (1972) estimated the uncertainty of $D_{molec, CH4, air}$ to be 3%. Any error on $D_{molec, CH4, air}$ will be absorbed by μ in the parameter estimation.

The diffusion coefficient of $^{13}CH_4$ was calculated from the diffusion coefficient of $^{12}CH_4$ with Eq. 2.24. The value of D_{molec} $^{12}CH_4$, air is estimated to be 1.0195 times the value of D_{molec} $^{13}CH_4$, air:

$$\frac{D_{molec,^{12}CH_4,air}}{D_{molec,^{13}CH_4,air}} = \sqrt{\frac{M_{^{13}CH_4}\left(M_{^{12}CH_4} + M_{air}\right)}{M_{^{12}CH_4}\left(M_{^{13}CH_4} + M_{air}\right)}} = 1.0195 \tag{5.7}$$

with $M_{air}= 29$ (78% N_2, 21%O_2 and 1% Ar)

The flux, N_i , can be calculated from the gas flow entering the bottom of the column:

$$N_i = \frac{p}{R \cdot T}\left(u \cdot y_{i,in}\right) \tag{5.8}$$

with $y_{i,in}$ the mole fraction of gas component i in the gas flow from the bottom. Because in steady state N_i is constant throughout the column, Eq. (5.5) can be integrated easily. It is written as:

$$\frac{\partial y_i}{\partial z} = -\frac{R \cdot T \cdot N_i}{p \cdot D_{i,matr}} + \frac{u \cdot y_i}{D_{i,matr}} \tag{5.9}$$

Combination with Eq. (5.8) and integration yields

$$\ln(y_i - y_{i,in}) = \frac{u}{D_{i,matr}}z + c \tag{5.10}$$

with c an integration constant.

On the basis of measurements of the CH_4 concentration and the CH_4 isotope abundance, the concentrations [$^{12}CH_4$] and [$^{13}CH_4$] are calculated. Equation (5.10) is fitted to experimental data of [$^{12}CH_4$] and [$^{13}CH_4$] for the determination of $D_{matr}(^{12}CH_4)$ and $D_{matr}(^{13}CH_4)$ by simple

linear regression. Substitution in Eq. (5.4) yields a set of two equations with two unknowns, ε/μ or $D_{molec,matr}/D_{molec,air}$ and α_{disp}, which can be solved.

5.3.2.3 Stefan-Maxwell

A more accurate way to calculate the advection and dispersion of gases is based on the Stefan-Maxwell equations (Eq. 2.4). Again the reasoning applies to dispersion as well. An equation of the same form as Eq. (5.4) was used to calculate $D_{ij,matr}$. Again, the molecular diffusion coefficients were calculated with Eq. (5.6), with coefficients A and s taken from Marrero and Mason (1972).

By distinguishing between $^{12}CH_4$ and $^{13}CH_4$ both CH_4 concentration and isotope abundance can be calculated at each point in the system.

Data was analyzed by the modelling and simulation software WEST developed by Hemmis NV (Kortrijk, Belgium). The differential Eq. 2.4 formed the basis of the model in WEST. WEST was used to fit the simulations to experimental data of CH_4 concentration and CH_4 isotope abundance for the estimation of $D_{molec,matr}/D_{molec,air}$, α_{disp} and d, as well as to obtain the standard errors of these parameters.

To obtain unbiased parameter estimations, the more accurate data should be given a higher weight than the less accurate data. Weights were introduced proportionally to the inverse of the measurement variance σ^2 (Dochain and Vanrolleghem, 2001):

$$J = \sum_{z=0}^{H} \left(\frac{1}{\sigma_y^2} \sum_i \left(y_{i,z} - \hat{y}_{i,z} \right)^2 + \frac{1}{\sigma_{\delta^{13}C}^2} \left(\delta^{13}C_z - \hat{\delta}^{13}C_z \right)^2 \right) \tag{5.11}$$

with J the objective function to minimize, z the depth, H the height of the column and $y_{i,z}$ the concentration of gas i at depth z

In this experiment the measurement errors were: $\sigma_{\delta^{13}C} = 0.6‰$ and $\sigma_{CH_4} = 0.017 \cdot [CH_4]$ (Chapter 3).

5.3.2.4 Headspace

Measurements revealed that the gas composition in the effluent of the system (top left in Fig. 5.1) differs from the gas composition at the top of the packed bed (top of the grey area in Fig. 5.1). This is because the headspace is not completely mixed, but contains a layer that is governed by upward advective flow and molecular diffusion, not mixing. For that reason we

considered a layer with thickness d (m) governed by free-air vertical advective flow and free air molecular diffusion at the bottom of the headspace into the model:

$$-\frac{p}{R \cdot T} \cdot \frac{y_{i,0} - y_{i,h}}{d} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_i \cdot y_{j,h} - N_j \cdot y_{i,h}}{D_{molec,ij}} \tag{5.12}$$

with $y_{i,0}$ the mole fraction of gas i at the top of the packed bed, $y_{i,h}$ the mole fraction in the headspace and d the thickness of the layer.

5.4 Results and discussion

5.4.1 Experimental results

Figure 5.2a shows the steady-state concentration profiles of CH_4 in the column at different air flow rates when air flows through the porous medium. Fig 5.2b shows the isotope abundance profiles for the same experiments. As expected, the CH_4 concentration decreases with increasing depth. The profiles become sharper with increasing air flow rates as the CH_4 molecules moving randomly into the column are increasingly flushed by the upflowing air. The relative ^{13}C abundance of CH_4 decreases with increasing depth as $^{13}CH_4$ diffuses into the column more slowly than $^{12}CH_4$.

Figure 5.3a and 5.3b show steady-state CH_4 concentration and isotope abundance profiles when CH_4 is the gas flowing through the column. The CH_4 concentration decreases as it flows up the column because the random movements of air into the porous medium dilute the CH_4. The abundance profiles pass through a maximum at 5-10 cm below the surface of the porous medium. The CH_4 is ^{13}C enriched throughout the column. This is because of the lower diffusion coefficient of $^{13}CH_4$, causing it to accumulate in comparison with $^{12}CH_4$. The CH_4 cannot be enriched in the outflow because its relative ^{13}C abundance equals the relative ^{13}C abundance of the CH_4 entering the system. Therefore, the $\delta^{13}C$ value decreases again in the top 5 cm of the porous medium, creating the maximum.

Fig. 5.2 (a) CH$_4$ concentration profiles for different air flow rates through the column; (b) relative isotope abundance profiles for different air flow rates through the column
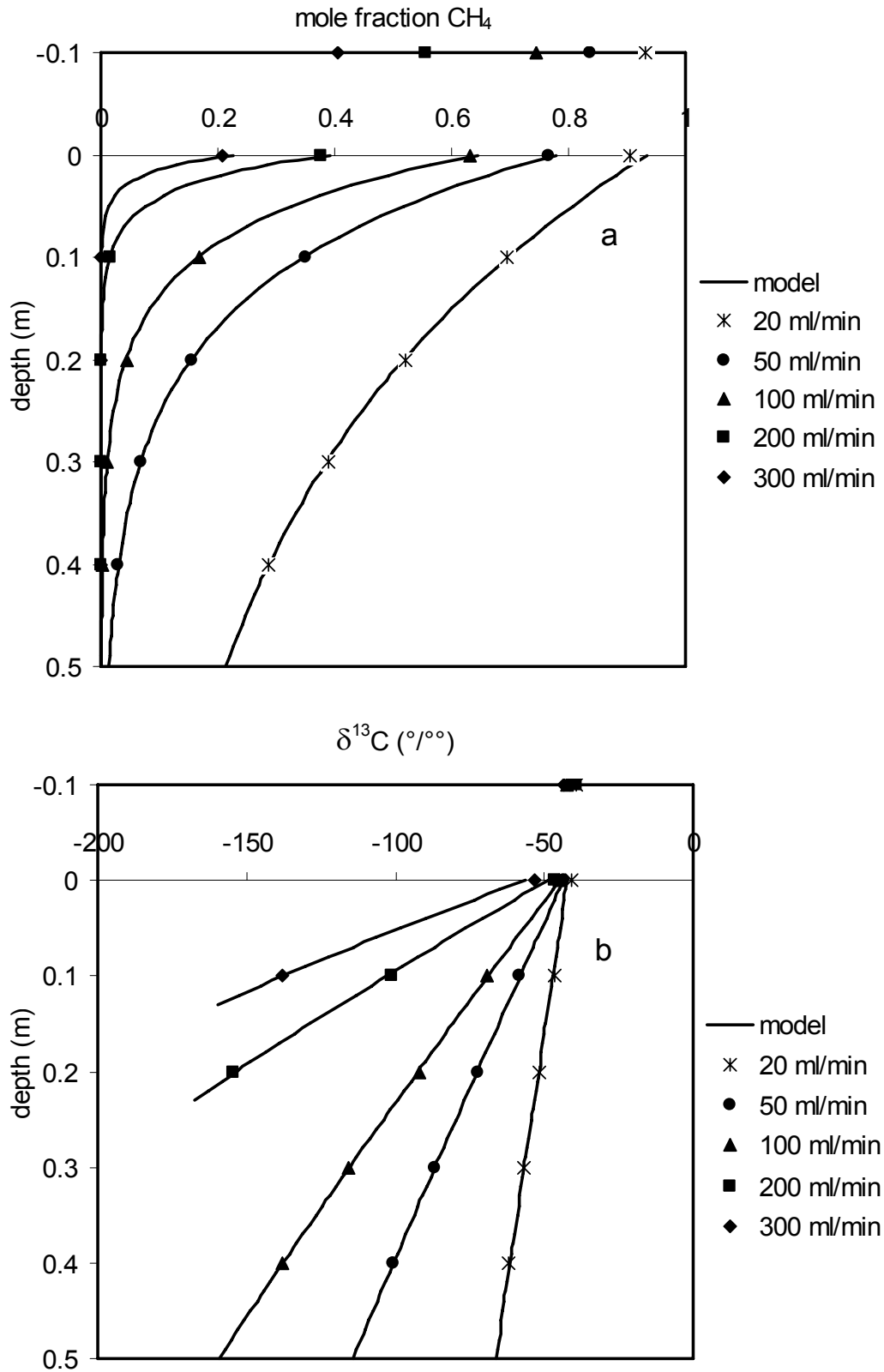
Fig. 5.3 (a) CH₄ concentration profiles for different CH₄ flow rates through the column;
(b) relative isotope abundance profiles for different air flow rates through the column
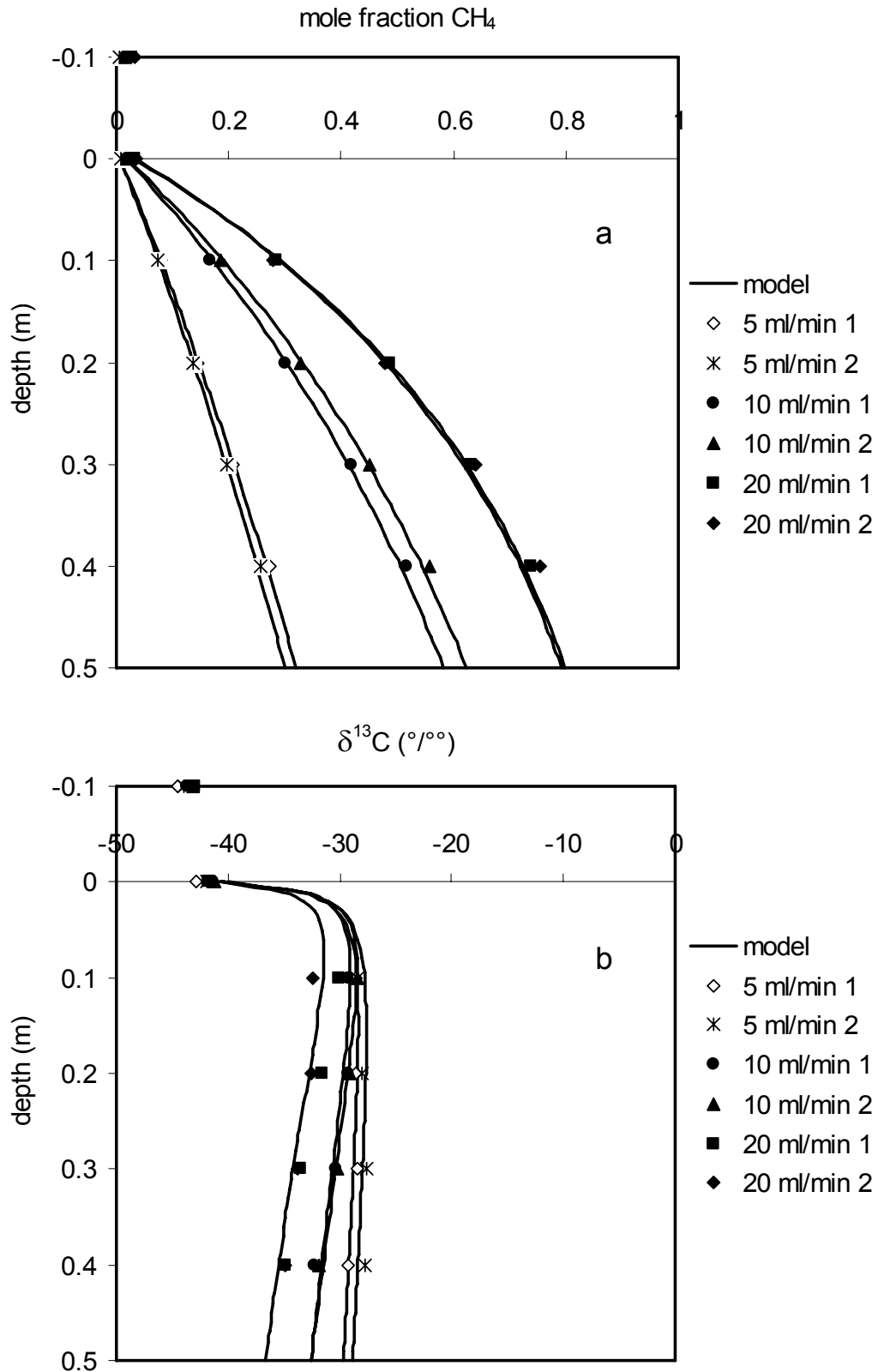
The profiles are very different when an interstitial velocity of 5×10^{-5} m s^{-1} (flow rate 20 ml min^{-1}) is exceeded. This is illustrated in Fig. 5.4a for the concentration profile and in Fig. 5.4b for the abundance profile. The concentration profile is linear and not as steep as would be expected from theory. The abundance profiles show a depletion of $^{13}CH_4$ at 50 ml min^{-1} and 100 ml min^{-1}. We hypothesize that buoyancy effects can create advective circulation of the gas in the column. Methane is lighter than air, so the gas density decreases with increasing depth into the column. If a preferential flow channel in the column creates a local area of CH_4 enrichment, then buoyancy will cause the gas to accelerate its upward movement further. Conversely if a constriction of the pores creates a local zone of CH_4 depletion then buoyancy will cause the gas in this zone to move downward, creating an advective cycle. We hypothesize that micro-scale diffusion smoothes out all concentration fluctuations up to a flow rate of 20 ml min^{-1}. Above that flow rate the heterogeneities develop too quickly to be stabilized by diffusion.

The problem of buoyancy-induced convection cycles has been studied extensively in the case of liquids heated from below (eg. Katto and Matsuoka, 1967; Kaviany, 1984). More recently, the problem was tackled for buoyancy effects due to composition changes in a liquid (Hassanzadeh et al., 2005). Convective cycles are governed by the stability of the flow pattern. The isotope signatures suggest that the most stable flow pattern features downward flow at the sides, where the gas samples were taken, and upward flow at the center.

For the determination of dispersion we only considered the experiments with either an air flow through the column, or a CH_4 flow not exceeding 20 ml min^{-1}.
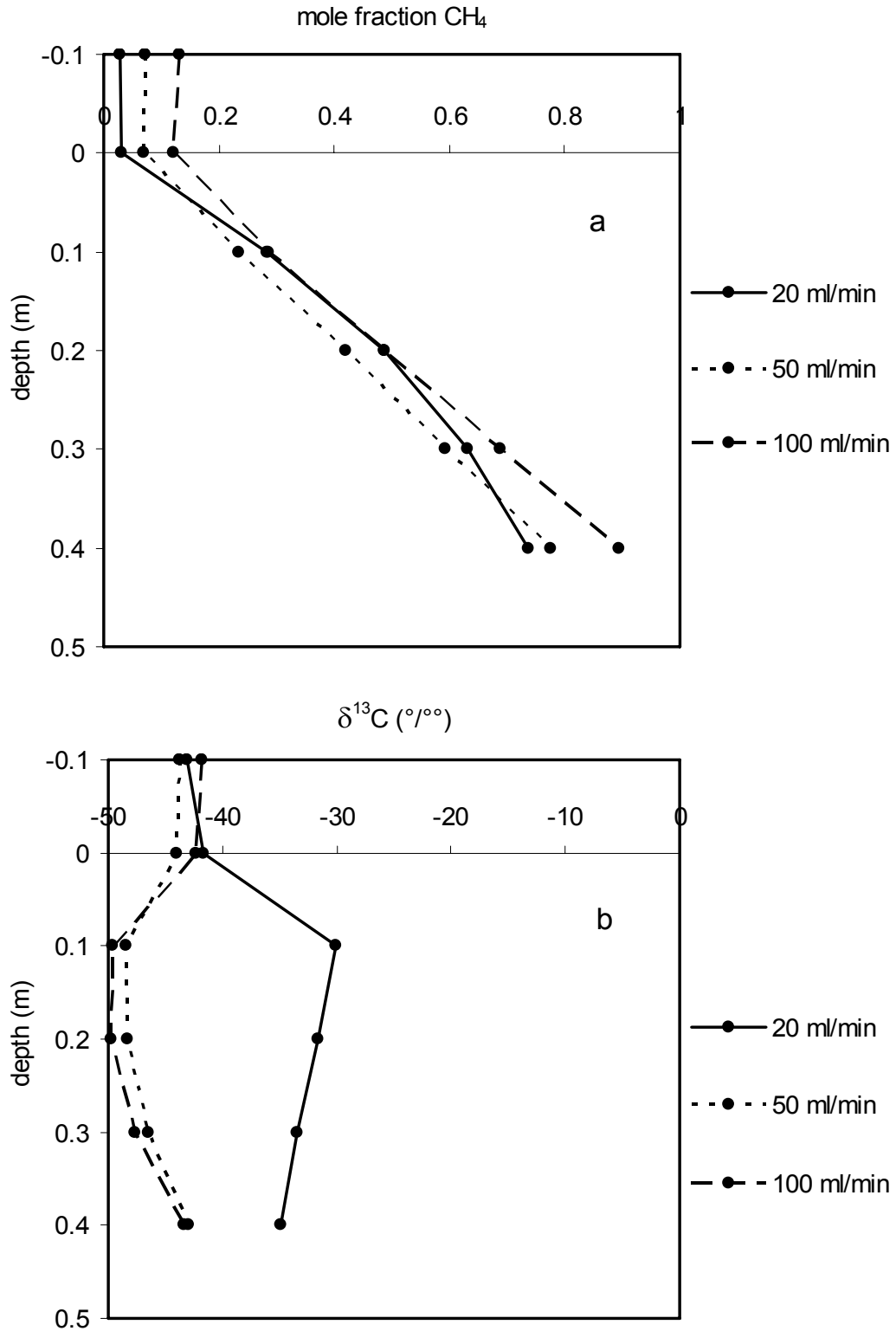
Fig. 5.4 (a) CH_4 concentration profiles for high CH_4 flow rates through the column; (b) relative isotope abundance profiles for high CH_4 flow rates through the column

5.4.2 Data analysis

Table 5.1 shows the values of α_{disp} obtained from the experimental data using Fick's law. For CH$_4$ flow through the column some experiments give a negative α_{disp} which is theoretically impossible. This might indicate that Fick's law is inadequate. However, the values of α_{disp} are small and the uncertainty of these numbers is large. Therefore, the negative sign of the estimated α_{disp} is insufficient to conclude the inadequacy of Fick's law at this point.

Table 5.1 Mass transport parameters estimated with Fick's law at different interstitial velocities

v (m s^{-1})	$D_{molec,matr}/D_{molec,air}$	α_{disp} (m)
Air through column		
5.13×10^{-05}	0.299±0.678	0.002±0.275
1.35×10^{-04}	0.280±0.228	0.0010±0.0350
2.40×10^{-04}	0.295±0.293	0.0007±0.0254
5.58×10^{-04}	0.282±2.121	0.0005±0.0791
9.49×10^{-04}	0.260	0.000787
CH$_4$ through column		
1.23×10^{-05}	0.269±0.553	0.004±0.938
1.18×10^{-05}	0.289±0.697	-0.018±1.234
2.83×10^{-05}	0.259±0.481	0.016±0.353
3.16×10^{-05}	0.266±0.595	0.005±0.391
5.38×10^{-05}	0.265±0.513	0.006±0.198
5.80×10^{-05}	0.299±1.441	-0.003±0.516

For the same experiments Table 5.2 shows the parameters calculated with the Stefan-Maxwell equations. As expected the thickness of the non-mixing air layer in the headspace is dependent on the gas flow rates. The flow rate of air through the headspace was larger than the flow rate of CH$_4$ through the headspace in the other experiments which explains the thinner air layer for the experiments with CH$_4$ through the column. A buoyancy effect in the headspace might also be a reason of the thinner non-mixing air layer.

The ratios $D_{molec,matr}/D_{molec,air}$ as calculated with the Stefan-Maxwell equations agree well with the ones obtained with Fick's law. Apparently CH$_4$ (^{12}CH$_4$ + ^{13}CH$_4$) and air can be considered as a binary mixture to a sufficient degree to account for their mixing ratios by Fick's law.

Millington (1959) derived the following equation for diffusion coefficients in dry porous media:

$$\frac{D_{molec,matr}}{D_{molec,air}} = \varepsilon^{4/3} \tag{5.13}$$

For our column this leads to a value of 0.252 for $D_{molec,matr}/D_{molec,air}$, which is close to the average value of 0.259 found here. Currie (1960) conducted experiments in different porous media consisting of spheres, and found that the following equation can be used:

$$\frac{D_{molec,matr}}{D_{molec,air}} = \varepsilon^m \tag{5.14}$$

with m ranging from 1.35 to 1.44.

In our case this leads to an estimated value of $D_{molec,matr}/D_{molec,air}$ of 0.226 to 0.248, not far from the value found here.

Table 5.2 Mass transport parameters estimated with Stefan-Maxwell equations. d is the thickness of the diffusive air layer above the porous matrix

v in column (m s^{-1})	d (m)	α_{disp} (m)	$D_{molec,matr}/D_{molec,air}$
Air			
5.13×10^{-05}	-0.014 ± 0.014	0.0134 ± 0.006	0.26 ± 0.02
1.35×10^{-04}	0.022 ± 0.007	0.0009 ± 0.0007	0.279 ± 0.006
2.40×10^{-04}	0.027 ± 0.008	0.0007 ± 0.0005	0.295 ± 0.007
5.58×10^{-04}	0.027 ± 0.006	0.0008 ± 0.0003	0.271 ± 0.011
9.49×10^{-04}	0.026 ± 0.003	0.0010 ± 0.0003	0.245 ± 0.018
CH$_4$			
1.23×10^{-05}	0.003 ± 0.002	0.07 ± 0.04	0.24 ± 0.02
1.18×10^{-05}	0.004 ± 0.002	0.05 ± 0.04	0.26 ± 0.02
2.83×10^{-05}	0.005 ± 0.002	0.029 ± 0.016	0.24 ± 0.02
3.16×10^{-05}	0.0039 ± 0.0015	0.017 ± 0.009	0.258 ± 0.015
5.38×10^{-05}	0.0033 ± 0.0017	0.017 ± 0.009	0.25 ± 0.02
5.80×10^{-05}	0.003 ± 0.003	0.026 ± 0.015	0.25 ± 0.04

All α_{disp} values are positive when calculated with the Stefan-Maxwell model, and deviate substantially from the values calculated with Fick's law. There appears to be a systematic underestimation of α_{disp} by Fick's law. This indicates that Fick's law is an inadequate approximation for the description of isotope fractionation effects in a case like the one presented here. The reason for the deviation is that Fick's law does not account for diffusion resulting from $^{12}CH_4$-$^{13}CH_4$ collisions, which will influence the diffusion coefficients. An approach that might potentially solve this problem within the framework of Fick's law is the Wilke approximation for calculating composition-dependent diffusion coefficients (Froment and Bischoff, 1990 p. 131). We conclude that Fick's law with constant diffusion coefficients is not recommended for modelling isotope fractionation effects.

This conclusion is in contrast with modelling studies of O_2 transfer and respiration and the resulting isotope fractionation effects. Aggarwal and Dillon (1998) and Hendry et al. (2002)

used Fick's law to model the transfer of $^{16,16}O_2$ and $^{16,18}O_2$ in soils. Angert et al. (2001) described these processes with a more basic conceptual model that bears some resemblance to Fick's law. However, there are several reasons why Fick's law is more acceptable in those cases than in ours. First, their system can be considered as a ternary gas mixture ($^{16,16}O_2$, $^{16,18}O_2$ and N_2) with one gas (N_2) stagnant, so it fits one of Jaynes and Rogowski (1983)'s criteria of applicability of Fick's law. Our system is quaternary ($^{12}CH_4$, $^{13}CH_4$, O_2 and N_2). Second, as the O_2 concentration cannot exceed 21%, the gas composition is more constant than in our case, so the diffusion coefficients change less with depth. Third, the diffusion coefficients of the different gas components differ more widely in our case than in theirs.

The value of α_{disp} estimated with the Stefan-Maxwell equations has a trend towards higher dispersivities for lower gas velocities (Fig. 5.5). This result was unexpected because it is normally assumed that α_{disp} is constant. An empirical equation for α_{disp} in function of the interstitial velocity was fitted through all experimental data:

$$\alpha_{disp} = \alpha_{disp,0} + \left(\alpha_{disp,\infty} - \alpha_{disp,0} \right) \exp(-a \cdot v) \tag{5.15}$$

with $\alpha_{disp,\infty} = 0.000744$ m, $\alpha_{disp,0} = 0.0849$ m and $a = 4.02 \times 10^4$ s m^{-1}

From Fig. 5.5 it is clear that Eq. 5.15 follows the experimental data well. The reason for the exponential relationship between the dispersivity and the interstitial velocity is unknown. A possible reason could be the turbulence generated by the air pump that was used to pump air in the headspace in certain experiments. If that were the case, we would expect that dispersion is low even at low interstitial velocities when both CH_4 and air are supplied by a gas bottle. However, the experiment at the lowest flow rate with air flowing through the column also gives a large value of α_{disp}, in spite of the fact that both air and CH_4 were supplied from a gas bottle. We conclude that the increase of α_{disp} at low velocities is not due to turbulence induced by the pump. An alternative explanation is atmospheric pressure fluctuations that create an oscillatory advective movement in the column. Auer et al. (1996) observed increased dispersion as a result of this "barometric pumping" in numerical experiments. Elberling et al. (1998) observed increased oxygen transfer into soils due to atmospheric pressure cycles in both field studies and models. The barometric pumping effect receives a growing interest from landfill researchers because the large internal gas volume in a landfill amplifies this oscillation effect. Poulsen et al. (2001) assumed that pressure oscillations have a pronounced effect on mass transfer in soils adjacent to landfills, and incorporated a dispersion coefficient in the top soil layer in their gas transfer model to account for that. At this point it is not clear

what the physical significance of Eq. 5.15 is, so it may not have a broad applicability. More research is required to establish the applicability of Eq. 5.15 in other situations.

For low gas velocities dispersion cannot be measured with traditional methods measuring the total dispersion as a function of the gas velocity because the mechanical dispersion is only a small fraction of the total dispersion. This is illustrated in Fig. 5.6, which shows the total dispersion as a function of the interstitial gas velocity for a binary mixture of CH_4 and N_2. From this figure it is only possible to calculate the dispersion for the experiments with larger flow rates.
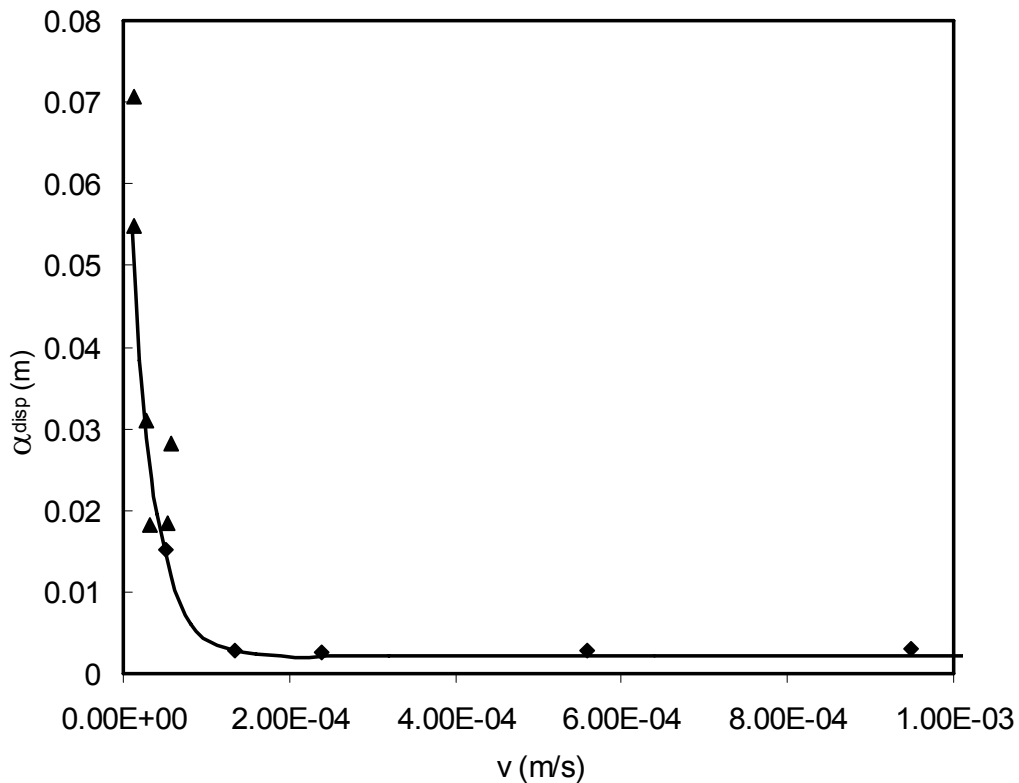

Fig. 5.5 α_{disp} from experiments (▲, ♦ CH_4 and air through column, respectively) and exponential model (line) versus interstitial gas velocity
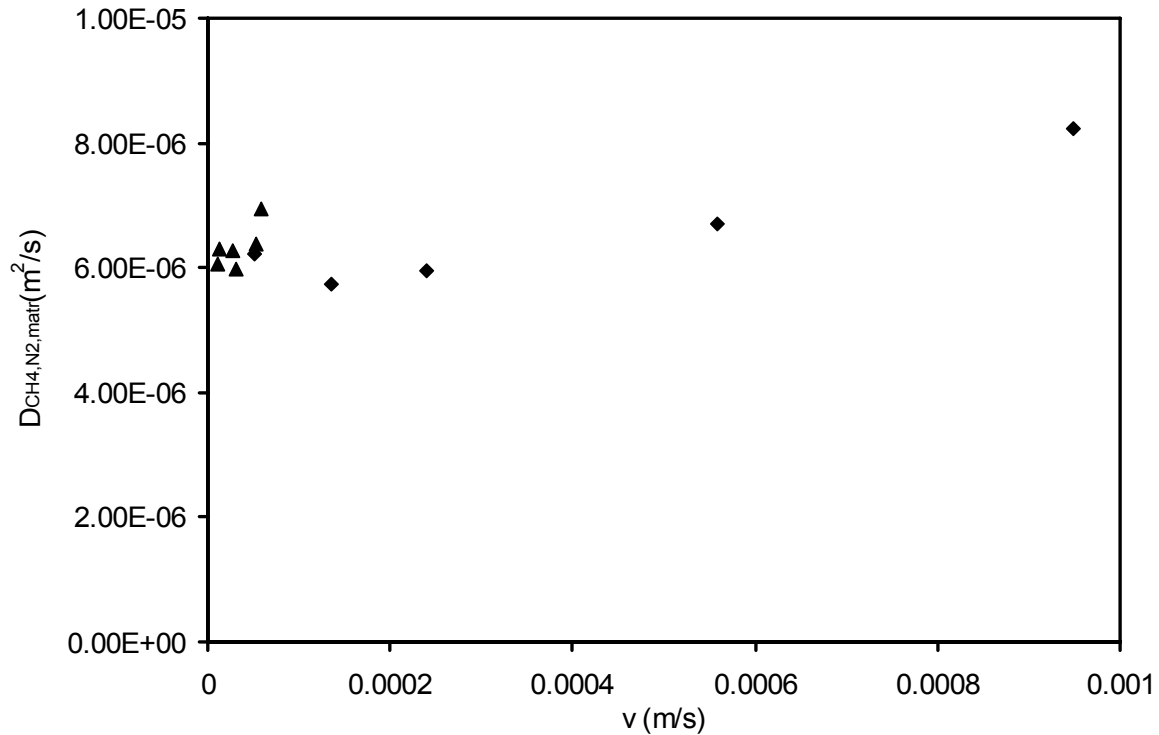
Fig. 5.6 Total binary dispersion between CH_4 and N_2 versus interstitial gas velocity ($\blacktriangle$, $\blacklozenge$ CH_4 and air through column, respectively)

In Fig. 5.7 the sensitivity of the concentration and isotopic profiles to α_{disp} around the optimal values is shown for two situations: a flow rate of 5 ml min^{-1} CH_4 (Fig. 5.7a and 5.7b) and 200 ml min^{-1} air (Fig. 5.7c and 5.7d) through the column. As expected a higher α_{disp} results in a lower isotope fractionation (Fig. 5.7b and 5.7d). At the lowest flow velocity of 5 ml min^{-1} CH_4 the sensitivity of the isotopic profile (Fig. 5.7b) and the concentrations is of the same magnitude. However the errors on concentration measurements, around 1%, are much larger than the errors on the isotopic content, less than 1‰. For this reason the isotope concentrations will be important to calculate the dispersivity at low gas velocities. At a gas velocity of 200 ml min^{-1} a larger effect is expected on the concentration profile. However, the estimated dispersivity is much lower (α_{disp}=0.001) than at 5ml min^{-1} (α_{disp}=0.07) for example. This results in a much lower sensitivity on the concentration profiles, again showing that isotopic measurements are needed to accurately estimate the dispersivity.

Fig. 5.7 (a) CH$_4$ concentration profiles for a flow rate of 5ml/min CH$_4$ through the column;
(b) relative isotope abundance profiles for a flow rate of 5ml/min CH$_4$ through the column
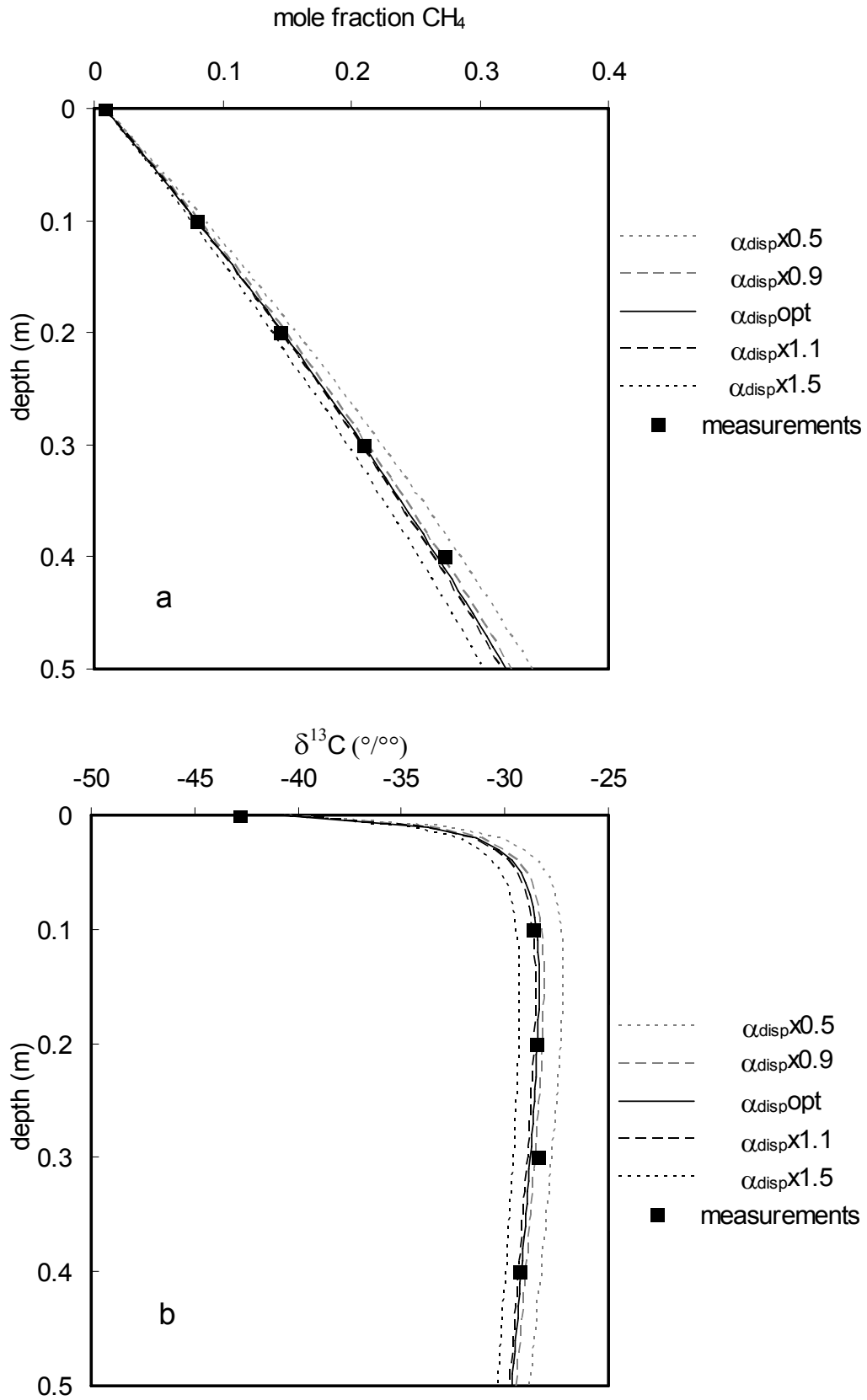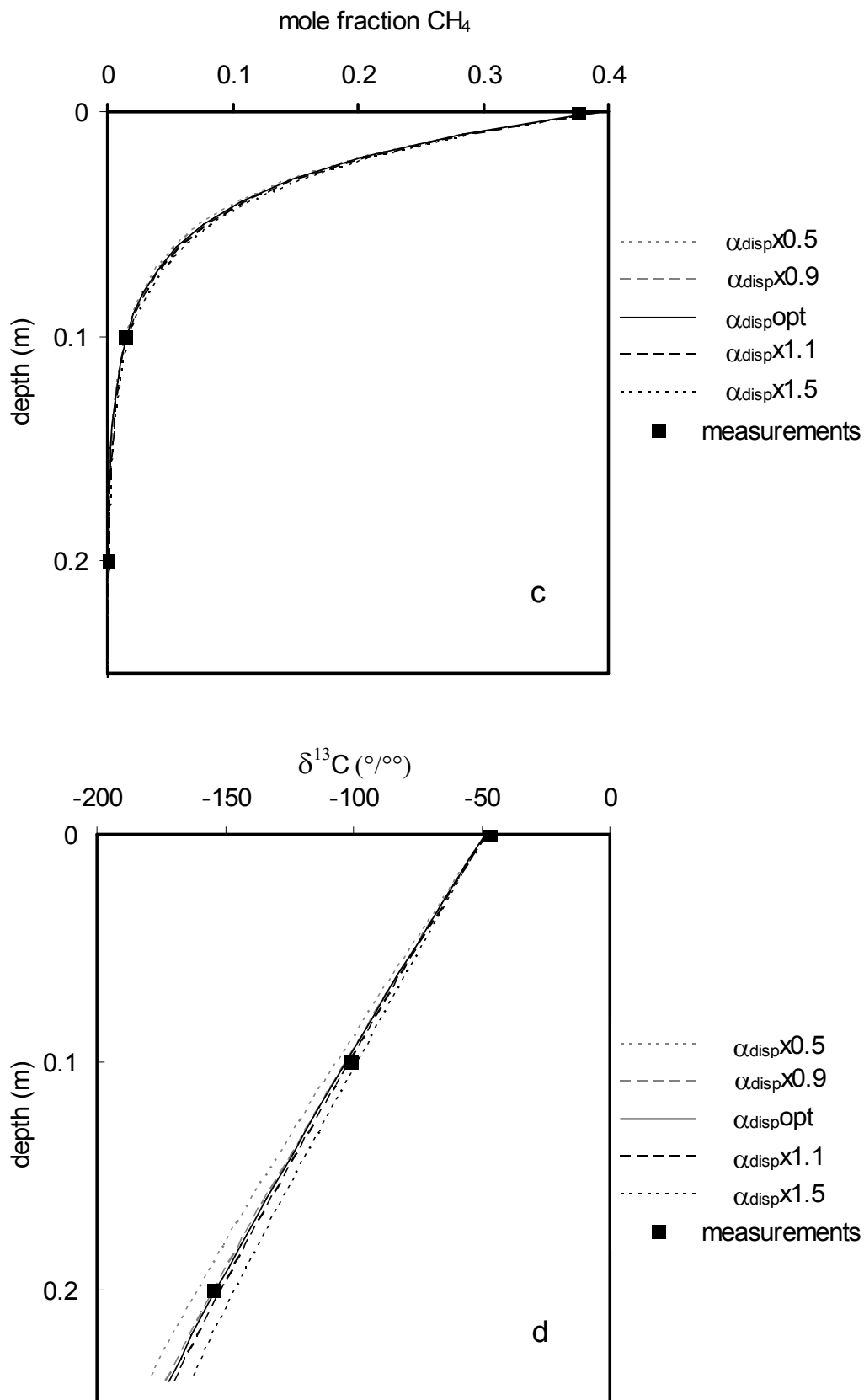
Fig. 5.7 (c) CH$_4$ concentration profiles for a flow rate of 200ml/min air through the column; (d) relative isotope abundance profiles for a flow rate of 200ml/min air through the column

Most experiments described in the literature were conducted with higher gas velocities than in the current experiment (1×10^{-5} to 1×10^{-3} m s^{-1}) because higher velocities are needed to reliably estimate mechanical dispersion from the change of the total dispersion versus flow velocity. At the high end of our experiments, where α_{disp} is fairly constant, the value is somewhat below, but close to the range found in the literature. Popovicova and Brusseau (1997) measured a value of 0.026 m for a column with glass beads (0.59 mm diameter) and flow rates between 3×10^{-3} m s^{-1} and 2.5×10^{-2} m s^{-1}. Constanza-Robinson and Brusseau (2002) found values for α_{disp} between 0.003 and 0.03 m for velocities between 0.5 and 1×10^{-3} m s^{-1} for a sand column. Other reported values for α_{disp} are 0.0017 m for a soil column with a gas velocity of 2.2×10^{-3} m s^{-1} (Garcia-Herruzo et al., 2000) and 0.00196 m for CH$_4$ gas through a sandy soil column (Ruiz et al., 1999). These values are close to the one found in this study for large gas velocities, where α_{disp} is fairly constant: 0.001 m.

In Chapter 4 α_{disp} is estimated together with other parameters in a calibration with a similar column as in this test but filled with soil instead of glass beads. For a low gas velocity of 1.3×10^{-5} m s^{-1} the result was 0.052 m, which confirms the results in Fig. 5.5.

5.5 Conclusions

Experiments with a glass beads-filled column showed that it is possible to measure both molecular diffusivity and mechanical dispersivity from a single steady-state experiment using isotopes. It was shown that Fick's law with constant diffusion coefficients is not adequate for analyzing the data and that the Stefan-Maxwell equations must be used. At interstitial gas velocities between 1.5×10^{-4} m s^{-1} and 10^{-3} m s^{-1} the dispersivity is constant at 0.001 m, but increases rapidly at decreasing gas velocities below 1.5×10^{-4} m s^{-1}, and can be as high as 0.07 to 0.08 m.

Chapter 6

Field study of carbon and deuterium fractionation in landfill covers

6.1 Abstract

At present there are no non-invasive measurement techniques for CH_4 oxidation in landfill cover soils that do not lead to biased estimates. A promising technique is based on stable isotope measurements, but De Visscher et al. (2004) showed that this technique leads to a systematic underestimation of the CH_4 oxidation. However, it was concluded that an approach combining computer modelling and deuterium isotope measurements might hold the key for an unbiased, non-invasive measurement technique. In this study, the CH_4 oxidation and transport model of Chapter 4 was tested on field data. Also in real landfill covers the model was able to fit the concentration profiles and isotopic profiles. Simulations indicate that the open system equation, which does not take into account diffusion fractionation, should give a better estimate for CH_4 oxidation when applied on δD measurements instead of δC because the fractionation factor for oxidation is 10 times larger for deuterium than for carbon.

6.2 Introduction

The CH_4 oxidation and transport model of Chapter 4 was shown suitable for simulation of column profiles. In this chapter the model will be tested on field data.

This research was conducted in collaboration with the Florida State University (Tallahassee), Department of Oceanography and the Department of Civil and Environmental Engineering. This laboratory has an extensive data set with concentration profiles and isotopic measurements on a landfill site. In particular, the possibility to measure deuterium isotopes was a great opportunity as D fractionation factors for CH_4 oxidation are much larger than for C. Deuterium measurements will not only give extra information for the quantification of oxidation but the signal should be more clear with less "noise" from the transport fractionation.

6.3 Materials and methods

6.3.1 Field data

Field data from measurement campaigns during the last two years at the Leon county landfill (Tallahassee) were used. The data was collected for the project 'Inexpensive approaches for

mitigating CH_4 emissions from landfills'. In this project, two cover layers, soil and compost, were tested as well as different depths of mulch (30 and 60 cm).

The dataset consists of box measurements and probe measurements (Fig. 6.1) on a monthly basis at several locations on the test fields. The probes (needles) were permanently installed on the landfill at different depths between 5 cm and 1 m (where the cover layer ends and the waste starts). From these probes samples were taken to measure the CO_2, O_2, N_2 and CH_4 gas concentrations on a gas chromatograph and to measure ^{13}C and D abundances with an IRMS.

Stable carbon isotopes abundances were measured by direct injection into a Hewlett Packard Gas Chromatograph coupled via a combustion interface to a Finnigan Mat Delta S Isotope Ratio Mass Spectrometer (GCC-IRMS). The ^{13}C samples with small concentrations (<4000 ppm) were cryogenically focused using a device coupled to the front end of the GC. The measurement errors were approximately 0.15‰ for $\delta^{13}C$ and 1‰ for δD (Department of Oceanography, Florida State University).

Around these probes, permanent collars were installed where a chamber can easily be placed on top of it at the time of the measurement. After closing the box the samples were taken to measure the concentration increase in time due to the CH_4 emissions. The emitted CH_4 flux was calculated from the slope of the concentration curve.

Fig. 6.1 Left: probe nest with collar, right: closed chamber

Although the dataset is nearly complete for two years, the quality of the data is not always good. Probes near to the surface are very sensitive to leaks and the sample volume is large making it unsure from which depth the gas is actually extracted. For this reason only data with profiles that could be theoretically explained was considered.

Because the IRMS to measure δD was not equipped with a cryogenically focusing device, only samples with a high concentration could be analyzed for D. For this reason the samples from probes nearest to the surface and the chambers were not analyzed.

6.3.2 Model validation

The method to validate the oxidation and diffusion model is different from the method to calibrate with column data in Chapter 4 because an important input parameter, the CH_4 influx, is unknown in a landfill. Only measurements of the emission flux can be made.

To estimate the CH_4 influx, an initial rough estimation is made, followed by a calibration to refine the estimate. A rough estimate of the influx can be made from the out-coming emission flux measured in the chambers around the probes together with a rough estimate of the CH_4 oxidation. The CH_4 oxidation can be estimated based on the isotope samples of the chambers with the open system equation (Eq. 2.22). This first simulation will show if it is possible to fit the concentration profiles and isotopic profiles with the available measurement data without doing a calibration.

Although the test covers were placed on hot spots, no observable emission flux was measured on many locations. As a starting point for the simulation of the model one dataset was chosen from a test field with a soil cover and a positive CH_4 emission. A positive emission is needed to estimate the incoming flux into the landfill cover.

After this simulation the model was calibrated to see if better results could be obtained by estimating the parameters that cannot be determined accurately from independent measurements. Both air filled porosity (AFP) and CH_4 influx were chosen as parameters and the model was fitted to the emitted CH_4 flux, isotopic signature measured in the chambers and the N_2 concentration profile.

The moisture content was measured at the time when the samples were taken with water content reflectometers (Campbell Scientific CR615) on 12 and 40 cm depth. Landfill cover soil is not a typical repacked soil as in laboratory setups but it is not an undisturbed soil either because it has been in place for only two years. Therefore the empirical equations that are available in the literature to calculate the diffusion coefficients based on the moisture content may not be accurate.

6.3.3 Incubation experiments

Some important parameters, the maximum oxidation rate, V_{max} and the fractionation factors for oxidation (α_{oxC} and α_{oxD}) are not measured in the field and had to be measured in an incubation experiment.

Samples from two different cover layers, soil and compost, were taken at the Leon county landfill (Tallahassee) at the same location where the data that was used for the model calibration came from. Mixed samples were taken at a depth of 20 cm, where the methanotrophic activity is expected to be the highest. Bottles (1l) were filled with the soil and CH_4 was added (12%). An amount of 70 g soil or 20 g compost was chosen because larger quantities would hinder the gas transport in the soil. Four setups were available, which makes two soils and two replicates. Samples were taken every morning and evening during 3 days to measure the CH_4 concentration and isotopic signature. With the Rayleigh equation (Eq. 3.12) the fractionation factors for oxidation can be calculated from the relation between CH_4 concentration and $\delta^{13}C$.

The maximum oxidation rate V_{max} (nmol kg soil DW^{-1} s^{-1}) is calculated by fitting the oxidation rate to a Michaelis-Menten equation (Eq 2.15):

$$R = V_{max} \frac{[CH_4]}{Km + [CH_4]}$$

6.2

with
R: oxidation rate (nmol kg soil DW^{-1} s^{-1})
Km: a constant
$[CH_4]$: CH_4 concentration

The setup (Fig. 6.2) developed by Dave Powelson (FSU, Tallahassee) enables to correct for the pressure decrease during the experiments. In biological CH_4 oxidation, one molecule CO_2 is produced and 2 molecules disappear: CH_4 and O_2 (Section 2.1). When the experiment is started from high concentrations of CH_4 and the oxidation rate was large this could cause a significant pressure decrease and a lack of oxygen. The samples of 20 ml out of a volume of 1000 ml also created a pressure decrease. The balloon (B in Fig. 6.2) worked as a pressure indicator. During the experiment the pressure was kept constant by adding pure oxygen. The use of pure oxygen instead of air also helped to prevent a lack of oxygen.

The setup described above is different from the setup described in Section 3.4.1.1 because there the applied CH_4 concentration was low (1-2%) and the sample volume needed for the gas chromatograph was small (100 µl). Under these conditions the pressure decrease is limited and the above mentioned measures are not needed.

For this research higher concentrations were needed to measure the D isotope concentrations and the sample volumes were larger so the setup by Dave Powelson was a better choice.
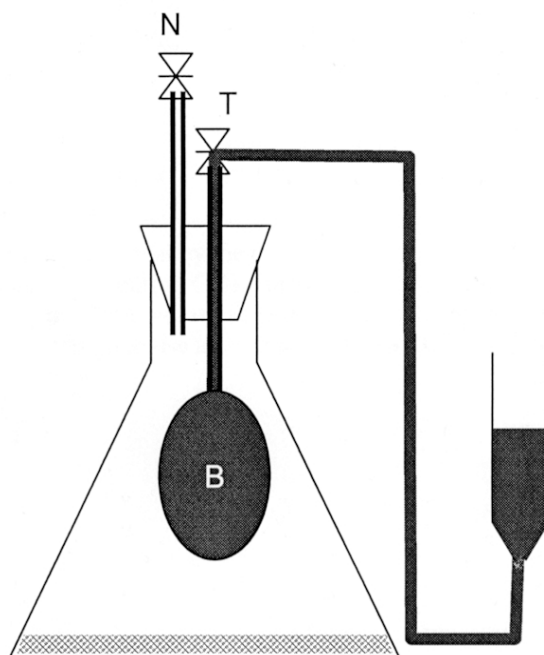
Fig. 6.2 Setup used for the incubation experiments (Powelson, oral communication)

6.4 Results and discussion

6.4.1 Incubation experiments

Table 6.1 presents the parameters obtained from the incubation experiments. The fractionation factor for carbon, α_{oxC}, is within the range of 1.01-1.03 found in literature (Snover and Quay, 2000). For the fractionation factor for D, $\alpha_{ox,D}$, few references for landfill cover soils are available, but the value of ten times the fractionation factor for C had been obtained before (Snover and Quay, 2000). The V_{max} for soil is lower than the values found for compost but both values are high, as also found in experiments with soils from enriched environments for example in Table 4.1 and from De Visscher et al., 1999.

Table 6.1 Parameters estimated from incubation experiments

	soil	compost
α_{oxC}	1.0213	1.0238
α_{oxD}	1.209	1.252
V_{max} (nmol.kg soil DW^{-1}.s^{-1})	250	1250

6.4.2 Modelling of field conditions

6.4.2.1 Model simulation

The simulation showed that the data from the chambers was not reliable enough to have a good estimate of the incoming CH_4 flux at the place of the probes. The modelled concentration profiles strongly deviated from the measured profiles indicating that incorrect data was used for the gas transport modelling. Apart from the advective flow, diffusion can be problematic as well.

6.4.2.2 Model calibration

In Fig. 6.3 the simulated concentration profiles are shown together with the measured ones on field 2B (soil cover) for the dataset of 3 September 2004. There is a fair agreement between the modeled and the measured profiles considering the uncertainties of some parameters and the measurements. The probe on 70 cm is leaking as it is unlikely that there is nitrogen at this depth and not at 50 cm (also seen at other dates). The soil consists of 2 layers: 60 cm sandy loam and 30 cm clay soil which was the original temporary cover. As there was less information about the clay layer, like air filled porosity, this layer is not taken into account and the model assumes a uniform layer with the properties of the sandy loam soil.
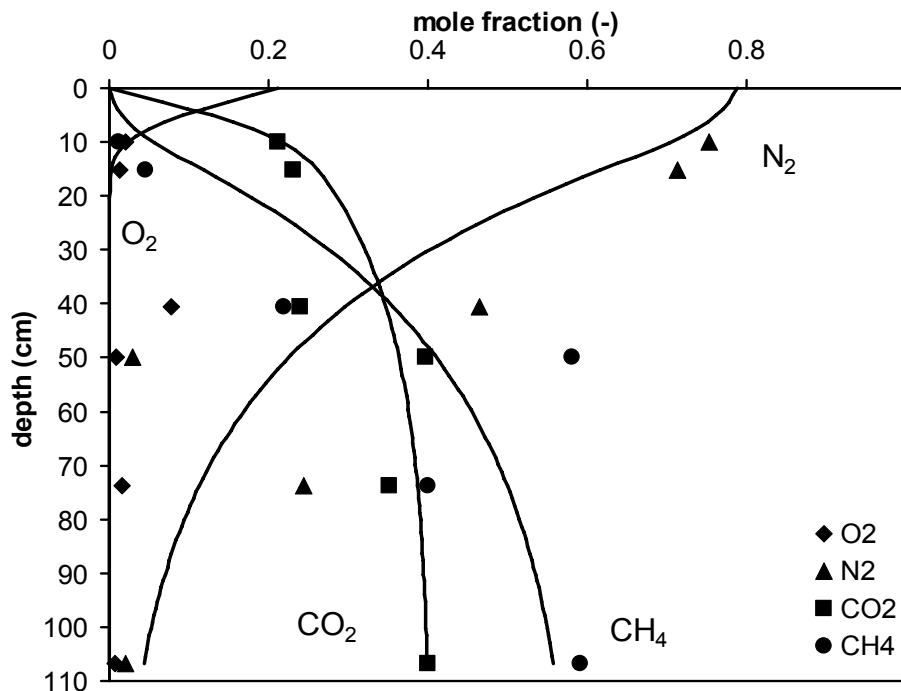

Fig. 6.3 Simulated and measured concentration profiles in the soil cover layer

In Fig. 6.4 the isotopic profile of the CH_4 is shown for carbon (Fig. 6.4a) and hydrogen (Fig. 6.4b). The isotopic content of the CH_4 flux coming into the cover soil (measurement) and the emitted CH_4 flux (simulated) is shown with arrows. For carbon isotopes, the measured isotope abundance of the emitted CH_4 is given as well. The isotopic signature of the CH_4 flux is not necessarily the same as the isotopic content of the CH_4 present in the soil. This is because of the fractionating effect of molecular diffusion in the gas phase. It is important for the calculation of CH_4 oxidation directly from isotopic contents with simple equations to use the CH_4 fluxes and not the concentrations. Although the $\delta^{13}C$-value of the emitted CH_4 gas and the emission flux (6.31×10^{-6} mol $m^{-2}s^{-1}$) were used as input data; the model was not capable of following the measured $\delta^{13}C$. The reason for this can be the extreme measurement of -35 ‰ at one of the 3 surrounding chambers where measurements are available; the other 2 measurements had a $\delta^{13}C$ around -48 ‰.

In the lower part of the soil there is no oxygen and the observed fractionation is caused by transport only. The fractionation factor for transport is the same for H and C but the scale of the graph for the D isotope abundance is ten times larger than the graph for C which makes the curves look different. Above 20 cm there is oxygen, so CH_4 oxidation is possible and this results in a large increase of the delta value for the D isotopes because the fractionation factor for oxidation is 10 times larger for H than for C.
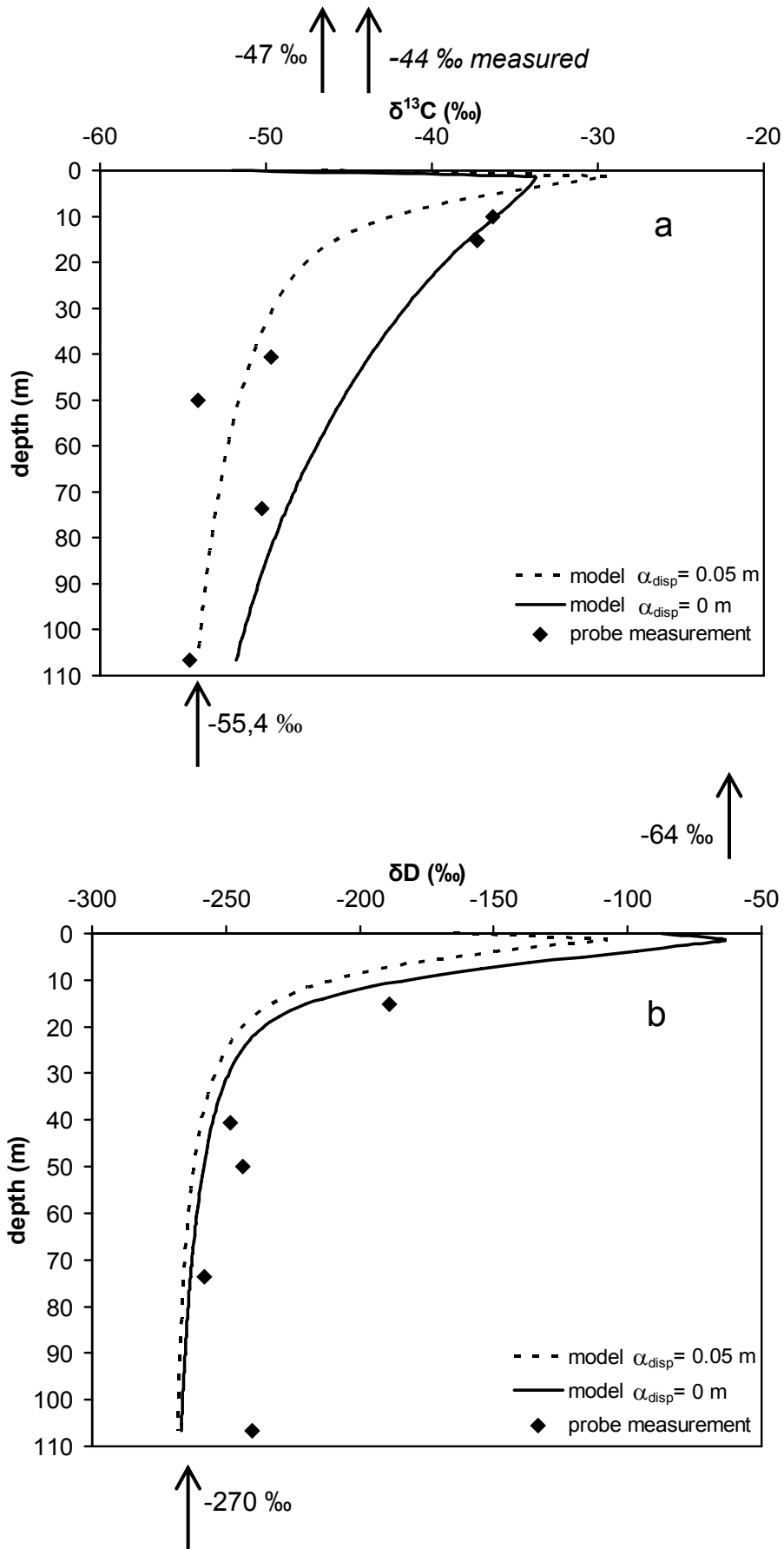
Fig. 6.4 Simulated and measured isotopic profiles in the soil cover layer for C (6.4a) and D (6.4b), arrows: isotopic signature of incoming and outgoing CH_4 flux.

In Chapter 4 a significant dispersion effect was found. A simulation adding the same dispersivity as found in this estimation is shown in fig 6.4 with dotted line. There is less fractionation in both istope profiles. For carbon this makes the deepest part of the observed profile better while the upper two sampling points are missed by the model and for D the already underestimation of the fractionation becomes worse.

A reason for these moderate results can be the strong influence of moisture variations on transport processes. Variations in moisture can be included in this model but were not used as there was no accurate data available.

The model was also applied on other datasets from other dates and from a test field covered with 60 cm of mulch (site 4). The results and problems were similar to the results on site 1 on 3 September 2004. Table 6.2 gives the most important parameters. Data from test fields with a compost cover were not used because there was no positive emission measured on nearly all dates and measuring points, which makes it difficult to calibrate the model.

The difference between the measured air filled porosity and the optimal one is small for the soil cover but this difference has a pronounced effect on the concentration profiles. For the deep mulch cover the air filled porosity could not be calculated, probably due to the kind of material.

While the material was more similar to compost than soil on site 4 the same V_{maxmax} as for the soil cover was used because with the compost value the model predicted almost complete oxidation although there was a significant emission flux measured . The reason for the high oxidation was the very high temperature in the mulch test field (Table 6.2).

Table 6.2 Fitted model parameters and outputs

	site 1 soil		site 4 deep mulch		
	3 sep 04	18 nov 04	19 jan 05	14 sep 05	10 aug 05
calculated δ^{13}C-value emitted CH_4 (‰)	-51.6	-52.1	-51.9	-51.3	-52.8
measured δ^{13}C-value emitted CH_4 (‰)	-44	-49.5	-44.3	-38.2	-51.1
calculated δD-value emitted CH_4 (‰)	-64.0	-107.5	-130.6	-100.4	-168.9
calculated total influx (mol.m^{-2}.s^{-1})	-8.8×10^{-5}	-3.4×10^{-5}	-1.3×10^{-4}	-1.3×10^{-4}	-6.6×10^{-5}
calculated emission flux (mol.m^{-2}.s^{-1})	-6.4×10^{-6}	-4.4×10^{-6}	-2.8×10^{-5}	-2.1×10^{-5}	-1.9×10^{-5}
measured emission flux (mol.m^{-2}.s^{-1})	-6.3×10^{-6}	-4.2×10^{-6}	-2.8×10^{-5}	-2.2×10^{-5}	-1.9×10^{-5}
AFP estimated	0.19	0.11	0.40	0.29	0.15
AFP measured	0.15	0.14	0.03	0	0
f_{ox} (%)	88%	79%	65%	73%	51%
T_{soil} (°C)	29	18.5	26	37.5	30.5

6.4.2.3 Comparison between traditional isotope technique and simulation model

In the traditional isotope method the oxidation percentage is calculated with a linear equation called the open system equation (Eq. 2.22). Alternatively the closed system equation used for incubations can also be used to calculate the CH_4 oxidation. In literature the open system equation is preferred because the soil cover layer is seen as an open system with an inflow and outflow of gas. The open system equation was derived for bacterial processes which take place in a completely mixed reactor (Monson and Hayes, 1980). However CH_4 oxidation takes place in a soil column where the CH_4 is gradually oxidized as it passes through the soil column. The application of the open system equation was never proven to be acceptable for such a soil column. For this reason there is some concern about the application of the open system equation to CH_4 oxidation in landfill cover soils. A method which is used at the Department of Oceanography from the Florida State University is to calculate the oxidation with the closed system equation together with the open system to provide a range in which the real oxidation percentage can be expected.

The oxidation percentage is calculated with both equations based on isotope signatures of the simulated CH_4 emission (Fig. 6.4). In Table 6.3 the results of both models are compared with the oxidation percentage given by the simulation model and the oxidation percentage calculated from the mean of the $\delta^{13}C$ emission measurements (Fig. 6.4). For carbon there is a large underestimation of the CH_4 oxidation by both the open and the closed system equation. The estimations of the CH_4 oxidation based on the D measurements comes very close to the simulated oxidation percent for both the open and the closed system equations. This shows that the equations that do not account for fractionation by diffusion give a better estimation when used on D measurements because the oxidation signal for D is larger. Note that the average of the results of the open system equation and the closed system equation applied to D, 87.5% is almost identical to the results of the simulation model. This indicates that a landfill cover soil is intermediate between an open system and a closed system. The oxidation percentage calculated from the chamber measurements is higher than would be expected from the simulated data for ^{13}C measurements; however as already indicated the extreme measurement of -35 ‰ has a large influence on the mean.

Table 6.3 Oxidation percentages calculated with different methods

Source of data		Simulated data	Measurements
Simulation model		88	
Isotopes	^{13}C	D	^{13}C
Closed system equation	17	76	44
Open system equation	17	99	53

6.5 Conclusions

The simulation model was able to fit the concentration profiles and isotopic profiles for a real landfill cover, although the measurements are not as accurate as in a column experiment and the CH_4 influx was unknown.

The isotopic profile of the carbon isotopes is largely caused by diffusion. Because of the high fractionation factor for oxidation there is less diffusion "noise" in the D signal than in the C signal. Simulations indicate that the open system equation, which does not take into account diffusion fractionation, should give a better estimate for CH_4 oxidation when applied on δD measurements instead of δC.

Conclusions and perspectives

Quantification of CH_4 oxidation in landfill cover soils is not an easy task because emissions are not homogeneous and any disturbance of the cover layer changes the emission. Isotope measurements allow making an estimate of the CH_4 oxidation efficiency without disturbing the soil. However, current isotope methods contain simplifications that may result in large uncertainties.

Modelling isotope specific processes in the cover layer allows to better understand which processes have an influence on isotope signatures in landfill gas. This can ultimately lead to a better quantification of CH_4 oxidation.

Biological fractionation factor

The isotope measurement method is based on the preference of bacteria for lighter isotopes, the biological fractionation factor, being measured in the laboratory. A good estimate of this parameter is important because small errors in the determination of this fractionation factor can lead to a significant error in the quantification of the CH_4 oxidation.

In this study the original model of Rayleigh for determination of the fractionation factor α_{ox} of CH_4 oxidation was compared with the two most common approximations, the simplified Rayleigh approach and the Coleman method.

The differences caused by using the simplified Rayleigh approach are small (< 0.05% for C, < 0.006% for H). So, this approach can be considered valid when the experiment is performed with unlabelled CH_4. However, further simplifications made by Coleman et al. (1981) lead to large errors, especially for H fractionation (up to 5% for C, up to 20% for H).

The advantage of the equation of Coleman et al. (1981) and the simplified Rayleigh approach is that α_{ox} can be estimated by simple linear regression. However, nowadays it is perfectly feasible to use non-linear parameter estimation. This makes these approximations unneeded in all systems where the same model of Rayleigh is used.

In the case of labelled systems, this is especially important when the fractionation is strong. For example Morasch et al. (2001) estimated the fractionation factor for D on labeled substrate with the simplified rayleigh approach, fortunately this was corrected by Hunkeler (2002).

In contrast, the simplified Rayleigh approach is always valid when fractionation is weak.

Simulation model

A simulation model for the calculation of mass transfer and CH_4 oxidation in landfill cover soils was developed. This model distinguishes between $^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$, and incorporates isotope fractionation by diffusion and CH_4 oxidation. After calibration of the model and introduction of a non-fractionating process, mechanical dispersion, there was an excellent agreement with the measured concentrations and ^{13}C abundances in a laboratory setup.

Simulations with and without fractionation by transport show that fractionation by diffusive and dispersive transport in this setup has a profound influence on the isotope profiles. Diffusion hides the oxidation and must therefore be accounted for in the calculation of CH_4 oxidation based on isotopes. The classical isotope method does not account for that.

Overall, 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.

Mechanical dispersion

The model calibration also revealed that mechanical dispersion can be important even if the gas velocities are low. Existing measurements of the dispersion parameter, α, in the gas phase are scarce and require a number of experiments at different gas velocities.

In this study a method for the determination of the dispersion coefficient based on isotopes was developed. Experiments with a glass beads-filled column showed that it is possible to measure both molecular diffusivity and mechanical dispersivity from a single steady-state experiment using isotopes. It was shown that Fick's law with constant diffusion coefficients is not adequate for analyzing the data and that the Stefan-Maxwell equations must be used. At interstitial gas velocities between 1.5×10^{-4} m s^{-1} and 10^{-3} m s^{-1} the dispersivity is constant at 0.001 m, but increases rapidly at decreasing gas velocities below 1.5×10^{-4} m s^{-1}, and can be as high as 0.07 to 0.08 m. An estimation of the dispersivity in the calibration of the CH_4 oxidation and transport model for a low gas velocity gave a result in the same range and thus confirms the results of the separate dispersion experiment.

Field application

The simulation model was also tested in a more realistic field application. The simulation model was able to fit the concentration profiles and isotopic profiles for a real landfill cover,

although the measurements are not as accurate as in a column experiment and the CH_4 influx was unknown.

The isotopic profile of the carbon isotopes was largely caused by diffusion. Because of its high fractionation factor for oxidation there was less diffusion "noise" in the D signal. Simulations indicate that the open system equation, which does not take into account diffusion fractionation, should give a better estimate for CH_4 oxidation when applied on δD measurements instead of $\delta^{13}C$.

Perspectives

In both the laboratory setup (Chapter 4) and the field experiment (Chapter 6) existing datasets were used. Although experimental design is very important there was no choice in this study. For example model simulations indicated that under the tested conditions most of the processes are occurring in the top of the soil column and extra measurements near the soil surface will probably give more information.

Unfortunately in this study low concentration emission samples could not be measured on D isotopic content. D isotope measurements of CH_4 emission samples can make it clear whether CH_4 transport fractionation is the only cause of the underestimation of the current isotope method. It is also possible that chamber measurements are not representative for the conditions in the soil column observed during the modelling as they are always a mixture of emissions across a certain surface.

The dispersion measurements in this study were done with glass beads and in a laboratory setup. Field measurements are necessary to check whether the observed trend to higher dispersion at low gas velocities also exist in landfill covers. If this is the case then mechanical dispersion should be taken into account in landfill gas modelling even if the gas velocities are low. Isotopes of CH_4 and CO_2 are not suitable for this assessment because oxidation processes are influencing the isotope signal. N_2 isotopes could be a solution if no disturbance occurs by biological processes like denitrification.

A simple correction for CH_4 transport fractionation is not available; however, combined measurements of ^{13}C and D isotopes can possibly be enough to estimate CH_4 oxidation. Indeed, the difference between C and H isotopes should be a direct measure for oxidation, as both isotopes have the same fractionation by diffusion.

While the current isotope method has shortcomings, it can still be used as a rough estimate, knowing that it provides an underestimation of the oxidation percentage. If possible, D isotopes should be used and in this case the fractionation factor should be calculated with the Rayleigh model and not with the approximation by Coleman et al. (1981).

References

Aggarwal P.K. and Dillon M.A., 1998. Stable isotope composition of molecular oxygen in soil gas and groundwater: A potentially robust tracer for diffusion and oxygen consumption processes. Geochimica et Cosmochimica Acta 62, 577-584.

Ambus P., Andersen B.L., Kemner M., Sørensen B. and Wille J., 2002. Natural carbon isotopes used to study methane consumption and production in soil. Isotopes in Environmental and Health Studies 38, 149-157.

Angert A., Luz B. and Yakir D., 2001. Fractionation of oxygen isotopes by respiration and diffusion in soils and its implications for the isotopic composition of atmospheric O_2. Global Biogeochemical Cycles. 15, 871-880.

Barker J.F. and Fritz P., 1981. Carbon isotope fractionation during microbial methane oxidation. Nature 293, 289-291.

Barlaz M.A., Green R., Chanton J.P., Goldsmith C.D. and Hater G.R., 2004. Evaluation of a biologically active cover for mitigation of landfill gas emissions. Environmental Science and Technology 38, 4891-4899.

Bender M. and Conrad R., 1992. Kinetics of CH_4 oxidation in oxic soils exposed to ambient air or high CH_4 mixing ratios. FEMS Microbiology Ecology 101, 261-270.

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

Blair N., Leu A., Munoz E., Olson J., Kwong E. and Des Marais D., 1985. Carbon isotopic fractionation in heterotrophic microbial metabolism. Applied and Environmental Microbiology 50, 996-1001.

Bodelier P.L.E. and Laanbroek H.J., 2004. Nitrogen as a regulatory factor of methane oxidation in soils and sediments. FEMS Microbiology Ecology 47, 265-277.

Boeckx P. and Van Cleemput O., 1996. Methane oxidation in a neutral landfill cover soil: Influence of moisture content, temperature, and nitrogen-turnover. Journal of Environmental Quality 25, 178-183.

Boeckx P., Van Cleemput O. and Villaralvo I., 1996. Methane emission from a landfill and the methane oxidising capacity of its covering soil. Soil Biology and Biochemistry 28, 1397-1405.

Bogner J.E., Spokas K.A. and 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.

Börjesson G., 1997. Methane Oxidation in Landfill Cover Soils. Ph.D. Thesis, Swedish University of Agricultural Sciences, Uppsala, 37p.

Börjesson G., Sundh I. and Svensson B., 2004. Microbial oxidation of CH_4 at different temperatures in landfill cover soils. FEMS Microbiology Ecology 48, 305-312.

Börjesson G., Sundh I., Tunlid A. and Sven B.H., 1998. Methane oxidation in landfill cover soils, as revealed by potential oxidation measurements and phospholipid fatty acid analyses. Soil Biology and Biochemistry 30, 1423-1433.

Bowman J.P., Sly L.I., Nichols P.D. and Haywerd A.C., 1993. Revised taxonomy of the methanotrophs: Description of Methylobacter gen. nov., emendation of Methylococcus, validation of Methylosinus and Methylocystis species, and a proposal that the family Methylococcaceae includes only the group I methanotrophs. International Journal of Systematic Bacteriology 43, 735-753.

Campbell G.S., 1974. A simple method for determining unsaturated conductivity from moisture retention data. Soil Science 117, 311-314.

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

Christophersen M., Holst H., Kjeldsen P. and Chanton J., 2001. Lateral gas transport in a soil adjacent to an old landfill: Factors governing emission and methane oxidation. Waste Management and Research 19, 126-143.

Coleman D.D., Risatti J.B. and Schoell M., 1981. Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria. Geochimica et Cosmochimica Acta 45, 1033-1037.

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

Crank J., 1967. The mathematics of diffusion. Oxford University Press.

Crank J., McFarlane N.R., Newby J.C., Paterson G.D. and Pedley J.B., 1981. Diffusion processes in environmental systems. Macmillan Ltd., London.

Currie J.A., 1960. Gaseous diffusion in porous media. Part 2. – Dry granular materials. Britisch Journal of Applied Physics 11, 318-324.

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

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

De Visscher A., Boeckx P and Van Cleemput O., 2007. Artificial methane sinks. In: Reay D.S., Hewitt N., Grace J. & Smith K.A. Greenhouse Gas Sinks. CABI Publishing, New York, p. 184-200.

De Visscher A., De Pourcq I. and Chanton J., 2004. Isotope fractionation effects by diffusion and methane oxidation in landfill cover soils. Journal of Geophysical Research 109, D18111, doi:10.129/2004JD004857.

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

Dlugokencky E.J., Houweling S., Bruhwiler L., Masarie K.A., Lang P.M., Miller J.B. and Tans P.P., 2003. Atmospheric methane levels off: Temporary pause or a new steady-state? Geophysical Research Letters, 30(19), doi:10.1029/2003GL018126.

Dochain D. and Vanrolleghem P.A., 2001. Dynamical modeling and estimation in wastewater treatment processes. IWA publishing, London, 360p.

EEA, 2006. Greenhouse gas emission trends and projections in Europe 2006. European Environment Agency, Copenhagen.

Egboka B.C.E., Cherry J.A., Farvolden R.N. and Frind E.O., 1983. Migration of contaminants in groundwater at a landfill: A case study. Journal of Hydrology 63, 51-80.

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

Engesgaard P, Jensen K.H., Molson J., Frind E.O. and Olsen H., 1996. Large-scale dispersion in a sandy aquifer: Simulation of subsurface transport of environmental tritium. Water Resources Research 32, 3253-3266.

Etheridge D.M., Pearman G.I. and Fraser P.J., 1992. Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core. Tellus 44B, 282-294.

Froment G.F. and Bischoff K.B., 1990. Chemical Reactor Analysis and Design. J. Wiley & Sons, New York, 664p.

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

Gebert J., Groengroeft A. and Miehlich G., 2003. Kinetics of microbial methane oxidation in biofilters. Waste Management 23, 609-619.

Gebert J., Groengroeft A., Schloter M. and Gattinger A., 2004. Community structure in a methanotroph biofilter as revealed by phospholipid fatty acid analysis. FEMS Microbiology Letters 240, 61-68.

Gelhar L.W., Welty C. and Rehfeldt K.R., 1992. A critical review of data on field-scale dispersion in aquifers. Water Resources Research 28, 1955-1974.

Graham D.W., Chaudhary J.A., Hanson R.S. and Arnold R.G., 1993. Factors affecting competition between type I and type II methanotrophs in two-organism, continuous-flow reactors. Microbial Ecology 25, 1-17.

Granli T. and Bockman O.C., 1994. Nitrous oxide from agriculture. Norwegian Journal of Agriculture Science 12, 7-128.

Hanson R.S. and Hanson T.E., 1996. Methanotrophic bacteria. Microbiological Reviews 60, 439-471.

Happell J.D., Chanton J.P., Whiting G.J. and Showers W.J., 1993. Stable isotopes as tracers of methane dynamics in everglades marshes with and without active populations of methane oxidizing bacteria. Journal of Geophysical Research 98D, 14771-14782.

Hassanzadeh H., Pooladi-Darvish M. and Keith D.W., 2005. Modelling of convective mixing in CO_2 storage. Journal of Canadian Petroleum Technology 44 (10), 43-51.

Hendry M.J., Wassenaar L.I. and Birkham T.K., 2002. Microbial respiration and diffusive transport of O_2, $^{16}O_2$, and $^{18}O^{16}O$ in unsaturated soils: A mesocosm experiment. Geochimica et Cosmochimica Acta 66, 3367-3374.

Higgins I.J., Best D.J. and Hammond R.C., 1980. New findings in methane-utilizing bacteria highlight their importance in the biosphere and their commercial potential. Nature 286, 561-564.

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

Hunkeler D., 2002. Quantification of isotope fractionation in experiments with deuterium-labeled substrate. Applied Environmental Microbiology 68, 5205-5207.

Hutchinson G.L. and Mosier A.R., 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Science Society of America Journal 45, 311-316.

IPCC, 1996. Climate change 1995. The science of climate change; Cambridge University Press, 572p.

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 and New York 881p.

Jaynes D.B. and Rogowski A.S., 1983. Applicability of Fick's law to gas diffusion. Soil Science Society of America Journal 47, 425-430.

Jin Y. and Jury W.A., 1996. Characterizing the dependence of gas diffusion coefficient on soil properties. Soil Science Society of America Journal 60, 66-71.

Katto Y. and Masuoka T., 1967. Criterion for the onset of convective flow in a fluid in a porous medium. International Journal of Heat and Mass Transfer 10, 297-309.

Kaviany M., 1984. Onset of thermal convection in a saturated porous medium: Experiment and analysis. International Journal of Heat and Mass Transfer 27, 2101-2110.

Kightley D., Nedwell D.B. and Cooper M., 1995. Capacity for Methane Oxidation in Landfill Cover Soils Measured in Laboratory-Scale Soil Microcosms. Applied and Environmental Microbiology 61, 592-601.

King S.L., Quay P.D. and Lansdown J.M., 1989. The ^{13}C/^{12}C kinetic isotope effect for soil oxidation of methane at ambient atmospheric concentrations. Journal of Geophysical Research 94, 18273-18277.

Kjeldsen P., Dalager A. and Broholm K., 1997. Attenuation of methane and nonmethane organic compounds in landfill gas affected soils. Journal of the Air and Waste Management Association 47, 1268-1275.

Krüger M., Frenzel P. and Conrad R., 2001. Microbial processes influencing methane emission from rice fields. Global Change Biology 7, 49-64.

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

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

Mandernack K.W., Kinney C.A., Coleman D., Huang Y.S., Freeman K.H. and Bogner J., 2000. The biogeochemical controls of N_2O production and emission in landfill cover soils: The role of methanotrophs in the nitrogen cycle. Environmental Microbiology 2, 298-309.

Mariotti J.C., Germon J.C., Hubert P., Kaiser P., Letolle R., Tardieux A. and Tardieux P., 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. Plant and Soil 62, 413-430.

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

Marshall T.J., 1959. The diffusion of gases through porous media. Journal of Soil Science 10, 79-82.

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

Mendoza C.A. and Frind E.O., 1990a. Advective-dispersive transport of dense organic vapors in the unsaturated zone. 1. Model development. Water Resources Research 26, 379-387.

Mendoza C.A. and Frind E.O., 1990b. Advective-dispersive transport of dense organic vapors in the unsaturated zone. 2. Sensitivity analysis. Water Resources Research 26, 388-398.

Miller L.G., Kalin R.M., McCauley S.E., Hamilton J.T.G., Harper D.B., Millet D.B., Oremland R.S. and Goldstein A.H., 2001. Large carbon isotope fractionation associated with oxidation of methyl halides by methylotrophic bacteria. Proceedings of the National Academy of Science of the USA 98, 5833-5837.

Millington R.J., 1959. Gas diffusion in porous media. Science 130, 100-102.

Millington R.J. and Quirk J.M., 1960. Transport in porous media. In: Van Beren F.A. et al. (ed.) Transactions of the International Congress on Soil Science, Madison, WI, 14-24 August 1960, Vol. 1 pp. 97-106. Elsevier, Amsterdam.

Millington R.J. and Quirk J.M., 1961. Permeability of porous solids. Transactions of the Faraday Society 57, 1200-1217.

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

Moldrup P., Olesen T., Schjonning P., Yamaguchi T. and Rolston D.E., 2000b. Predicting the gas diffusion in undisturbed soil from soil water characteristics. Soil Science Society of America Journal 64, 94–100.

Monod J., 1958. Recherches sur la croissance des cultures bactériennes. Ph. D Thesis 1942. 2nd edition. Hermann, Paris, France, 210p.

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

Morasch B., Richnow H. H., Schink B. and Meckenstock R. U., 2001. Stable Hydrogen and Carbon Isotope Fractionation during Microbial Toluene Degradation: Mechanistic and Environmental Aspects. Applied and Environmental Microbiology 67, 4842-4849.

Nozhevnikova A., Glagolev M., Nekrasova V., Einola J., Sormunen K. and Rintala J., 2003. The analysis of methods for measurement of methane oxidation in landfills. Water Science and Technology 48(4), 45-52.

Nozhevnikova A., Nekrasova V., Lebedev V.S. and Lifshits A.B., 1993. Microbiological processes in landfills. Water Science and Technology 27(2), 243-252.

Oonk J. and Boom A., 1995. Landfill Gas Formation, Recovery and Emissions. TNO rapport R95-203, Apeldoorn, The Netherlands.

Panikov N.S., 1995. Microbial growth kinetics. Chapman & Hall, London, 328p.

Park S.Y., Brown K.W. and Thomas J.C., 2004. The use of biofilters to reduce atmospheric methane emissions from landfills: Part I. Biofilter design. Water Air and Soil Pollution 155, 63–85.

Penman H.L., 1940. Gas and vapour movements in the soil. I. The diffusion of vapours through porous solids. Journal of Agricultural Science 30, 437-462.

Perera L.A.K., Achari G.J. and Hettiaratchi P.A., 2002a. Determination of Source Strength of Landfill Gas: A Numerical Modeling Approach. Journal of Environmental Engineering 128, 461-471.

Perera M.D.N., Hettiaratchi J.P.A.and Achari G., 2002b. A mathematical modeling approach to improve the point estimation of landfill gas surface emissions using the flux chamber technique. Journal of Environmental Engineering and Science. 1, 451-463.

Popovicova J. and 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.

Poulsen T.G., Christophersen M., Moldrup P. and Kjeldsen P., 2001. Modeling lateral gas transport in soil adjacent to old landfill. Journal of Environmental Engineering 127, 145-153.

Powelson D., Chanton J., Abichou T. and Morales J., 2006. Methane Oxidation in Compost and Water Spreading Biofilters. Waste Management & Research, in press.

Powelson, D. oral communication. Florida, Tallahassee.

Rayleigh J.W.S., 1896. Theoretical considerations respecting the separation of gases by diffusion and similar processes. Philosophical Magazine 42, 493-498.

Reddi L.N. and Inyang H.I., 2000. Geoenvironmental engineering: principles and applications, Dekker, New York, 494 p.

Roslev P. and King G.M., 1994. Survival and recovery of methanotrophic bacteria starved under oxic and anoxic conditions. Applied Environmental Microbiology 60, 2602-2608.

Ruiz J., Bilbao R. and 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.

Sahimi M., 1993. Flow phenomena in rocks: From continuum models to fractals, percolation, cellular automata, and simulated annealing. Reviews of Modern Physics 65, 1393-1534.

Scanlon B.R., Nicot J.P. and Massmann J.W., 2002. Soil Gas Movement in Unsaturated Systems. In: Warrick, A.W. (Eds.), Soil Physics Companion, CRC press, Boca Raton, USA, 297-341.

Scharff H., Martha A., van Rijn D.M.M., Hensen A., van den Bulk W.C.M., Flechard C., Oonk J., Vroon R., De Visscher A. and Boeckx P., 2003. A Comparison of Measurement Methods to Determine Landfill Methane Emissions. Novem, Utrecht, The Netherlands.

Scott K.M., Lu X., Cavanaugh C.M. and Liu J.S., 2004. Optimal methods for estimating kinetic isotope effects from different forms of the Rayleigh distillation equation. Geochimica et Cosmochimica Acta 68, 443-442, doi:10.1016/S0016-7037(03)00459-9.

Sharpe P.J.H. and DeMichele D.W., 1977. Reaction kinetics in poikilotherm development. Journal of Theoretical Biology 64, 649-670.

Snover A.K. and P.D. Quay, 2000. Hydrogen and carbon kinetic isotope effects during soil uptake of atmospheric methane. Global Biogeochemical Cycles 14, 25-39.

Stein V.B., Hettiaratchi J.P.A. and 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. and Saint-Fort R., 2004. Methane oxidation and EPS formation in compost: Effect of oxygen concentration. Environmental Pollution 129, 305-314.

Wise M.G., McArthur J.V. and Shimkets L.J., 1999. Methanotrophic diversity in landfill soil: Isolation of novel type I and type II methanotrophs whose presence was suggested by

culture-independent 16S ribosomal DNA analysis. Applied and Environmental Microbiology 65, 4887-4897.

Wuebbles D., Hayhoe K., 2002. Atmospheric methane and global change. Earth-Science Reviews 57, 177–210.

Curriculum Vitae

Personalia

Naam: Koenraad Mahieu

Adres: Halfuurdreef 35

8210 Veldegem

Tel. 050/279654

    0498/626206

E-mail Koenraad.Mahieu@lid.kviv.be

Burgerlijke staat: Ongehuwd

Nationaliteit: Belg

Geboren te Torhout op 10/9/1979

Opleiding

Lagere school te Veldegem

Humaniora St. Lodewijkscollege Brugge (wiskunde-wetenschappen)

Universitaire studie Universiteit Gent

    Bio-ingenieur in de Milieutechnologie

    Geslaagd met onderscheiding

    Eindwerk: modelbouw van actief slib flocculatie d.m.v. een populatiebalansmodel

        Promotor: Prof. Dr. ir. P.A. Vanrolleghem

        Begeleider: ir. I. Nopens

Milieucoördinator type A (Syntra West, Kortrijk)

Talenkennis

Nederlands: moedertaal

Frans: goed

Engels: goed

Duits: schriftelijk

Professionele activiteiten

2006 - 2003 Doctoraatstudent op BOF project:

    Modelgebaseerde interpretatie van isotopenratio's: Theoretische ontwikkeling en

    toepassing op methaanoxidatie in stortafdekgronden

Artikels in internationale tijdschrijften met peer review

Mahieu K., De Visscher A., Vanrolleghem P.A. and 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. and Van Cleemput O. Gas dispersion in porous media: new measurement technique using stable isotopes. (Submitted).

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O. Modelling of stable isotope fractionation by methane oxidation and diffusion in landfill cover soils (submitted).

Nopens I., Koegst T., Mahieu K. and Vanrolleghem P.A. 2005. PBM and activated sludge flocculation: from experimental data to calibrated model. AIChe Journal 51, 1548-1557.

Artikels in andere tijdschrijften

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O. 2003. Isotope fractionation by microbial methane oxidation: improved determination. Communications in agricultural and applied biological sciences 68(3), 193-196.

Congres proceedings

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O. Isotope Fractionation by Microbial Methane Oxidation: Improved Determination. Proceedings 3rd International Landfill Research Symposium, 2004, Sapporo, Japan, p. 79-81.

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O. Modelling of stable isotope fractionation by methane oxidation and diffusion in landfill cover soils. Proceedings 6th Benelux IRMS user Group meeting, 2005 Gent, p. 37-38.

Mahieu K., De Visscher A., Vanrolleghem P.A. and Van Cleemput O. Improved quantification of methane oxidation in landfill cover soils by numerical modeling of stable isotope fractionation. Proceedings Sardinia 2005, Tenth International Waste Management and Landfill Symposium, 2005, Sardinia.

Woelders H., Oonk H., Hensen A., Mahieu K., De Visscher A., Van Velthoven F. and Overzet D. Enhancing methane oxidation in landfill top-layers result of field trials. Proceedings Sardinia 2005, Tenth International Waste Management and Landfill Symposium, 2005, Sardinia.

Reports

Oonk H., Hensen A., Mahieu K., De Visscher A., Van Velthoven F. and Woelders H., 2004. Verbeterde methaanoxidatie in toplagen van stortplaatsen. TNO-rapport R2004/377, TNO, Apeldoorn.

Varia

Posterprijs op 3rd International Landfill Research Symposium, 2004, Sapporo, Japan

Studieverblijf Januari-maart 2006 aan het Department of Oceanography Florida State University (Tallahassee).