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

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Introduction

- Methane contributes to the greenhouse effect.
- Landfills are an important source of methane.
- But in the cover layer a part of the methane is oxidized to CO_2.
- Difficult to quantify methane oxidation.
- Isotope fractionation is a promising method.

Background

-Methane oxidation:

$$CH_4 + (1+x)O_2 \Rightarrow xCO_2 + {}_2H_2O + (1+x)C_{org}$$

- Bacteria oxidize the ^{12}C-isotope slightly faster than the ^{13}C-isotope.
- The fractionation factor, α, is calculated from batch experiments.
- Isotope ratios are measured at the waste and at the top of the landfill.

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

Background

- Methane transport
  - advection: no fractionation
  - diffusion: fractionation
  - dispersion: no fractionation

=> Mathematical models needed to predict isotopic profiles.

Simulation model for gas diffusion and methane oxidation (De Visscher and Van Cleemput, 2003)

- Layer model for (CH_4,O_2,N_2,CO_2)
- Mass balance

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

- Diffusion by Stefan Maxwell equation

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

- Michaelis-Menten kinetics for methane oxidation

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

Extensions of Simulation model for isotope fractionation

- Binary diffusion coefficients for isotopes (Marrero and Mason, 1972):

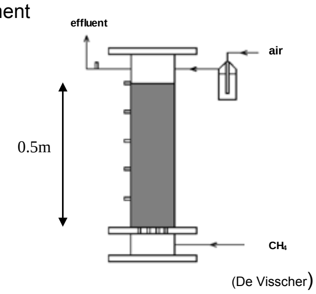
$$D_{ij} \propto \frac{1}{\sqrt{\frac{M_i . M_j}{M_i + M_j}}} \qquad \Rightarrow \frac{D_{^{12}CH_4,N_2}}{D_{^{13}CH_4,N_2}} = 1.0193$$

- Oxidation

$$r_{^{13}CH_4} = \frac{r_{CH_4} . y_{^{13}CH_4}}{\alpha_C y_{CH_4}} \qquad r_{^{12}CH_4} = r_{CH_4} - r_{^{13}CH_4}$$

Experimental setup

Column experiment



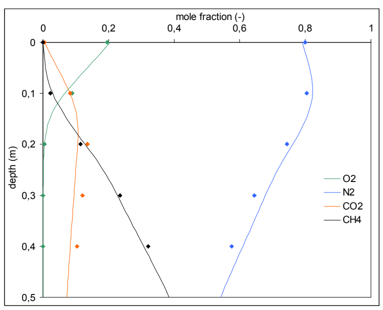
(De Visscher)

Used experimental data (Depourcq)

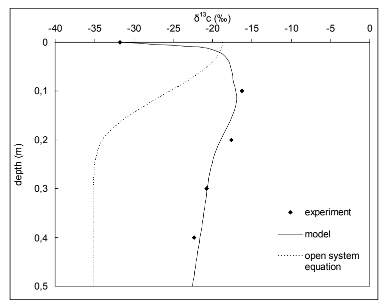
- Column experiment: concentration and isotopic profiles
- Fractionation factor: 1.0183

  estimated from batch experiment
- Vmax profile measured in batch experiments
- Moisture profile measured after breakup of column: water production by methane oxidation

Results: Concentration Profiles



Results: Isotopic Profiles



Results: Parameters

$$D_{soil,ij} = \frac{\varepsilon^{1+b}}{\phi} D_{gas,ij} + \alpha_{disp}.u$$

α_{disp} = 0.052204 m

b = 1.097779

$$V\max,\max = 2.67.10^{-6} \frac{mol\ CH_4}{kg_{soil} DW.s}$$

stoichiometry: $x = 0.75 \frac{mol\ CO_2}{mol\ CH_4}$

Conclusions and future research

- Concentration profiles and isotopic profiles can be described with the used model
- Deuterium measurements can give more information because the isotope fractionation is larger.
- This model can help for a better quantification of methane oxidation.