

Isotope fractionation by microbial methane oxidation: improved determination



Koenraad Mahieu¹, Alex De Visscher¹, Peter A. Vanrolleghem² and Oswald Van Cleemput¹

¹Laboratory of Applied Physical Chemistry (ISOFYS)

²BIOMATH, Department of Applied Mathematics, Biometrics and Process Control
Ghent University, Coupure links 653, B-9000 Ghent

Introduction

Methane oxidation can reduce methane emissions from landfills.

Bacteria oxidize the ¹²C-isotope slightly faster than the ¹³C-isotope. The result is an increase of the ¹³C/¹²C ratio, R, from the remaining methane.

This fractionation between ¹²C-CH₄ and ¹³C-CH₄, can be used to measure methane oxidation if the fractionation factor, α, is known.

α is calculated from batch experiments with a simplified model.

Objective

Investigating the impact of the simplifications in the model on the estimation of α.

Methods

➤ The isotope ratios, R, are measured as delta values:

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

With R_{st} the isotope ratio of a standard

➤ Mathematical model

$$\frac{d^{13}C}{d^{12}C} = \frac{^{13}C}{^{12}C} \quad \text{Rayleigh (1896)}$$

$$\ln \left(\frac{CH_4}{CH_{4,0}} \right) = \frac{\alpha}{1-\alpha} \ln \left(\frac{1000 + \delta^{13}C}{1000 + \delta^{13}C_0} \right) + \ln \left(\frac{1 + \frac{\delta^{13}C \cdot R_{st} + R_{st}}{1000}}{1 + \frac{\delta^{13}C_0 \cdot R_{st} + R_{st}}{1000}} \right)$$

$$\delta^{13}C \approx \delta^{13}C_0 \quad \text{or} \quad ^{12}C \approx CH_4$$

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

$$\ln \left(\frac{CH_4}{CH_{4,0}} \right) = \frac{\alpha}{1-\alpha} \cdot \frac{\delta^{13}C - \delta^{13}C_0}{1000} \quad \text{Coleman (1981)}$$

⇒ α estimated by linear regression

The approximations of Coleman (1981) suppose a small |δ|-value and δ¹³C-interval in the batch experiment

➤ Estimate of difference between models:

Simulations with exact model and reestimation of α with approximated models

Results

➤ C fractionation

Approximation ¹²C=CH₄

Errors remain small (<0,5%) for all values of α and initial δ¹³C₀

Coleman (1981)

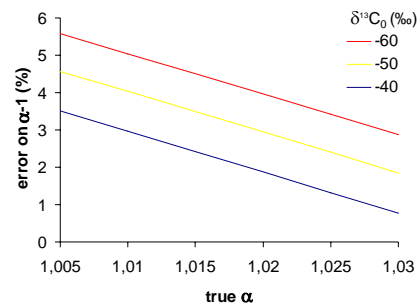


Fig 1. Differences on α-1 (%)

Errors several percentages on α-1 and increasing for lower δ¹³C₀ and lower α (Fig 1.)

➤ H fractionation

$$\alpha_H \gg \alpha_C \quad \text{and} \quad |\delta D_0| \gg |\delta^{13}C_0|$$

⇒ Errors up to 10% for approximation Coleman

Conclusions

- Error on the estimated α with the approximation ¹²C=CH₄ is small
- Further simplifications (Coleman) give larger errors ⇒ unacceptable for H-fractionation
- Nonlinear parameter estimation possible ⇒ the simplifications in Coleman's model are no longer necessary
- The method of Coleman can be helpful to get an initial guess of α for the nonlinear parameter estimation.

References

Coleman, D. D., Risatti, J.B. & Schoell, M. (1981). *Geochimica et Cosmochimica Acta*, 45, 1033-1037.

Rayleigh, J. W. S. (1896). *Philosophical Magazine*, s.5.42, 493-498.

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