

Research paper

Modelling methane formation in sediments of tropical lakes focusing on syntrophic acetate oxidation: Dynamic and static carbon isotope equations



Vasily Vavilin^{a,*}, Sergey Rytov^a, Ralf Conrad^b

^a Water Problems Institute, Russian Academy of Sciences, 3 Gubkina Str., Moscow 119333, Russian Federation

^b Max Planck Institute for Terrestrial Microbiology, Karl-von-Frisch-Strasse 10, 35043 Marburg, Germany

ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form 25 August 2017

Accepted 28 August 2017

Available online 13 September 2017

Keywords:

Cellulose methanization

Competition for acetate

Fraction of methane produced from H₂/CO₂

Kinetic isotope effect

Sediments of tropical lakes

Syntrophic acetate oxidation

ABSTRACT

A dynamic model including isotope variables has proved to be an effective tool for evaluating the relative importance of the processes that are taking place in parallel and compete for the same substrate. We present a mathematical description of cellulose conversion into methane and carbon dioxide in the anoxic sediments of three floodplain tropical lakes that were investigated before. Parallel processes of acetoclastic methanogenesis and syntrophic acetate oxidation competing for acetate and gaseous and dissolved H₂, CO₂, and CH₄ are considered in dynamic equations for total and ¹³C carbon in CH₄ and CO₂. During cellulose microbial transformation, in accordance with experimental data and modelling, a greater volume of CH₄ than CO₂ is produced due to the higher CO₂ solubility. Changes in the concentration of ¹³C contained in CH₄ and CO₂ allowed specifying the pathway of cellulose degradation. We have shown that neglect of syntrophic acetate oxidation results in unrealistically large fractionation factors for hydrogenotrophic methanogenesis, indicating that syntrophic acetate oxidation is of crucial importance in spite of its being fairly slow as compared to other processes. The model reveals that, in the absence of acetate oxidizers, the fraction of methane, f_C , produced from H₂/CO₂ equals 0.33, while in the presence of acetate oxidizers, it is significantly higher ($f_C \approx 0.59$ in Jatoba Lake and $f_C \approx 0.53$ in Mussura Lake). In contrast to Jatoba and Mussura Lakes, in sediments of Batata Lake with much smaller initial microbial populations increasing during incubation, the acetoclastic methanogenesis dominates initially with a f_C value of less than 0.1, but later the hydrogenotrophic methanogenesis becomes the dominant process, with a f_C value of about 0.73 at the end of incubation. The high value of $f_C = 0.641 \pm 0.133$ is confirmed for 14 Brazilian lakes investigated before. Modelling has shown that the difference between the isotope signatures in methane and carbon dioxide is an informative index to indicate the contribution of syntrophic acetate oxidation for methane production from sediments. The Δ value increases when acetate oxidation becomes significant. The dynamics of carbon isotope signatures in methane and carbon dioxide improve the static isotope equations. In contrast to specific assessments ensuing from the static isotopic equations, the dynamic model enables taking changes in the whole set of experimental data and analyzing the overall system behavior at various model parameters.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Methane (CH₄) is the second most important greenhouse gas. Its concentration has significantly increased as a result of human activity, contributing to global warming (Wuebbles and Hayhoe, 2002; Bousquet et al., 2006; Kirschke et al., 2013). Wetlands are the largest natural source of the greenhouse CH₄ to the atmosphere

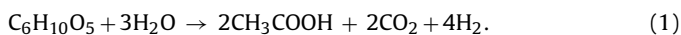
(Matthews and Fung, 1987; Nahlik and Mitsch, 2011). Tropical wetlands (including shallow lakes) have been estimated to produce about 50% of the natural wetland CH₄ emissions and explain a large portion of the observed methane variability (Ringeval et al., 2014). Lakes within the floodplains of tropical rivers have been found to be a significant source of atmospheric CH₄ (Devol et al., 1990; Smith et al., 2000; Marani and Alvala, 2007).

The formation of CH₄ from cellulosic material (C₆H₁₀O₅)_n is catalyzed by several types of microorganisms, which participate in depolymerization (hydrolysis), enzymatic acidogenesis, acetogenesis, and methanogenesis (Lynd et al., 2002). The major products

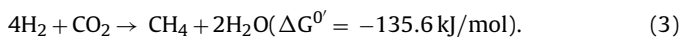
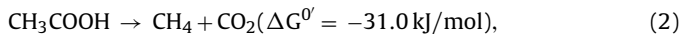
* Corresponding author.

E-mail addresses: vavilin@iwp.ru, vavilin@hotmail.com (V. Vavilin).

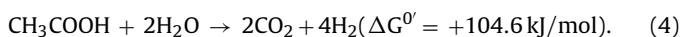
of enzymatic degradation of cellulose are monosaccharides, which are then transformed into volatile fatty acids (VFA) such as acetate (CH_3COOH), hydrogen (H_2), and carbon dioxide (CO_2):



The main substrates for the methanogenic microorganisms are acetate and H_2/CO_2 (Zinder, 1993), performing acetoclastic and hydrogenotrophic methanogenesis, respectively:



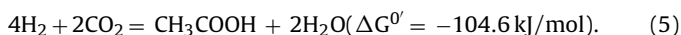
It is commonly accepted (Conrad, 2005) that acetoclastic methanogenesis contributes about 70% to the total production of CH_4 . However, the relative contributions of different acetoclastic and hydrogenotrophic methanogenic microorganisms to CH_4 formation depend on environmental factors. Thus, at a higher temperature or in the presence of compounds such as ammonia or volatile fatty acids (VFA), acetate is oxidized to H_2 and CO_2 (Schnurer et al., 1994; Cord-Ruwisch et al., 1998; Schink, 2002; Hattori, 2008):



This energetically unfavorable reaction, called *syntrophic acetate oxidation*, is performed by acetate-oxidizing microorganisms coupled with hydrogenotrophic methanogens.

Evidently, acetoclastic methanogens and acetate oxidizers compete for the same substrate (acetate). Syntrophs are generally considered to be slow growers. Ammonia and acetate concentration, hydraulic retention time, temperature and methanogenic population structure are important to influence the acetate conversion pathway (Westerholm, 2012). Recently, Vavilin and Rytov (2017) simulating Grossin-Debattista's laboratory data (2011) on mesophilic acetate methanization have shown that, at very low initial concentrations of acetate-oxidizers in inoculum, the acetate-oxidizers dominate eventually all the other acetate-consumers when the initial ammonium concentration is high.

At low temperatures, the homoacetogenesis may occur that is the reversion of acetate oxidation (Conrad et al., 1989; Vavilin et al., 2000; Kotsyurbenko et al., 2001; Hattori, 2008):



Homoacetogens and hydrogenotrophic methanogens compete for the same substrate (H_2/CO_2).

The kinetic isotope effect is defined as a change in the chemical reaction rate when the atom in the reactant molecule is replaced by its isotope. It is common (Craig, 1957) to describe the isotopic composition in delta notation per mil (‰) relative to an international standard, R_{std} , as

$$\delta[\text{‰}] = 10^3 \left(\frac{R}{R_{std}} - 1 \right), \quad (6)$$

where R and R_{std} are the isotope ratios in the sample and standard sample, respectively. The stable carbon isotope signature ($\delta^{13}\text{C}$) is expressed in ‰ deviations from $^{13}\text{C}/^{12}\text{C}$ ratio of 0.0112372 in Pee Dee Belemnite (PDB) carbonate used as the standard.

In chemical processes, the isotopic fractionation is the enrichment of one isotope relative to the other. Hayes (1993) defined the isotopic fractionation factor (IFF) for reaction $A \rightarrow B$ as the ratio:

$$\alpha_{A \rightarrow B} = \frac{\delta A + 1000}{\delta B + 1000}, \quad (7)$$

where δA and δB are the isotopic signatures of substrate A and product B . The degree of isotopic fractionation can be also quantified with the more distinctive *enrichment factor*, $\epsilon[\text{‰}] = (1/\alpha - 1) \times 1000$, because α -values usually deviate only slightly from 1. In the case of

low natural $^{13}\text{C}/^{12}\text{C}$ ratios, the hydrogenotrophic methanogenesis exhibits a much stronger IFF than the acetoclastic methanogenesis. To obtain information about the dominating CH_4 production pathway, an apparent IFF between CO_2 and CH_4 is used (Whiticar, 1986):

$$\alpha_c^{ap} = \frac{\delta^{13}\text{CO}_2 + 1000}{\delta^{13}\text{CH}_4 + 1000}. \quad (8)$$

The purpose of this study is to clarify methanization processes in the tropical lake sediments that were studied earlier by Conrad et al. (2010, 2011). Taking into account the amounts of CH_4 and CO_2 produced during the batch tests, and changes in their carbon isotope values, we can simulate the parallel processes of acetoclastic methanogenesis and acetate oxidation, which both compete for acetate. Dynamic and static isotope equations are used and compared in our modelling.

2. Materials and methods

2.1. Description of the batch experiments

A detailed description of experiments was presented earlier (Conrad et al., 2010, 2011). Samples of sediments were taken from floodplain lakes of the Amazon and Pantanal regions in Brazil. The area and depth of the lakes change considerably due to seasonal flood pulses. Sediment cores were taken and the upper 0–3 cm of sediments was used in batch experiments at 25 °C. Similar production rates of CH_4 and CO_2 (4.0 ± 3.8 and $3.8 \pm 3.3 \text{ nmol h}^{-1} \text{gdw}^{-1}$, respectively) were obtained for 16 Brazilian Lakes. Gas samples were taken from the incubated bottles and analyzed for CO_2 , CH_4 , $\delta^{13}\text{CO}_2$, and $\delta^{13}\text{CH}_4$. At the end of incubation, the bottles were sacrificed for sampling of the liquid phase, which was analyzed for acetate and other VFA. During sediment incubations, propionate and other VFA were also detected (Conrad et al., 2011), but only in the presence of CH_3F (which inhibits acetoclastic methanogenesis) and with concentrations much less than the acetate concentration.

In our modeling, we simulated the experimental data from the sediments of Jatoba, Mussura, and Batata Lakes. Water temperature over the sediments of Batata and Mussura Lakes was 31 °C and 30 °C, respectively. About 9-mL (Jatoba) and 12-mL (Batata and Mussura) aliquots of the sediments were transferred in triplicate into 27-mL (Jatoba) and 60-mL (Batata and Mussura) sterile tubes and incubated anaerobically at 25 °C.

2.2. Model

2.2.1. Unified approach to describe the dynamics of isotope fractionation in microbial substrate transformation

Rayleigh distillation equation for gas mixture diffusion (Rayleigh, 1896) is commonly used to calculate isotope fractionation:

$$R_t/R_0 = f^{(1/\alpha-1)}, \quad (9)$$

where R_0 and R_t are the substrate isotope ratios at the beginning and a later time moment t , respectively; $f = C_t/C_0$ is the unreacted fraction of the substrate with C_0 and C_t being the concentrations of the substrate at the beginning and at the end of time interval t , respectively; α is the kinetic fractionation coefficient between the substrate and the product in a closed and perfectly mixed system. Rayleigh equation is deduced from the first-order kinetics of substrate transformation with $\alpha = k^l/k^h$, where k^l and k^h are the first-order kinetic coefficients for the isotopically depleted (lighter) and enriched (heavier) substrates, respectively. The Rayleigh equation is valid for any type of substrate kinetics (Vavilin and Rytov, 2015).

Download English Version:

<https://daneshyari.com/en/article/5742015>

Download Persian Version:

<https://daneshyari.com/article/5742015>

[Daneshyari.com](https://daneshyari.com)