Animal Feed Science and Technology 194 (2014) 71–80

Contents lists available at ScienceDirect

Animal Feed Science and Technology

journal homepage: www.elsevier.com/locate/anifeedsci

Temperature, but not submersion or orientation, influences the rate of sulphur hexafluoride release from permeation tubes used for estimation of ruminant methane emissions

M.H. Deighton[a,b,*], S.R.O. Williams[a], K.R. Lassey[c], M.C. Hannah[a], T.M. Boland[d], R.J. Eckard[b], P.J. Moate[a]

[a] Agriculture Research Division, Department of Environment and Primary Industries, Ellinbank 3821, VIC, Australia
[b] Melbourne School of Land and Environment, The University of Melbourne, Parkville 3010, VIC, Australia
[c] Lassey Research and Education Ltd., 4 Witako Street, Lower Hutt 5011, New Zealand
[d] School of Agriculture and Food Science, University College Dublin, Belfield, Dublin 4, Ireland

ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form 17 April 2014
Accepted 14 May 2014

Keywords:
Sulphur hexafluoride tracer technique
Polytetrafluoroethylene
Membrane
Permeation
Arrhenius
Methane emission

ABSTRACT

Predictable release of sulphur hexafluoride (SF_6) tracer gas from permeation tubes into the reticulo-rumen is necessary to estimate methane emissions from ruminants using the SF_6 tracer technique. Any discrepancy between the laboratory determined rate of SF_6 release from permeation tubes and the actual rate of release in the reticulo-rumen would bias calculated methane emissions. The purpose of this investigation was to determine the effect of temperature, submersion and orientation on the rate of SF_6 release from permeation tubes. Four experiments were undertaken. Experiment 1 determined that release of SF_6 increased by 2.5 ± 0.14% per degree Celsius increase in temperature between 37 and 41 °C ($P < 0.001$). Experiment 2 determined that the Arrhenius equation can be used to describe the temperature dependence of SF_6 release rate from permeation tubes between 0 and 70 °C, consistent with a change in release rate of 2.3 ± 0.08% per degree Celsius change in temperature. Experiment 3 determined that submersion of permeation tubes in water did not affect the rate of SF_6 release ($P = 0.13$). Experiment 4 determined that SF_6 release rate was not influenced by permeation tube orientation ($P = 0.42$). In addition we determined the activation energy of permeation, E_p, describing the overall temperature dependence of SF_6 permeation flux from permeation tubes, to be 18,424 ± 680 J/mol. This research implies that the short-term release rate of SF_6 from permeation tubes within the reticulo-rumen will vary in response to temperature change due to animal, diet and/or environmental factors. A short term decrease in temperature of reticulo-rumen contents, induced by drinking cold water, is expected to have a larger influence on the accuracy of estimated methane emission derived from time-averaged sampling periods less than 24 h. Use of the SF_6 technique to detect differences in enteric methane emissions due to diet or between animal species may be confounded by diet or genetic effects on body temperature. Unless the effect of temperature is managed through careful implementation of the technique, substantial errors could be caused as illustrated by the following example: a +2 °C error in calibration temperature (41 °C), and a −2 °C discrepancy between the actual (37 °C) and assumed reticulo-rumen temperature (39 °C), could bias estimated methane emissions by approximately +10%.

Abbreviations: PTFE, polytetrafluoroethylene; SF_6, sulphur hexafluoride.

* Corresponding author. Tel.: +61 3 5624 2222; fax: +61 3 5624 2248.
E-mail address: matthew.deighton@depi.vic.gov.au (M.H. Deighton).

http://dx.doi.org/10.1016/j.anifeedsci.2014.05.006
0377-8401/© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The emission of enteric methane from ruminants can be determined using a calibrated tracer technique developed by Zimmerman (1993) and first deployed by Johnson et al. (1994). The tracer technique enables determination of methane emissions from individual animals within grazing or housed systems without the need for confinement. The technique requires the release of a tracer gas (sulphur hexafluoride, SF_6) at a known rate into the reticulo-rumen. Release of SF_6 at a known rate is achieved using a calibrated slow-release device (permeation tube). At 39 °C brass permeation tubes contain both gaseous and non-gaseous SF_6 with a vapour pressure of 32.5 bar (Funke et al., 2001). Permeation tubes typically emit between 2 and 10 mg of SF_6 gas per day *via* a permeable polytetrafluoroethylene (PTFE) membrane and sintered stainless steel frit (Lassey et al., 2001). Measurement of the gas mixing ratios of methane and SF_6 in air that is enriched with expired and/or eructated gases collected from about an animal's mouth and nostrils enables calculation of that animal's enteric methane emission (Eq. (1); Williams et al., 2011);

$$R_{CH_4} = R_{SF_6} \frac{[CH_4]_M - [CH_4]_{BG}}{[SF_6]_M - [SF_6]_{BG}} \times \frac{MW_{CH_4}}{MW_{SF_6}} \times 1000 \quad (1)$$

where the rate of methane emission $\left(R_{CH_4};\, g/d\right)$ is equal to the release rate of SF_6 $\left(R_{SF_6};\, mg/d\right)$ from a permeation tube in the reticulo-rumen, multiplied by the background adjusted mixing ratios of methane and SF_6 within a representative time-averaged sample of gases collected from each animal. The measured mixing ratios of methane ($[CH_4]_M$) and SF_6 ($[SF_6]_M$) in this sample are corrected by subtracting the background mixing ratios of these gases ($[CH_4]_{BG}$, $[SF_6]_{BG}$) within concurrently collected samples of ambient air. Mixing ratios of methane are expressed in parts per million (μmol/mol) while those of SF_6 are expressed in parts per trillion (pmol/mol) of the collected air sample. The molecular mass of methane $\left(MW_{CH_4}\right)$ is 16, and that of SF_6 $\left(MW_{SF_6}\right)$ is 146. The multiplier of 1000 accounts for the disparate units of $[CH_4]$ and $[SF_6]$ and R_{SF_6} so that R_{CH_4} is expressed as g CH_4/d.

The rate of methane emission varies considerably throughout the day according to feeding pattern (Aguerre et al., 2011; Grainger et al., 2007), therefore it is necessary to ensure that the rate of sample collection and SF_6 tracer gas release from permeation tubes remain constant throughout the sampling period. Vital to the accurate estimation of methane emissions *in vivo* during the gas sampling period is the predicted SF_6 release rate $\left(R_{SF_6}\right)$.

The predicted rate of SF_6 release (mg/d) from permeation tubes in the reticulo-rumen is based on a pre-experimental determination of the rate of permeation tube mass loss during laboratory incubation, hereafter referred to as calibration. Calibration is generally conducted at a temperature of 39 °C (Lassey et al., 2001) since the mean temperature of the rumen is generally considered to be 39 °C (*e.g.* Brody et al., 1955). It is assumed that all permeation tube mass loss during calibration is attributable to release of SF_6 gas. During calibration of SF_6 release rate, permeation tubes are typically dry and in a consistent orientation (vertical or horizontal). It has previously been demonstrated that permeation across the PTFE membrane is the sole route of SF_6 release from permeation tubes, with no leakage occurring *via* the nylon washer or its seal against the brass tube (Deighton et al., 2013). It has also been reported that the rate of SF_6 release from permeation tubes is temperature dependent; in fact SF_6 release from permeation tubes can be inhibited completely by cooling tubes to −80 °C (Deighton et al., 2011).

The temperature dependence of gas permeation is generally described by the Arrhenius relationship (*e.g.* Namieśnik, 1984; Mitchell, 2000). Generally, in the Arrhenius equation (Eq. (2)), k refers to a reaction rate constant. In this application of the Arrhenius equation, k_1 refers to the rate of permeation or release rate of SF_6 (mol/d) from the permeation tube at a specific absolute temperature T_1 (K), while k_2 refers to the release rate when the absolute temperature is T_2, R is the gas constant (8.314 J/mol per degree), and E_p refers to the activation energy of permeation (J/mol) (Maron and Prutton, 1969).

$$\ln \frac{k_2}{k_1} = \frac{E_p}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \quad (2)$$

Namieśnik (1984) reported that the permeation rate of gases may vary by as much as 10% for a 1 °C change in temperature about an unspecified temperature. More recently Bárbaro et al. (2008) measured the SF_6 release rate from 10 permeation tubes and reported that the release rate increased by 3% per K between 308 and 316 K (*i.e.* 35 and 43 °C). However, the experimental procedure used to draw this conclusion was not described. Thus, in view of such discrepant reports of the sensitivity of SF_6 permeation rate to temperature the actual sensitivity remains uncertain.

A predictable release of SF_6 from permeation tubes within the reticulo-rumen is critical for accurate determination of enteric methane emissions. Any difference in SF_6 release rate from permeation tubes immersed in the reticulo-rumen, compared to the release rate determined in the laboratory would bias estimates of methane emissions. Rochette et al. (2012) reported that the rate of SF_6 release from permeation tubes, with mean SF_6 release rate of 1.7 mg/d, decreased following first but not subsequent incubation in a liquid environment. This finding led Rochette et al. (2012) to propose that the rate of SF_6 release from permeation tubes should be determined following an initial incubation in a liquid medium, preferably in the rumen. If accepted this proposal will require a change to the way that the SF_6 release rate from permeation tubes has been determined since development of the technique in 1993.

In addition to the effect of changes in temperature and incubation media, the rate of SF_6 release may also change if tubes have a different orientation in the reticulo-rumen than during laboratory determination of SF_6 release rates. It is currently