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Declining sulphur hexafluoride permeability of polytetrafluoroethylene membranes causes overestimation of calculated ruminant methane emissions using the tracer technique

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ABSTRACT

Predictable release of sulphur hexafluoride (SF_6) from permeation tubes is critical for determination of enteric methane emissions from ruminants using the calibrated tracer technique. Experiments comparing respiration chambers and the SF_6 technique indicate that prolonged deployment of SF_6 tubes causes overestimation of methane emissions. We report three studies investigating release rate of SF_6 from permeation tubes. Experiment 1 investigated if SF_6 was released by routes other than the polytetrafluoroethylene (PTFE) membrane. Replacement of the membrane with an impervious disk prevented SF_6 release, confirming that SF_6 release occurs only through the PTFE membrane. Experiment 2 investigated the effect of frit exposure to the rumen environment and reticulo-rumen residence duration upon SF_6 release rate. Three treatments were applied: (i) tubes with exposed frits (Control), (ii) tubes with exposed frits previously incubated for 152 d in the reticulo-rumen (Exposed-frit) and (iii) tubes incorporating an external membrane to prevent frit contamination during 152 d incubation in the reticulo-rumen (Protected-frit). These tubes were then used to determine methane yield. Tubes of each treatment were also retained in an incubator to determine SF_6 release rate concurrent to the *in vivo* experiment. Decline of SF_6 release was not related to frit exposure to the reticulo-rumen environment. Methane yield determined using Exposed-frit and Protected-frit tubes was 21% greater than that estimated with Control tubes ($P<0.01$). Concurrent SF_6 release, from Exposed-frit and Protected-frit tubes retained within an incubator was similarly reduced by 22% relative to Control tubes, indicating that decline of SF_6 release rate is a function of time elapsed post-calibration, unrelated to tube reticulo-rumen residence duration *per se*. Experiment 3 was conducted to determine the cause of the *in vivo* decline in SF_6 release. Three pre-treatments were applied to PTFE membranes; untreated (Control-PTFE), 165 d rumen exposure (Rumen-PTFE) and 165 d SF_6 exposure (SF_6-PTFE). Pre-treated membranes were used to construct new permeation tubes. Release rate from SF_6-PTFE tubes was 36% less than from control tubes and 35% less than from Rumen-PTFE tubes ($P<0.001$). Release rate from Rumen-PTFE tubes did not differ from control tubes ($P>0.05$). Post-calibration decline in SF_6 release rate from permeation tubes results from exposure of PTFE membranes to SF_6 rather than reticulo-rumen

Abbreviations: DMI, dry matter intake; PTFE, polytetrafluoroethylene; SF_6, sulphur hexafluoride.

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exposure. We conclude that 'dry' incubation of permeation tubes in a laboratory to determine the rate of SF_6 release is valid. However, post-calibration decline in SF_6 release must be accounted for to prevent over-estimation of methane emissions.

1. Introduction

Respiration chambers and the calibrated SF_6 tracer technique are the main methods used to estimate enteric methane emissions from individual ruminant animals. The respiration chamber technique (Grainger et al., 2007), confines animals in a chamber and the air flow-rate and the mixing ratio (concentration) of methane in the chamber air intake and exhaust are measured. Respiration chambers enable precise determination of methane emissions, but their use is limited by high capital and running costs. In contrast, the calibrated tracer technique can be used on large numbers of animals simultaneously due to the lower cost of the gas sampling apparatus. The tracer technique is currently the only method that can be used to quantify daily methane emissions from large numbers of individual animals without the need for their confinement.

Use of sulphur hexafluoride (SF_6) as a tracer gas for the determination of ruminant methane emissions was pioneered by Zimmerman (1993) and first used experimentally in ruminants by Johnson et al. (1994). The technique enables estimation of enteric methane emissions *via* the mouth and nostrils. The concentration of SF_6 tracer gas in a collected air sample is dependent upon the rate of SF_6 release from a small SF_6 emitting permeation tube within the reticulo-rumen, the quantity of expired and eructated gases and the dilution of these gases in ambient air corrected for the background concentration of SF_6. Release of SF_6 from the permeation tube occurs *via* permeation through a thin polytetrafluoroethylene (PTFE) membrane, supported by an external, yet highly porous, sintered metal frit (Fig. 1).

There are a number of factors that influence the precision with which methane emissions can be estimated using the SF_6 tracer technique. An important factor is the release rate of SF_6 tracer gas. The predicted release-rate *in vivo* is determined by measurement of SF_6 mass loss from permeation tubes during laboratory incubation at 39 °C prior to each experiment (Johnson et al., 1994). Also affecting methane emission, calculated using Eq. (1), is the accuracy of extrapolation of the pre-determined SF_6 release rate to predict the actual rate of release during subsequent gas sampling periods. Lassey et al. (2001) have shown that SF_6 release rate declines over time and that relative to a prediction based on a linear regression of SF_6 mass loss *versus* time, a quadratic equation can be used to improve prediction of SF_6 release rate *in vivo*. These authors also proposed a "quality control" procedure in which additional permeation tubes within each batch are retained in an incubator at 39 °C to determine the mean decline in SF_6 release rate concurrent with deployment of similar permeation tubes in animals. The estimated SF_6 release rate within animals may then be corrected on the basis of the change in release rate of the laboratory incubated tubes.

Deviation of the actual release rate of SF_6 from the predicted rate during a given gas measurement period will inversely bias the resulting estimate of methane emission. For example, a 5% reduction in the actual release rate of SF_6 in the reticulo-rumen, relative to the predicted release rate, will result in the overestimation of daily methane emissions by 5% and *visa versa*.

Eleven experiments using both respiration chambers and the SF_6 tracer technique have been reported in the scientific literature (Table 1). These experiments did not focus on the influence of time after reticulo-rumen deployment of permeation tubes on methane emissions as calculated by the SF_6 technique. Moreover, none of these authors reported using the "quality control" procedure proposed by Lassey et al. (2001) despite using SF_6 permeation tubes up to 250 d after insertion into the reticulo-rumen. Taken collectively, the data from these eleven experiments indicates the presence of a systematic bias related to time elapsed following permeation tube deployment (Fig. 2).

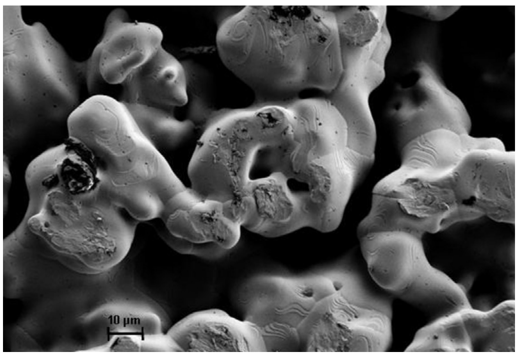

Fig. 1. Scanning electron micrograph (2000× magnification) of a highly porous sintered stainless-steel frit used in the construction of SF_6 permeation tubes.