RESEARCH ARTICLE

A dual tracer ratio method for comparative emission measurements in an experimental dairy housing

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Abstract

Agriculture, and in particular dairy farming, is an important source of ammonia (NH₃) and non-carbon dioxide greenhouse gas (GHG) emissions. This calls for the development and quantification of effective mitigation strategies. Our study presents the implementation of a dual tracer ratio method in a novel experimental dairy housing with two identical, but spatially separated housing areas. Modular design and flexible floor elements allow the assessment of structural, process engineering and organisational abatement measures at practical scale. Thereby, the emission reduction potential of specific abatement measures can be quantified in relation to a reference system. Emissions in the naturally ventilated housing are determined by continuous dosing of two artificial tracers (sulphur hexafluoride SF₆, trifluoromethylsulphur pentafluoride SF₅CF₃) and their real-time detection in the ppt range with an optimized GC-ECD method. The two tracers are dosed into different experimental sections, which enables the independent assessment of both housing areas. Mass flow emissions of NH₃ and GHGs are quantified by areal dosing of tracer gases and multipoint sampling as well as real-time analysis of both tracer and target gases. Validation experiments demonstrate that the technique is suitable for both areal and point emission sources and achieves an uncertainty of less than 10 % for the mass emissions of NH₃, methane (CH₄) and carbon dioxide (CO₂), which is superior to other currently available methods. Comparative emission measurements in this experimental dairy housing will provide reliable, currently unavailable information on emissions for Swiss dairy farming and demonstrate
the reduction potential of mitigation measures for NH$_3$, GHGs and potentially other pollutants.

Keywords: Experimental dairy housing; Tracer ratio method; Comparative emission measurement; Ammonia; Greenhouse gas

**Graphical Abstract**

Validation of the dual tracer ratio method:
High accuracy and sensitivity for quantification of NH$_3$ and GHG emissions
Suitability for areal and point sources
Minimal cross-contamination of experimental sections
Equivalence of SF$_6$ / SF$_6$CF$_3$
1. Introduction

Agricultural activities, in particular livestock farming, contribute significantly to global NH$_3$ and GHG emissions (Ciais et al., 2013). In Switzerland, NH$_3$ and non-CO$_2$ GHG (e.g. methane and nitrous oxide) emissions from agriculture even dominate the anthropogenic load. According to model calculations, 94% of total NH$_3$ emissions in Switzerland were attributed to farming in 2007, a third of which can be traced to livestock housing (Achermann et al., 2009; Kupper et al., 2013). Similarly, 81% of methane (CH$_4$) and 79% of nitrous oxide (N$_2$O) emissions in Switzerland originated from agriculture in 2014 (FOEN, 2016), with CH$_4$ being primarily produced by enteric fermentation of ruminants (Hiller et al., 2014; Eyer et al., 2016; Röckmann et al., 2016) and N$_2$O mainly emitted by microbial activities in natural and fertilized soils (Mohn et al., 2012; Fowler et al., 2013; Mohn et al., 2013; Wolf et al., 2015).

To effectively mitigate NH$_3$ and GHG emissions from livestock housing, structural, process engineering, organisational and nutritional reduction strategies must be developed and quantified. A recent meta-analysis by Bougouin et al. (2016) of 16 published studies reveals a wide spread in NH$_3$ emissions of naturally ventilated dairy cattle housing from 7.4 to 106 g NH$_3$ cow$^{-1}$ d$^{-1}$. Nearly half of the heterogeneity in this data set can be explained by flooring (slatted floor, solid floor), temperature, season, milk yield and diet (crude protein, dry matter intake). Further interpretation of the data is hindered by the limited availability of driving variables, and by inconsistencies between measurement techniques. Previous Swiss studies using a dual tracer ratio method on six commercial farms with solid floors and an outdoor exercise area,
showed large variations in daily mean NH$_3$ emissions, ranging from 6 to 67 g LU$^{-1}$ d$^{-1}$ (LU livestock unit, 1 LU = 500 kg live weight). Here, the main explanatory variables were climatic conditions (temperature, wind speed) and urea content in the milk (Schrade et al., 2012). Given this pronounced variability, it would be highly beneficial to evaluate the reduction potential of mitigation measures in relation to a reference system with comparable climatic, herd and nutritional conditions.

Several approaches have been used to determine NH$_3$ and GHG emissions from naturally-ventilated dairy housing, most of them using a tracer technique with known source strength and measuring its concentration in the housing with respect to background conditions (Teye and Hautala, 2007). The involved tracer can be either artificial (e.g. SF$_6$), or natural / metabolic such as heat (Von Wachenfelt et al., 2001; CIGR, 2002) or CO$_2$ produced by the animals (Pedersen et al., 1998; Pedersen et al., 2008; Bai et al., 2016). CO$_2$ and heat balance methods are cheap, rapidly deployable methods to determine ventilation rates at a practical scale but they are based on a number of general assumptions (e.g. respiration quotient) which strongly limit their accuracy. More specifically, these balance methods require a minimal CO$_2$ concentration or temperature difference between the inside and the outdoor air (Pedersen et al., 1998). This makes them unsuited for naturally ventilated housings with large openings, and housing systems with an outdoor exercise area.

A well-established approach to determine ventilation rates in buildings is to dose an artificial tracer gas (Sherman, 1990). These methods are also applicable to naturally ventilated housings (Calvet et al., 2013) and areal
sources like outdoor exercise areas and open slurry storages (Griffith et al., 2008; Keck et al., 2011; Schrade et al., 2012) because the mass flow of the tracer can be adapted to the dilution ratio. Several variants of tracer ratio methods have been used in naturally ventilated cattle housings (see Table S1 in the supplementary file), differing in the choice of the tracer gas (e.g. SF$_6$, carbon monoxide CO or Krypton-85 $^{85}$Kr), the positioning of tracer gas release and sampling system as well as in the dosing procedure (concentration decay versus constant tracer gas release). The most frequently used tracer gas for emission measurements in livestock husbandry is SF$_6$. It is chemically extremely stable, non-toxic, and has a background concentration in ambient air of only a few ppt. Its molecular mass is about five times higher than ambient air. Therefore, it is typically diluted, i.e. mixed with compressed air or nitrogen to approach the density of ambient air (e.g. Berry et al., 2005; Schrade et al., 2012; Schiefler, 2013; Mendes et al., 2015; Edouard et al., 2016). In addition to SF$_6$, Schrade et al. (2007) used SF$_5$CF$_3$, which has very similar characteristics as SF$_6$, as a second tracer to distinguish between indoor and outdoor emissions.

To calculate accurate emission values, however, several metrics must be evaluated: most importantly, the tracer gas release must sufficiently mimic the release of the target substances from surfaces (e.g. NH$_3$) or animals (CH$_4$, CO$_2$), which can be achieved by tracer gas dosing next to the emitting areas or objects (Demmers et al., 1998; Schneider et al., 2006; Schrade et al., 2012; Mendes et al., 2015; Edouard et al., 2016). Second, the sample must be representative, preferably homogenously mixed, and independent of the wind
situation, which is better achieved when using pooled sampling (Mendes et al., 2015; Edouard et al., 2016).

In this study, a dual tracer ratio method was implemented in a new experimental dairy housing for comparative emission measurements at Agroscope, Tänikon. The aim of the study was to validate the optimized tracer ratio method with respect to the equivalence of the two tracer gases and the capability of the developed technique to quantify areal and point emission sources. In addition, the accuracy and sensitivity for mass flow emissions of NH$_3$ and GHGs was tested and finally the potential to trace cross-contamination between experimental areas was evaluated.
2. Materials and Methods

2.1 Experimental dairy housing

The experimental dairy housing, built in 2014 – 2015, is located in north-eastern Switzerland in Aadorf at Waldegg (47°49'N, 8°92'E, around 550 m a.s.l.). The location is ideally suited due to its large distance to other emission sources. In addition, the site provides the possibility to position the building axis orthogonal to prevailing wind directions, which is an important criterion to minimize cross-contamination between different housing sections. Representative measurements of wind direction distribution were conducted in the planning phase of the housing between February 2010 and July 2011, applying two ultrasonic anemometer (WindObserver, Gill Instruments, GB; WindMaster, Gill Instruments, GB) at 1.5 and 5 m height, indicating mostly south-westerly (47% of time) and north-easterly (30%) wind directions (Fig. 1).
Fig. 1. Average distribution of the wind direction at Waldegg near Tänikon (a). The photo indicates the orientation of the building axis of the experimental housing orthogonal to the prevailing wind directions. The yellow and blue dots indicate locations, in the surrounding of the housing, with NH3 passive samplers (Schrade et al., 2012). While at the yellow dots monthly average concentrations are determined, at the blue dot NH3 background concentrations are determined for every measurement period. The red dot indicates the sampling site for the GHG background measurements (b).

The housing consists of two experimental areas, each for 20 cows with three rows of cubicles with straw (Fig. 2). The basic concept with two identical sections provides the opportunity for the progressive development and testing of NH3 and GHG reduction strategies (housing concept, exercise area design, feeding stalls, manure removal management, diet, etc.) and for efficient comparative quantification of their reduction potential (Schrade et al., 2015). The experimental areas are naturally ventilated without thermal insulation and with flexible curtains as facades. Outdoor exercise areas are arranged lengthways to the experimental areas in the south-west. In the centre section of the building (utility area) the milking parlour, analytics, and office are situated.
Fig. 2. Photograph of the experimental dairy housing for emission measurements of Agroscope near Tänikon, Switzerland (a): Schematic top view of the housing with two experimental sections for comparative emission measurements, reference and treatment, and the centre section in the middle (b).
2.2 Implementation of the dual tracer gas ratio method

2.2.1 Tracer gas release

To determine emissions under natural ventilation, a tracer ratio method with two
different tracer gases SF$_6$ and SF$_5$CF$_3$ and constant dosing is applied (Schrade
et al., 2012). To trace cross contamination between experimental sections,
individual tracer gases are applied to reference and treatment area (Table 1).

Constant flows of the diluted tracer gases (2000 ppm SF$_6$ or SF$_5$CF$_3$ in synthetic
air, rel. uncertainty ±2%, Messer Schweiz AG, Switzerland) are adjusted using
mass flow controllers (GSC, 2 L min$^{-1}$, high performance, uncertainty ±0.3 % of
maximum flow, Vögtlin Instruments Inc., Switzerland). The tracer gases are
directed to the experimental sections via stainless steel tubing (ID 4 mm,
Interalloy, Switzerland). SF$_6$ impurities in the SF$_5$CF$_3$ tracer (1% SF$_6$ in SF$_5$CF$_3$,
absolute uncertainty ±1%) specified by the SF$_5$CF$_3$ manufacturer
(Fluorochemika, Poland SP.Z00.) are considered during data analysis. Tracer
gas flows are set according to ventilation conditions (curtains open / closed etc.)
to adjust analysed tracer gas concentrations in an optimal range (> 50 ppt,
<1500 ppt SF$_6$ and SF$_5$CF$_3$). Depending on the adjusted flow of the diluted
tracer gases, measurement campaigns of several weeks up to months are
feasible with one high pressure cylinder. Within the experimental areas, tracer
gases are distributed homogeneously using 18 critical orifices (hole diameter 30
µm, Lenox Laser Inc., USA) mounted at ground level (10 to 15 cm above floor)
equidistantly next to the walking aisles to mimic the emission sources (Fig. 3).
Five additional orifices are installed in the outdoor exercise area and deployed
depending on the experimental design, reflecting the proportionality of indoor
and outdoor emissions (Schrade, 2009). Flow rates for individual orifices are
monitored before and after every measuring campaign using a mass flow meter (GSM, Vögtlin Instruments Inc., Switzerland), and individual orifices agreed within ±10% (one standard deviation (SD)). Stainless steel tubes and critical orifices are protected with metal profiles from damage by animals and contamination with excrements and dirt.

Table 1 Positions of tracer gas dosing and tracer as well as target gas sampling used for cross contamination experiments and intended emission measurements. Tracer gas dosing during the validation experiments may deviate and is therefore given in Table S2 in the supplementary file.

<table>
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<th>Reference section 1</th>
<th>Centre section</th>
<th>Treatment section 2</th>
<th>Background</th>
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<td>Tracer gas dosing</td>
<td>SF₅CF₃</td>
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<td>Tracer gas sampling</td>
<td>SF₆, SF₅CF₃</td>
<td>SF₆, SF₅CF₃</td>
<td>SF₆, SF₅CF₃</td>
<td>SF₆, SF₅CF₃</td>
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<tr>
<td>Target gas sampling</td>
<td>NH₃, CH₄, CO₂, N₂O</td>
<td>NH₃, CH₄, CO₂, N₂O</td>
<td>NH₃, CH₄, CO₂, N₂O</td>
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Fig. 3. Implementation of the dual tracer ratio method in the experimental dairy housing. The dosing grids used to distribute the tracer gases are shown for the reference section (a). Grid 1, drawn in grey, with 18 capillaries is the standard grid used to distribute tracer gases. Grid 2 and 3, drawn in blue and green, with 18 and 5 capillaries, respectively are applied in the validation experiments, described in Table S2 in the supplementary file, only. Cross section through the building showing the height of the tracer gas dosing grids (colour coding for grid 1-3) and the air sampling grid installed at 2.5 m height with 24 capillaries (b).
2.2.2 Gas sampling

Integrative air samples in each section are collected using 24 glass orifices (2.5 m above ground, hole diameter 250 μm, Thermo-Instruments, Germany and Louwers, The Netherlands) protected with PTFE membrane filters (TE 38, 37 mm, GE Whatman Plc, UK) and directed via PTFE tubes (OD 8 mm, Maagtechnic AG, Switzerland) to an air-conditioned trailer placed in the utility area (Fig. 2). Six additional orifices are installed in the outdoor exercise area and used depending on the experimental design. Flow rates for individual orifices are monitored before and after every measuring period using a mass flow meter (GSM, Vögtlin Instruments Inc., Switzerland), and individual orifices agreed within ±10% (±1 SD).

In addition to air sampling from both experimental sections of the housing, measuring gas is collected from the utility area in the centre section (Fig. 2), as well as the background site around 30 m south-east, i.e. perpendicular to the prevailing wind direction, of the experimental housing (Fig. 1). The two additional sites are equipped with seven (utility area) and eight (background) orifices. Sample gas from these locations (reference and treatment area, utility area, background site) is continuously drawn using four separate membrane pumps (ME 2C, Vacuubrand, Germany). Air flows are around 10 L min⁻¹ for reference and treatment area and around 2.5 L min⁻¹ for the centre section and the background site and delivered to separate 2 L Teflon flasks (Semadeni AG, Switzerland), which serve as mixing containers and pressure compensation vessels. Gas samples from the Teflon flasks are extracted sequentially, 10 min per sample, using a gauge head selector switch (10 position common outlet...
flow-path selector, EUTA-2LSC10MWESLF, Vici AG International, Switzerland) and directed to the analyzers). The operation of the selector switch, and thus the measuring sequence, is controlled via the “external valve sequencer option” of the GHG CRDS analyzer (model G2301, Picarro Inc., USA). The applied repetitive measuring sequence (10 minutes per setting) for the respective experiment is given in Table S2 in the supplementary file.

2.2.3 Gas analysis

Air samples are analysed for SF$_6$ and SF$_5$CF$_3$ by gas chromatography with electron capture detection (GC-ECD, 7890A, Agilent Technologies AG, Switzerland). A GC configuration with custom-made molecular-sieve 5Å column (60 / 80 mesh, ID = 3.7 mm, L = 4 m, Applied Science Inc., USA), a HayeSep Q column (80 / 100 mesh, ID = 3.7 mm, L = 50 cm, Sigma Aldrich Inc., Switzerland) and a carrier gas flow of 50 mL min$^{-1}$ (N$_2$ 6.0, Messer Schweiz AG, Switzerland) are used. Operating temperatures are 300 °C for the ECD, 120 °C for the column and 120 °C for the injector. The detection limits are 2 ppt for both SF$_6$ and SF$_5$CF$_3$. Low analytical detection limits are required to avoid extensive dosing and emissions of these potent greenhouse gases. In the current setup the greenhouse warming potential (GWP) of the added diluted SF$_6$ and SF$_5$CF$_3$ tracer gases was substantially lower than the GWP of animal emissions from the housing. Tracer gas concentrations (SF$_6$, SF$_5$CF$_3$) are referenced against commercial standard gases (102.1 ± 2 ppt SF$_6$, 848 ± 17 ppt SF$_6$, Tracertech GmbH, Germany, 14.8 ± 0.3 ppm SF$_5$CF$_3$, Carbagas AG, Switzerland). As commercial SF$_5$CF$_3$ standards are not available at low concentrations, higher concentration standards are diluted and the dilution ratio determined using a
CH₄ bootstrap gas. In addition, tracer gas concentrations are referenced to the SF₆ scale provided by NOAA GMD ESRL and a gravimetric standard for SF₆ and SF₅CF₃ provided by University of Bristol.

NH₃, CH₄ and CO₂ concentrations are analysed with two cavity ring-down spectrometers (CRDS1, NH₃: model G2103, CRDS2, CH₄, CO₂: model G2301, Picarro Inc., USA), N₂O and CO are measured with a quantum cascade laser absorption spectrometer (QCLAS, QC-TILDAS-CS, Aerodyne Inc., USA) after drying with a Nafion permeation device (PD-100T-72, Perma Pure, USA). The precisions of the laser spectrometers, according to manufacturer specification are: < 0.07 ppb NH₃, < 0.22 ppb CH₄, < 25 ppb CO₂, < 0.01 ppb N₂O and < 0.05 ppb CO. CH₄, CO₂ and N₂O concentrations are referenced to the respective scales provided by NOAA GMD ESRL via regular (every 12 hours) analysis of pressurized air (727.2 ± 0.04 ppm CO₂, 11537.0 ± 21.7 ppb CH₄, 351.0 ± 0.11 ppb N₂O, ± 1 SD, n = 3) calibrated by WCC-Empa (Zellweger et al., 2012; Zellweger et al., 2016). NH₃ measurements are referenced to commercial gas standards (20 ppm NH₃, Messer Schweiz AG, Switzerland) diluted with synthetic air (Messer Schweiz AG, Switzerland). The exact NH₃ concentration in the diluted standards is confirmed by absorption in diluted sulfuric acid and subsequent ion chromatography (ICS 3000, Thermo Scientific™ Dionex™ ion chromatography, Switzerland) (Mohn et al., 2004).

To confine tracer (SF₆, SF₅CF₃) and target gas (NH₃, CH₄, CO₂, N₂O) concentration changes to emissions from the experimental dairy housing, a correction for variations in background concentrations was applied. For SF₆ and SF₅CF₃, a constant offset correction was applied (8.0 ppt SF₆, 0.15 ppt...
SF\(_5\)CF\(_3\)). While the SF\(_6\) background concentration was determined over a 24 hours period in March 2016 (8.0 ± 0.2 ppt), for SF\(_5\)CF\(_3\) ambient concentrations are below the analytical detection limit and therefore a literature value was used (Sturges et al., 2012). The validity of stable SF\(_6\) and SF\(_5\)CF\(_3\) background concentrations was assured by regular measurements at the background site (Fig. 1). CH\(_4\), CO\(_2\) and N\(_2\)O concentrations in the housing were corrected for diurnal changes in background concentrations using a linear spline algorithm. Details on the sampling frequency are given in Table S2 in the supplementary file. For NH\(_3\) correction, a background concentration is determined for the respective measuring period with a NH\(_3\) passive sampler positioned around 100 m north-west of the housing (Fig. 1) (Schrade et al., 2012).

2.2.4 Emissions calculation

The quantification of emissions with the tracer ratio method is based on the assumption that the tracer gas (SF\(_6\), SF\(_5\)CF\(_3\)) behaves in the same way as the target gas (NH\(_3\), GHG) and thus mimics the emitting source (Demmers et al., 2001). The mass flow of the target gas (\(\dot{m}_{\text{target}}\)) is calculated from the ratio of the background corrected target (\(c_{\text{target}}\)) and tracer gas concentration (\(c_{\text{tracer}}\)) and the mass flow of the tracer gas (\(\dot{m}_{\text{tracer}}\)) as given in Eq. (1):

\[
\dot{m}_{\text{target}} = \frac{\dot{m}_{\text{tracer}} \times c_{\text{target}}}{c_{\text{tracer}}} \tag{1}
\]

2.3 Wind data measurements

Wind statistics were measured using 3D ultrasonic anemometers measuring at 1 Hz (experiments 2.4.2, 2.4.3, 2.4.4, 2.4.5; USA-1-Scientific, METEK,
Elmshorn, Germany) or 10 Hz (experiments 2.4.1 and 2.4.6 Ultra-sonic
Anemometer 3D, Adolf Thies GmbH & Co. KG, Göttingen, Germany) at a height
of 10 m, 60 m south-west of the housing. In addition, wind direction and speed
were measured in the middle of each experimental section and the outdoor
exercise area, at a height of 2.5 m, using 3D ultrasonic anemometers
(Ultrasonic Anemometer 3D, Adolf Thies GmbH & Co. KG, Göttingen,
Germany).

2.4 Validation experiments

To validate the dual tracer ratio method, targeted experiments were completed
to confirm the two tracer gases perform similarly and the method is suitable to
quantify areal as well as point emission sources, determine the accuracy and
sensitivity of the method for NH₃ and GHG emissions and assess any cross
contamination between the experimental sections (Table S2 in the
supplementary file). The term “accuracy” defines the closeness of the
agreement between the result of a measurement and a true value of the
measurand (JCGM, 2008).

2.4.1 Equivalence of tracer gases

This experiment tests the basic assumption of the dual tracer ratio method that
both tracer gases (SF₆, SF₅CF₃) distribute similarly and are analyzed reliably by
GC-ECD. The general setup and specifications of components are according to
2.2, but constant flows of both tracer gases (150 mL min⁻¹ SF₆, 150 mL min⁻¹
SF₅CF₃) are combined in one stainless steel line, and both tracer gases are
distributed with the same set of critical orifices in one experimental area (Fig. 3).
Tracer gas concentrations are analyzed by GC-ECD with ten minutes temporal resolution over five consecutive days and interpreted with respect to agreement between the observed and the predicted SF$_6$ to SF$_5$CF$_3$ concentration ratio. The experiment was conducted under normal farming conditions (with cows etc.) to cover the most relevant and challenging experimental settings. The standard deviation of ten minutes and of daily average values are used as a measure for the uncertainty in the observed SF$_6$ / SF$_5$CF$_3$ concentration ratios. Predicted SF$_6$ to SF$_5$CF$_3$ concentration ratios are calculated from tracer gas concentrations and flows taking into consideration manufacturer specification on SF$_6$ impurities in the SF$_5$CF$_3$ tracer. The uncertainty of the predicted SF$_6$ to SF$_5$CF$_3$ concentration ratios is estimated based on the given uncertainty contributions using the laws of error propagation.

2.4.2 Suitability of the tracer ratio method to quantify areal emission sources

To test the suitability of the tracer ratio method to quantitatively assess areal emission sources, SF$_6$ was used as a tracer, and SF$_5$CF$_3$ was dosed into the same experimental section, simulating the areal emission source of a target substance. For the primary tracer gas (SF$_6$), the permanently installed grid of dosing orifices was applied, while the target substance (SF$_5$CF$_3$) was distributed via a second, independent grid with 18 orifices (hole diameter 30 $\mu$m, Lenox Laser Inc., USA) (Fig. 3). Flows of both tracer gases (SF$_6$, SF$_5$CF$_3$) were 100 mL min$^{-1}$. Photos indicating the position of the SF$_5$CF$_3$ grid are given in the supplementary file (Fig. S1). The experiment was conducted in two variants, each during three to four days, with open and closed curtains, to simulate
different ventilation situations. Predicted SF₆ / SF₅CF₃ concentration ratios and uncertainties are calculated and interpreted as detailed in 2.4.1.

2.4.3 Suitability of the tracer ratio method to quantify point emission sources

The suitability of the tracer ratio method to quantify point emission sources is tested in an experiment similar to 2.4.2, but the second tracer gas (SF₅CF₃), used as a target substance to simulate the point emission source, is dosed into the housing with just one tube equipped with five collocated orifices (hole diameter 30 μm, Lenox Laser Inc., USA). Total flows of the two tracer gases (SF₆, SF₅CF₃) were 100 mL min⁻¹. The SF₅CF₃ emission source was positioned in the middle of the experimental section (Fig. 3), as indicated on a photo in the supplementary file (Fig. S2). Predicted SF₆ / SF₅CF₃ concentration ratios and uncertainties are calculated and interpreted as detailed in 2.4.1. Experiments were conducted over three consecutive days.

2.4.4 Accuracy of the tracer ratio method to quantify GHG emissions

Prior to the experiments the housing was thoroughly cleaned to minimize diffuse microbial CH₄ and N₂O release. Nonetheless, there were some remaining activities from slurry storage. SF₆ was distributed homogeneously into one experimental area using the permanently installed grid of critical orifices, the target gas (CH₄ or N₂O) was dosed into the same section via a second, independent grid equipped with 18 orifices (hole diameter 30 μm, Lenox Laser Inc., USA) (Fig. 3). Concentrations and flows of target gases were: 1860 mL min⁻¹ (rel. uncertainty ±2%, primary flow meter DryCal DC-2, Bios International Corp., USA) 49.66% CH₄ in N₂ (rel. uncertainty ±1%); 598 mL min⁻¹ (rel.
uncertainty ±2%, primary flow meter DryCal DC-2, Bios International Corp., USA) 39.86% N₂O in N₂ (rel. uncertainty ±1%). Flows were normalized to standard conditions (0°C, 1013 mbar).

Predicted CH₄ and N₂O emissions and the respective uncertainties are calculated from the concentration and the volume flow of the target gas. Experimentally determined CH₄ and N₂O emissions are calculated from analysed SF₆ and target gas concentrations and the mass flow of SF₆ into the section according to Eq. (1). The SF₆ mass flow is determined from the concentration and the flow (100 mL min⁻¹) of the distributed tracer gas, divided by the molar volume (Vₐ = 22.414 L mol⁻¹) and multiplied with its molecular mass (146.05 g mol⁻¹). Uncertainties of the experimentally determined CH₄ and N₂O mass flow emissions are estimated from uncertainties in the SF₆ mass flow and the analytical uncertainties in SF₆, CH₄ and N₂O determination.

2.4.5 Sensitivity of the tracer ratio method

The sensitivity of the tracer ratio method is assessed based on an experiment, where tracer gas (SF₆) is dosed into an empty (without cattle) and carefully cleaned experimental area using the permanently installed grid of critical orifices (Fig. 3). Over four days gas is sampled from this section, SF₆ and target gas (NH₃, CH₄, CO₂, N₂O) concentrations are analyzed, background corrected and integrative emissions calculated according to Eq. (1). The detected target gas emissions are caused by several parameters, including the analytical precision, “non-perfect” background correction estimates introducing an offset in emission estimates and residual emissions from the cleaned but previously used shed. In this manuscript target gas emissions of the empty housing are
used as a practical approach to describe the sensitivity of the trace ratio method in relation to emissions under normal operation of the housing (e.g. 20 cows). Residual emissions from the shed, however, display baseline emissions and do not impair the sensitivity of the chosen approach. In addition, NH₃ passive sampler measurements were conducted from 3 to 8 July 2015 in the housing prior to the first move-in with the cows (21.7.2015) to test the suitability of the NH₃ background correction.

2.4.6 Cross-contamination between experimental sections

Cross-contamination between experimental sections is assessed with an experiment dosing constant flows (100 mL min⁻¹) of both tracer gases (SF₆, SF₅CF₃) in individual areas under normal operation of the housing. Over four days, gas is sampled from both sections, and the tracer gas concentrations are analyzed by GC-ECD and corrected for concentrations in background air. The tracer gas concentrations in the respective other area, called cross-contamination, are then interpreted with respect to experimental conditions, e.g. milking time where cows were in the center section, wind speed, and wind direction.
3. Results and discussion

Within this section, the basic assumptions of the dual tracer ratio method are tested, and performance characteristics for future emission measurements at the experimental dairy housing are identified and discussed.

3.1 Equivalence of tracer gases

SF₆ and SF₅CF₃ concentrations exhibit a comparable temporal trend indicating that both tracers distribute similarly and are analyzed reliably by GC-ECD (Fig. 4). Variations in tracer gas concentrations in the course of the day are attributed to changes in ventilation conditions (e.g. wind speed) affecting the dilution with ambient unpolluted air. SF₆ / SF₅CF₃ concentration ratios calculated for individual 10 minute values show small temporary variations of 1.03 ± 0.02 (±1 SD), while daily averaged values are distinctly more stable (1.03 ± 0.002). The temporal variability of the analyzed 10 minutes SF₆ / SF₅CF₃ ratios might be due to temporal fluctuations in the tracer gas flows or variations in tracer gas analysis. Experimentally determined SF₆ / SF₅CF₃ concentration ratios exhibit only a very small systematic offset from the predicted value (1.02 ± 0.05), well within their estimated uncertainties, indicating, that both tracers can be considered as equivalent for the chosen experimental setup.
Fig. 4. SF$_6$ and SF$_5$CF$_3$ concentrations show a comparable temporal pattern when dosed through the same tubing into one housing section of the experimental dairy housing. Daily averaged SF$_6$ / SF$_5$CF$_3$ ratios (red points, 1.03 ± 0.002) agree with predicted values (1.02 ± 0.05) within their uncertainties indicating equivalence of both tracer gases (a). Plotting concentrations of SF$_5$CF$_3$ versus SF$_6$ indicates equivalence of both tracer gases for all wind speeds (b). All indicated uncertainties are ±1 SD.

3.2 Suitability of tracer ratio method to quantify areal and point emission sources

Dosing a second tracer gas (SF$_5$CF$_3$) via an additional, in-between grid of orifices results in larger temporal variations of SF$_6$ / SF$_5$CF$_3$ concentration ratio values (Fig. 5) than dosing through the same orifices. In addition, the temporal variability of 10 minutes averaged values increased from areal dosing (closed curtains: 0.13; open curtains: 0.12, 1 SD) to dosing as a point source (0.24). Both effects can be rationalized by incomplete mixing (limited mimicking) of the two tracer gases induced by spatial separation of the SF$_6$ and SF$_5$CF$_3$ dosing orifices. This may be less severe for actual emission measurements where the sources (e.g. NH$_3$) and the tracer gas dosing are less spatially separated. Daily averaged SF$_6$ / SF$_5$CF$_3$ concentration ratios (areal source: closed curtains: 1.06 ± 0.05, Fig. 5 A - B, open curtains: 1.01 ± 0.03, Fig. 5 C - D, point source: 0.98
± 0.07, Fig. 5 E - F), agree with the predicted ratio (1.02 ± 0.05) well within their uncertainty limits. This indicates that the applied tracer ratio method is appropriate to quantify daily averaged mass flow emissions of both areal and point sources with low uncertainty. The experiment with point emission source represents a worst case scenario, as the number of point sources, e.g. cows emitting CH₄, in the housing under realistic operating is typically 20, much higher than the five orifices employed in the test scenario.
Fig. 5. SF₆ and SF₅CF₃ concentrations as well as concentration ratios in the course of three or four measuring days. Daily averaged SF₆ / SF₅CF₃ concentration ratios for areal emission sources and closed (1.06 ± 0.05, a, b), open curtains (1.01 ± 0.03, c, d) as well as point emission sources (0.97 ± 0.07, e, f) exhibit agreement with the predicted values (1.02 ± 0.05) within uncertainty limits. Temporal variations of individual measurements increase from areal to point dosing of the target substance due to stronger spatial separation. All indicated uncertainties are ±1 SD.
Our results agree with observations of Mendes et al. (2015), who reported homogeneous mixing of an artificial tracer gas (SF₆) with two target gases (CO₂, NH₃) above the animal occupied zone (> 2 m height). However, in contrast to their experiments, which rely on individual bag and impinger measurements (seven samples per height), our study is based on real-time analyzers, which enables temporal averaging and allows interpretation of data with respect to different ventilation conditions (e.g. wind speeds). Similar to our results, the study of Demmers et al. (2001) displayed good pollutant recovery (105 - 108 %), but only for low wind speeds. In contrast to our setup, the tracer gas was distributed as a point or line source, and gas sampling was conducted at individual spots rather than in a grid over the whole emitting area. This may well explain that Demmers et al. (2001) observed substantial deviations of mass flow emissions for high wind speeds (94-122 %), which they attributed to inappropriate positioning of the sampling and tracer gas dosing points, as well as to enhanced background concentrations. In summary, the presented areal tracer gas dosing and multipoint sampling has proven to be a very robust approach to quantify mass flow emissions of both point and areal emissions sources from a naturally ventilated housing.

3.3 Accuracy of the tracer ratio method to quantify GHG emissions

Daily averaged CH₄ and N₂O mass flows determined with the tracer ratio method (920 ± 51 g d⁻¹ CH₄, 604 ± 44 g d⁻¹ N₂O, ±1 SD) agree with the predicted values (952 ± 20 g d⁻¹ CH₄, 674 ± 14 g d⁻¹ N₂O) within their expanded uncertainty limits (Fig. 6). The temporal variability of daily average values and individual 10 min measurements (920 ± 242 g d⁻¹ CH₄, 604 ± 224 g d⁻¹ N₂O) is
satisfactory, but higher than for SF₅CF₃ dosing. This indicates, that in addition
to differences in dosing schemes between tracer (SF₆) and target gas (CH₄,
N₂O, SF₅CF₃), target gas distribution and analysis of the two GHGs might be
impaired by additional parameters. The temporal variability of N₂O and CH₄
mass flow emissions, as compared to SF₅CF₃, might be enhanced due to
differences in gas density of the target components (N₂O: 2.0 g l⁻¹, CH₄: 0.7 g
l⁻¹) compared to air (1.3 g l⁻¹) or different response times of the analysers (GC –
ECD: SF₆, SF₅CF₃; QCLAS + Nafion dryer: N₂O; CRDS: CH₄). Both effects do
not apply for SF₅CF₃, which was analysed simultaneously with SF₆ in the
identical gas samples and highly diluted offering similar density than air. These
effects, however, cannot explain the observed systematic low recovery for CH₄
(-3 %) and N₂O (-10 %) mass flow emissions, compared to predicted values.
One plausible explanation for this might be that the gas specific correction
factors of the mass flow controllers used for CH₄ and N₂O addition, and
determined prior to the experiments with a primary flow meter, were not valid
under the experimental conditions (high outlet pressure).
Fig. 6. Concentration of SF₆, CH₄ and emission of CH₄ (a) as well as concentration of SF₆, N₂O and emission of N₂O (b) during three measuring days. Daily mean CH₄ and N₂O emissions are consistent with the mass flows of both gases dosed into the experimental sections, within their uncertainty limits. Indicated uncertainties are equivalent to ±1 SD.

In summary, the observed recovery (90 – 97%) for GHG mass emissions, determined with the implemented tracer ratio method, is superior to the few available validation studies published so far (Demmers et al., 2001; Calvet et al., 2013; Ogink et al., 2013). The uncertainty for gas emissions from mechanically ventilated livestock buildings, which are supposed to provide highest data reliability, is expected to be at best 10 % of the measured value (Calvet et al., 2013). For natural ventilated buildings the uncertainty for the determination of the ventilation rate alone is estimated to be between 10 % for tracer techniques and up to 40 or even 100 % for CO₂, heat or moisture balances, CFD calculations or pressure difference methods. The selection of gas sampling locations, effective dosing of tracers near emitting surfaces and the detection of inlets and outlets were identified as most critical parameters for improving measurement accuracy of the tracer gas approach (Calvet et al., 2013; Ogink et al., 2013). The combination of areal tracer gas dosing and
multipoint sampling, background correction, and high precision analysis of tracer and target substances in the present study significantly reduced the uncertainty of the determined gas emissions. A further reduction in uncertainty can be expected when calculating relative emissions of a treatment to a reference area.

For NH₃ the above approach was not adapted, due to the high toxicity of the gas and well known adsorption phenomena especially on wetted surfaces (ground, walls, ceiling). Alternatively, quantitative transfer of NH₃ through the sampling line was tested by purging the line with ultrapure water and analysis of the effluent for NH₄⁺ by ion chromatography. The residual NH₄⁺ in the sample line was always below 2 % of the cumulative NH₃. In addition, the accuracy of the laser spectroscopic analytical technique for NH₃ was tested against the manual reference method for emission measurements of NH₃ and gaseous ammonium compounds (VDI, 2017), absorption in aqueous H₂SO₄ and NH₄⁺ analysis by ion chromatography. Results by the reference method were 2 - 12 % higher, probably due to the inclusion of gaseous ammonium compounds (data not shown).

3.4 Sensitivity of the tracer ratio method

For CO₂, background corrected emissions in the empty (without cattle) and cleaned experimental dairy housing were \(-0.06 \pm 1.5 \text{ kg d}^{-1}\) (average daily value \(\pm 1 \text{ SD}\)), compared to 200 - 300 kg d\(^{-1}\) CO₂ under typical measurement conditions, with 20 cows in the housing. As illustrated in Fig. 7, the sensitivity of the tracer ratio method is mainly given by the capability for background
correction, i.e. to separate and subtract emissions in the close vicinity of the housing. This is especially important for calm nights with CO₂ accumulation in the nocturnal boundary layer, most probably due to emissions from soils in the surrounding of the housing (Mohn et al., 2008).

For CH₄, N₂O and NH₃, emissions in the empty housing were 21.0 ± 30.0 g d⁻¹ CH₄, 4.5 ± 1.3 g d⁻¹ N₂O and 29.5 ± 4.3 g d⁻¹ NH₃, indicating remaining emissions in the building or in the close vicinity, which cannot be eliminated by the background correction. This is visualized in Fig. 7, where the CH₄ concentration in the housing is clearly higher than at the background site. Emissions in the housing might be due to residual soiling of surfaces (e.g. straw mattresses) in the building, or remains of slurry in the channel or storage. Therefore, in this specific setup, residual, i.e. baseline emissions rather than an
analytical detection limit given by the tracer ratio method itself dominate the sensitivity of the analytical concept. Compared to emissions under typical measurement conditions, with 20 cows in the housing (8000-9000 g d\(^{-1}\) CH\(_4\), 600–900 g d\(^{-1}\) NH\(_3\), 4-5 g d\(^{-1}\) N\(_2\)O), baseline emissions are below 1 % for CH\(_4\), 3-5 % for NH\(_3\) but up to 100 % for N\(_2\)O. Therefore, we conclude that the tracer ratio method with background correction, as it was employed in this study, is appropriate to determine CO\(_2\), CH\(_4\) and NH\(_3\) mass emissions from the housing, but N\(_2\)O emissions are rather small and dominated by miscellaneous sources other than dairy cows and freshly polluted surfaces (Wolf et al., 2015). The suitability of the background measurement site was monitored by the analysis of SF\(_6\) and SF\(_5\)CF\(_3\), which would indicate the influence of housing emissions at the background location.

3.5 Cross-contamination between experimental sections

One feature of the dual tracer approach is that cross-contaminations between experimental areas are readily apparent by enhanced concentrations of the tracer gas (SF\(_6\), SF\(_5\)CF\(_3\)) in the respective other section. At wind speeds above 2 m s\(^{-1}\) tracer gas concentrations in the dosing area are around 100 – 400 ppt and mostly below detection limit in the other section, while concentrations increase for lower wind speeds above 1000 ppt for the dosing and 20-40 ppt in the second experimental area (Fig. 8). From these observations it can be concluded that cross-contamination between sections is in the lower percentage range for both high and low wind speeds irrespective of the wind direction. Moreover, this information is available by default as a quality control for every future measuring campaign to assure the validity of the data. If cross-
contamination between both experimental sections exceeds a preset target value (e.g. 10%), the respective data could be flagged and either filtered out or corrected.

Fig. 8. Tracer gas concentrations in the dosing section (filled symbols) and in the respective other housing section (open symbols) indicating minimal cross-contamination between experimental areas. Dislocation of tracer gases was only observed for low wind speeds irrespective of the wind direction.

4. Conclusion

This manuscript describes the design and construction of a naturally ventilated experimental dairy housing for the progressive development and testing of NH₃ and GHG reduction strategies. The building consists of two spatially separated housing sections, a treatment and a reference area, which allows comparative measurement conditions (e.g. climatic conditions) at practical scale. To quantify mass emissions of NH₃, CH₄, CO₂, and N₂O a tracer ratio method with areal
dosing of tracer gases and multipoint sampling as well as real-time analysis of tracer and target gases was implemented. Different, but equivalent tracer gases (SF₆, SF₅CF₃) are used for the treatment and reference section to trace cross-contamination. The areal tracer gas dosing was successfully validated for its suitability to mimic areal and point emission sources, with the temporal variability of the second being higher due to not completely congruent spatial areas. The accuracy of the tracer ratio method was demonstrated by CH₄ and N₂O addition experiments and the uncertainty of this approach shown to be in the 3-10 % range superior to existing alternative approaches. The sensitivity of the tracer ratio method was studied in the empty housing and shown to be sufficiently high to determine NH₃, CH₄ and CO₂ mass flow emissions. Cross-contamination between the experimental sections of the housing is monitored on a routine basis but was shown to be below the detection limit or in the low percentage range for the relevant meteorological conditions. In summary, the experimental dairy housing provides a unique platform to reliably quantify mass flow emissions of NH₃ and the GHGs from a naturally ventilated dairy housing and quantify the reduction potential of mitigation options.

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