1   **RESEARCH ARTICLE**

2   **A dual tracer ratio method for comparative emission**

3   **measurements in an experimental dairy housing**

4   Joachim Mohn[a, *], Kerstin Zeyer[a], Margret Keck[b], Markus Keller[b], Michael

5   Zähner[b], Jernej Poteko[b, c], Lukas Emmenegger[a], and Sabine Schrade[b]

6   [a] Laboratory for Air Pollution / Environmental Technology, Empa,

7   Überlandstrasse 129, 8600 Dübendorf, Switzerland

8   [b] Agroscope, Tänikon 1, 8356 Ettenhausen, Switzerland

9   [c] Institute of Agricultural Sciences, Animal Nutrition, ETH Zurich,

10   Universitätstrasse 2, 8092 Zürich, Switzerland

11   * Corresponding author

12   E-mail addresses:

13   joachim.mohn@empa.ch (J. Mohn),

14   kerstin.zeyer@empa.ch (K. Zeyer),

15   margret.keck@agroscope.admin.ch (M. Keck),

16   markus.keller@agroscope.admin.ch (M. Keller),

17   michael.zaehner@agroscope.admin.ch (M. Zähner),

18   jernej.poteko@agroscope.admin.ch (J. Poteko),

19   lukas.emmenegger@empa.ch (L. Emmenegger),

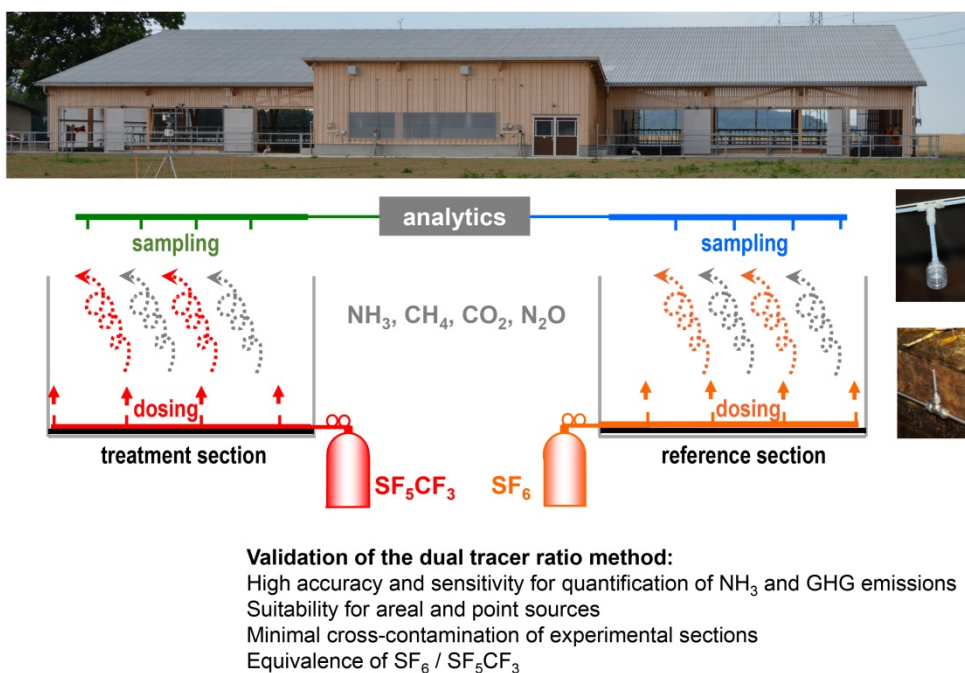20   sabine.schrade@agroscope.admin.ch (S. Schrade).

21

Abstract

Agriculture, and in particular dairy farming, is an important source of ammonia (NH_3) 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 SF_6, trifluoromethylsulphur pentafluoride SF_5CF_3) 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 NH_3 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 NH_3, methane (CH_4) and carbon dioxide (CO_2), 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

45 the reduction potential of mitigation measures for NH_3, GHGs and potentially

46 other pollutants.

49 **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_5CF_3

50

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_2O) 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_2O 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,

75   showed large variations in daily mean NH_3 emissions, ranging from 6 to 67

76   g LU^{-1} d^{-1} (LU livestock unit, 1 LU = 500 kg live weight). Here, the main

77   explanatory variables were climatic conditions (temperature, wind speed) and

78   urea content in the milk (Schrade et al., 2012). Given this pronounced

79   variability, it would be highly beneficial to evaluate the reduction potential of

80   mitigation measures in relation to a reference system with comparable climatic,

81   herd and nutritional conditions.

82   Several approaches have been used to determine NH_3 and GHG emissions

83   from naturally-ventilated dairy housing, most of them using a tracer technique

84   with known source strength and measuring its concentration in the housing with

85   respect to background conditions (Teye and Hautala, 2007). The involved tracer

86   can be either artificial (e.g. SF_6), or natural / metabolic such as heat (Von

87   Wachenfelt et al., 2001; CIGR, 2002) or CO_2 produced by the animals

88   (Pedersen et al., 1998; Pedersen et al., 2008; Bai et al., 2016). CO_2 and heat

89   balance methods are cheap, rapidly deployable methods to determine

90   ventilation rates at a practical scale but they are based on a number of general

91   assumptions (e.g. respiration quotient) which strongly limit their accuracy. More

92   specifically, these balance methods require a minimal CO_2 concentration or

93   temperature difference between the inside and the outdoor air (Pedersen et al.,

94   1998). This makes them unsuited for naturally ventilated housings with large

95   openings, and housing systems with an outdoor exercise area.

96   A well-established approach to determine ventilation rates in buildings is to

97   dose an artificial tracer gas (Sherman, 1990). These methods are also

98   applicable to naturally ventilated housings (Calvet et al., 2013) and areal

99 sources like outdoor exercise areas and open slurry storages (Griffith et al.,

100 2008; Keck et al., 2011; Schrade et al., 2012) because the mass flow of the

101 tracer can be adapted to the dilution ratio. Several variants of tracer ratio

102 methods have been used in naturally ventilated cattle housings (see Table S1 in

103 the supplementary file), differing in the choice of the tracer gas (e.g. SF_6,

104 carbon monoxide CO or Krypton-85 ^{85}Kr), the positioning of tracer gas release

105 and sampling system as well as in the dosing procedure (concentration decay

106 versus constant tracer gas release). The most frequently used tracer gas for

107 emission measurements in livestock husbandry is SF_6. It is chemically

108 extremely stable, non-toxic, and has a background concentration in ambient air

109 of only a few ppt. Its molecular mass is about five times higher than ambient air.

110 Therefore, it is typically diluted, i.e. mixed with compressed air or nitrogen to

111 approach the density of ambient air (e.g. Berry et al., 2005; Schrade et al.,

112 2012; Schiefler, 2013; Mendes et al., 2015; Edouard et al., 2016). In addition to

113 SF_6, Schrade et al. (2007) used SF_5CF_3, which has very similar characteristics

114 as SF_6, as a second tracer to distinguish between indoor and outdoor

115 emissions.

116 To calculate accurate emission values, however, several metrics must be

117 evaluated: most importantly, the tracer gas release must sufficiently mimic the

118 release of the target substances from surfaces (e.g. NH_3) or animals (CH_4,

119 CO_2), which can be achieved by tracer gas dosing next to the emitting areas or

120 objects (Demmers et al., 1998; Schneider et al., 2006; Schrade et al., 2012;

121 Mendes et al., 2015; Edouard et al., 2016). Second, the sample must be

122 representative, preferably homogenously mixed, and independent of the wind

123   situation, which is better achieved when using pooled sampling (Mendes et al.,

124   2015; Edouard et al., 2016).

125   In this study, a dual tracer ratio method was implemented in a new experimental

126   dairy housing for comparative emission measurements at Agroscope, Tänikon.

127   The aim of the study was to validate the optimized tracer ratio method with

128   respect to the equivalence of the two tracer gases and the capability of the

129   developed technique to quantify areal and point emission sources. In addition,

130   the accuracy and sensitivity for mass flow emissions of NH_3 and GHGs was

131   tested and finally the potential to trace cross-contamination between

132   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 Istruments, GB) at 1.5 and 5 m height, indicating mostly south-westerly (47% of time) and north-easterly (30%) wind directions (Fig. 1).
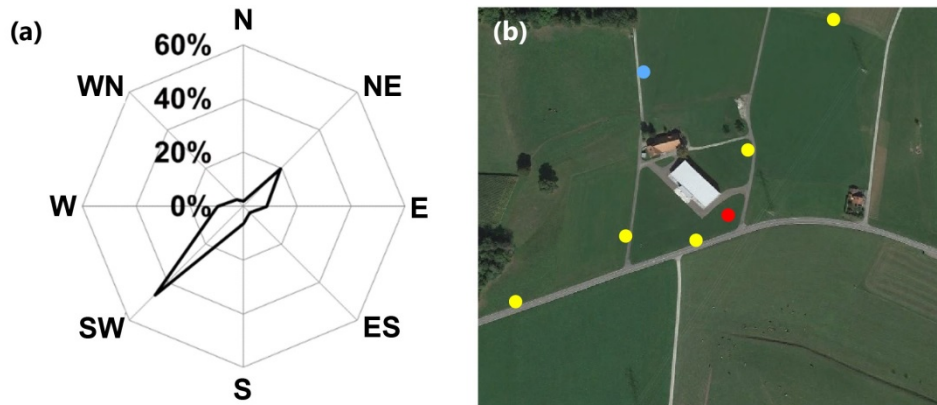
147

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 NH_3 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.
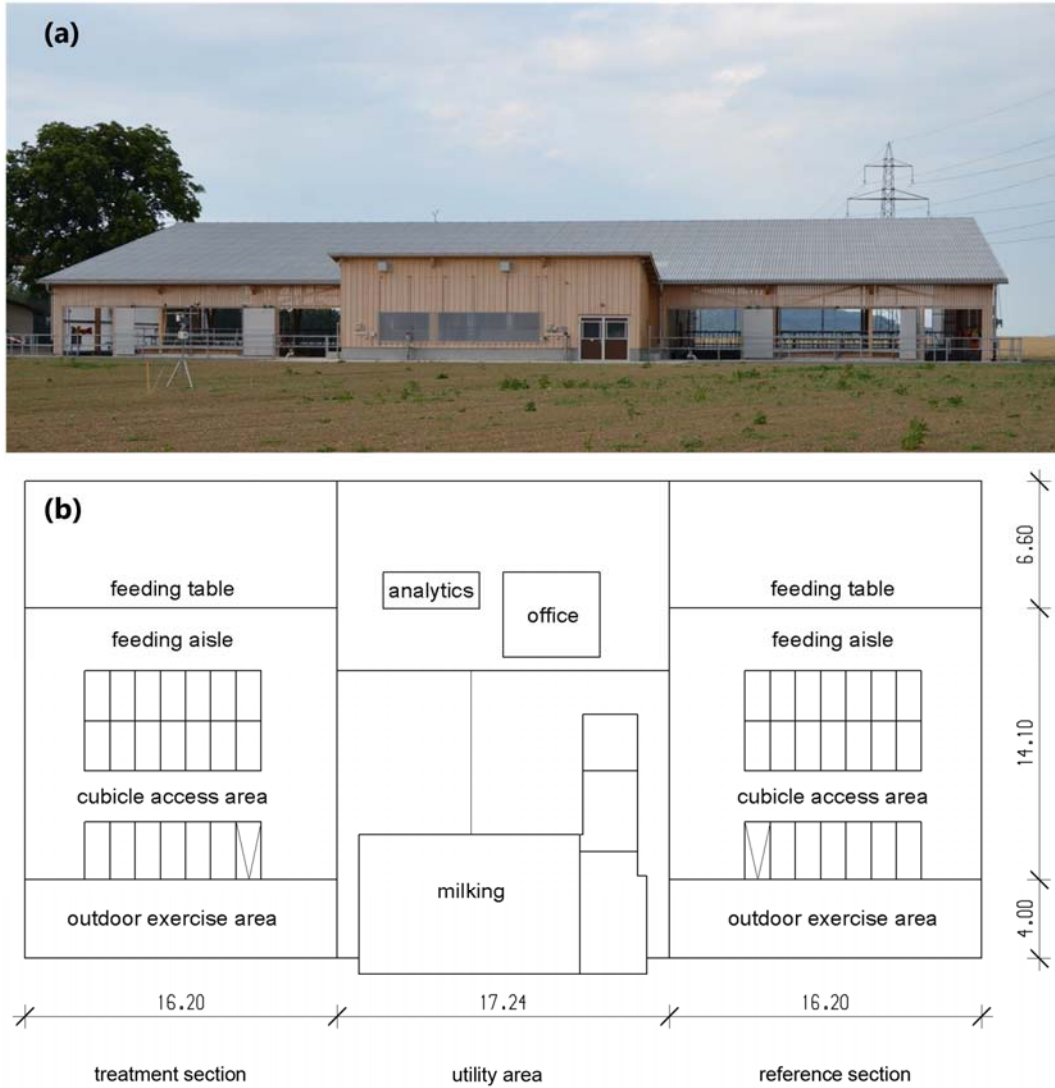
164

165

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).

169 *2.2   Implementation of the dual tracer gas ratio method*

170 *2.2.1 Tracer gas release*

171 To determine emissions under natural ventilation, a tracer ratio method with two

172 different tracer gases SF_6 and SF_5CF_3 and constant dosing is applied (Schrade

173 et al., 2012). To trace cross contamination between experimental sections,

174 individual tracer gases are applied to reference and treatment area (Table 1).

175 Constant flows of the diluted tracer gases (2000 ppm SF_6 or SF_5CF_3 in synthetic

176 air, rel. uncertainty ±2%, Messer Schweiz AG, Switzerland) are adjusted using

177 mass flow controllers (GSC, 2 L min^{-1}, high performance, uncertainty ±0.3 % of

178 maximum flow, Vögtlin Instruments Inc., Switzerland). The tracer gases are

179 directed to the experimental sections via stainless steel tubing (ID 4 mm,

180 Interalloy, Switzerland). SF_6 impurities in the SF_5CF_3 tracer (1% SF_6 in SF_5CF_3,

181 absolute   uncertainty   ±1%)   specified   by   the SF_5CF_3 manufacturer

182 (Fluorochemika, Poland SP.Z00.) are considered during data analysis. Tracer

183 gas flows are set according to ventilation conditions (curtains open / closed etc.)

184 to adjust analysed tracer gas concentrations in an optimal range (> 50 ppt,

185 <1500 ppt SF_6 and SF_5CF_3). Depending on the adjusted flow of the diluted

186 tracer gases, measurement campaigns of several weeks up to months are

187 feasible with one high pressure cylinder. Within the experimental areas, tracer

188 gases are distributed homogeneously using 18 critical orifices (hole diameter 30

189 µm, Lenox Laser Inc., USA) mounted at ground level (10 to 15 cm above floor)

190 equidistantly next to the walking aisles to mimic the emission sources (Fig. 3).

191 Five additional orifices are installed in the outdoor exercise area and deployed

192 depending on the experimental design, reflecting the proportionality of indoor

193 and outdoor emissions (Schrade, 2009). Flow rates for individual orifices are

194 monitored before and after every measuring campaign using a mass flow meter

195 (GSM, Vögtlin Instruments Inc., Switzerland), and individual orifices agreed

196 within ±10% (one standard deviation (SD)). Stainless steel tubes and critical

197 orifices are protected with metal profiles from damage by animals and

198 contamination with excrements and dirt.

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

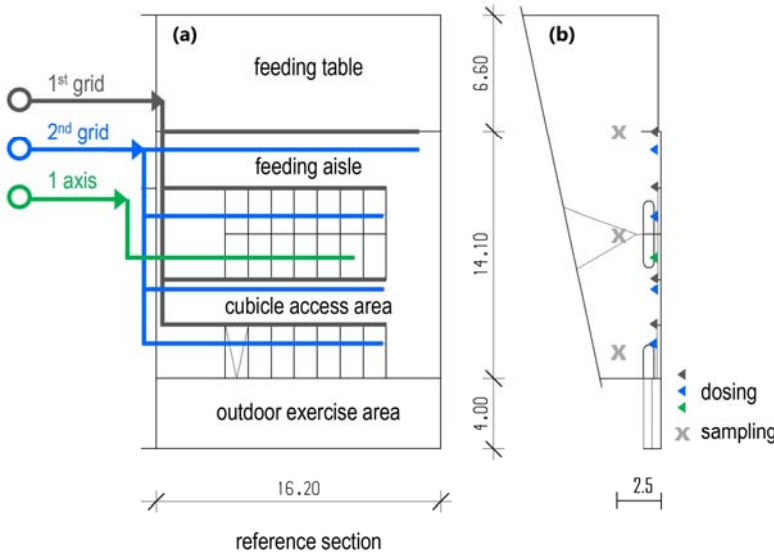|	Reference section 1	Centre section	Treatment section 2	Background
Tracer gas dosing	SF_5CF_3	-	SF_6	-
Tracer gas sampling	SF_6, SF_5CF_3	SF_6, SF_5CF_3	SF_6, SF_5CF_3	SF_6, SF_5CF_3
Target gas sampling	NH_3, CH_4, CO_2, N_2O	NH_3, CH_4, CO_2, N_2O	NH_3, CH_4, CO_2, N_2O	NH_3, CH_4, CO_2, N_2O

202

203

204 Fig. 3. Implementation of the dual tracer ratio method in the experimental dairy housing. The dosing grids
205 used to distribute the tracer gases are shown for the reference section (a). Grid 1, drawn in grey, with 18
206 capillaries is the standard grid used to distribute tracer gases. Grid 2 and 3, drawn in blue and green, with
207 18 and 5 capillaries, respectively are applied in the validation experiments, described in Table S2 in the
208 supplementary file, only. Cross section through the building showing the height of the tracer gas dosing
209 grids (colour coding for grid 1-3) and the air sampling grid installed at 2.5 m height with 24 capillaries (b).

210   *2.2.2 Gas sampling*

211   Integrative air samples in each section are collected using 24 glass orifices (2.5

212   m above ground, hole diameter 250 μm, Thermo-Instruments, Germany and

213   Louwers, The Netherlands) protected with PTFE membrane filters (TE 38, 37

214   mm, GE Whatman Plc, UK) and directed via PTFE tubes (OD 8 mm,

215   Maagtechnic AG, Switzerland) to an air-conditioned trailer placed in the utility

216   area (Fig. 2). Six additional orifices are installed in the outdoor exercise area

217   and used depending on the experimental design. Flow rates for individual

218   orifices are monitored before and after every measuring period using a mass

219   flow meter (GSM, Vögtlin Instruments Inc., Switzerland), and individual orifices

220   agreed within ±10% (±1 SD).

221   In addition to air sampling from both experimental sections of the housing,

222   measuring gas is collected from the utility area in the centre section (Fig. 2), as

223   well as the background site around 30 m south-east, i.e. perpendicular to the

224   prevailing wind direction, of the experimental housing (Fig. 1). The two

225   additional sites are equipped with seven (utility area) and eight (background)

226   orifices. Sample gas from these locations (reference and treatment area, utility

227   area, background site) is continuously drawn using four separate membrane

228   pumps (ME 2C, Vacuubrand, Germany). Air flows are around 10 L min^{-1} for

229   reference and treatment area and around 2.5 L min^{-1} for the centre section and

230   the background site and delivered to separate 2 L Teflon flasks (Semadeni AG,

231   Switzerland), which serve as mixing containers and pressure compensation

232   vessels. Gas samples from the Teflon flasks are extracted sequentially, 10 min

233   per sample, using a gauge head selector switch (10 position common outlet

13

234 flow-path selector, EUTA-2LSC10MWESLF, Vici AG International, Switzerland)

235 and directed to the analyzers). The operation of the selector switch, and thus

236 the measuring sequence, is controlled via the "external valve sequencer option"

237 of the GHG CRDS analyzer (model G2301, Picarro Inc., USA). The applied

238 repetitive measuring sequence (10 minutes per setting) for the respective

239 experiment is given in Table S2 in the supplementary file.

240 *2.2.3 Gas analysis*

241 Air samples are analysed for SF_6 and SF_5CF_3 by gas chromatography with

242 electron capture detection (GC-ECD, 7890A, Agilent Technologies AG,

243 Switzerland). A GC configuration with custom-made molecular-sieve 5Å column

244 (60 / 80 mesh, ID = 3.7 mm, L = 4 m, Applied Science Inc., USA), a HayeSep Q

245 column (80 / 100 mesh, ID = 3.7 mm, L = 50 cm, Sigma Aldrich Inc.,

246 Switzerland) and a carrier gas flow of 50 mL min^{-1} (N_2 6.0, Messer Schweiz AG,

247 Switzerland) are used. Operating temperatures are 300 °C for the ECD, 120 °C

248 for the column and 120 °C for the injector. The detection limits are 2 ppt for both

249 SF_6 and SF_5CF_3. Low analytical detection limits are required to avoid extensive

250 dosing and emissions of these potent greenhouse gases. In the current setup

251 the greenhouse warming potential (GWP) of the added diluted SF_6 and SF_5CF_3

252 tracer gases was substantially lower than the GWP of animal emissions from

253 the housing. Tracer gas concentrations (SF_6, SF_5CF_3) are referenced against

254 commercial standard gases (102.1 ± 2 ppt SF_6, 848 ± 17 ppt SF_6, Tracertech

255 GmbH, Germany, 14.8 ± 0.3 ppm SF_5CF_3, Carbagas AG, Switzerland). As

256 commercial SF_5CF_3 standards are not available at low concentrations, higher

257 concentration standards are diluted and the dilution ratio determined using a

258   CH_4 bootstrap gas. In addition, tracer gas concentrations are referenced to the

259   SF_6 scale provided by NOAA GMD ESRL and a gravimetric standard for SF_6

260   and SF_5CF_3 provided by University of Bristol.

261   NH_3, CH_4 and CO_2 concentrations are analysed with two cavity ring-down

262   spectrometers (CRDS1, NH_3: model G2103, CRDS2, CH_4, CO_2: model G2301,

263   Picarro Inc., USA), N_2O and CO are measured with a quantum cascade laser

264   absorption spectrometer (QCLAS, QC-TILDAS-CS, Aerodyne Inc., USA) after

265   drying with a Nafion permeation device (PD-100T-72, Perma Pure, USA). The

266   precisions of the laser spectrometers, according to manufacturer specification

267   are: < 0.07 ppb NH_3, < 0.22 ppb CH_4, < 25 ppb CO_2, < 0.01 ppb N_2O and < 0.05

268   ppb CO. CH_4, CO_2 and N_2O concentrations are referenced to the respective

269   scales provided by NOAA GMD ESRL via regular (every 12 hours) analysis of

270   pressurized air (727.2 ± 0.04 ppm CO_2, 11537.0 ± 21.7 ppb CH_4, 351.0 ± 0.11

271   ppb N_2O, ± 1 SD, n = 3) calibrated by WCC-Empa (Zellweger et al., 2012;

272   Zellweger et al., 2016). NH_3 measurements are referenced to commercial gas

273   standards (20 ppm NH_3, Messer Schweiz AG, Switzerland) diluted with

274   synthetic air (Messer Schweiz AG, Switzerland). The exact NH_3 concentration in

275   the diluted standards is confirmed by absorption in diluted sulfuric acid and

276   subsequent ion chromatography (ICS 3000, Thermo Scientific™ Dionex™ ion

277   chromatography, Switzerland) (Mohn et al., 2004).

278   To confine tracer (SF_6, SF_5CF_3) and target gas (NH_3, CH_4, CO_2, N_2O)

279   concentration changes to emissions from the experimental dairy housing, a

280   correction for variations in background concentrations was applied. For SF_6 and

281   SF_5CF_3, a constant offset correction was applied (8.0 ppt SF_6, 0.15 ppt

282   SF_5CF_3). While the SF_6 background concentration was determined over a 24

283   hours period in March 2016 (8.0 ± 0.2 ppt), for SF_5CF_3 ambient concentrations

284   are below the analytical detection limit and therefore a literature value was used

285   (Sturges et al., 2012). The validity of stable SF_6 and SF_5CF_3 background

286   concentrations was assured by regular measurements at the background site

287   (Fig. 1). CH_4, CO_2 and N_2O concentrations in the housing were corrected for

288   diurnal changes in background concentrations using a linear spline algorithm.

289   Details on the sampling frequency are given in Table S2 in the supplementary

290   file. For NH_3 correction, a background concentration is determined for the

291   respective measuring period with a NH_3 passive sampler positioned around 100

292   m north-west of the housing (Fig. 1) (Schrade et al., 2012).

293   *2.2.4   Emissions calculation*

294   The quantification of emissions with the tracer ratio method is based on the

295   assumption that the tracer gas (SF_6, SF_5CF_3) behaves in the same way as the

296   target gas (NH_3, GHG) and thus mimics the emitting source (Demmers et al.,

297   2001). The mass flow of the target gas ($\dot{m}_{target}$) is calculated from the ratio of the

298   background corrected target (c_{target}) and tracer gas concentration (c_{tracer}) and the

299   mass flow of the tracer gas ($\dot{m}_{tracer}$) as given in Eq. (1):

300   $$\dot{m}_{target} = \frac{\dot{m}_{tracer} \times c_{target}}{c_{tracer}} \qquad (1)$$

301   *2.3   Wind data measurements*

302   Wind statistics were measured using 3D ultrasonic anemometers measuring at

303   1 Hz (experiments 2.4.2, 2.4.3, 2.4.4, 2.4.5; USA-1-Scientific, METEK,

16

304   Elmshorn, Germany) or 10 Hz (experiments 2.4.1 and 2.4.6 Ultra-sonic

305   Anemometer 3D, Adolf Thies GmbH & Co. KG, Göttingen, Germany) at a height

306   of 10 m, 60 m south-west of the housing. In addition, wind direction and speed

307   were measured in the middle of each experimental section and the outdoor

308   exercise area, at a height of 2.5 m, using 3D ultrasonic anemometers

309   (Ultrasonic Anemometer 3D, Adolf Thies GmbH & Co. KG, Göttingen,

310   Germany).

311   *2.4   Validation experiments*

312   To validate the dual tracer ratio method, targeted experiments were completed

313   to confirm the two tracer gases perform similarly and the method is suitable to

314   quantify areal as well as point emission sources, determine the accuracy and

315   sensitivity of the method for NH_3 and GHG emissions and asses any cross

316   contamination between the experimental sections (Table S2 in the

317   supplementary file). The term "accuracy" defines the closeness of the

318   agreement between the result of a measurement and a true value of the

319   measurand (JCGM, 2008).

320   *2.4.1 Equivalence of tracer gases*

321   This experiment tests the basic assumption of the dual tracer ratio method that

322   both tracer gases (SF_6, SF_5CF_3) distribute similarly and are analyzed reliably by

323   GC-ECD. The general setup and specifications of components are according to

324   2.2, but constant flows of both tracer gases (150 mL min^{-1} SF_6, 150 mL min^{-1}

325   SF_5CF_3) are combined in one stainless steel line, and both tracer gases are

326   distributed with the same set of critical orifices in one experimental area (Fig. 3).

327 Tracer gas concentrations are analyzed by GC-ECD with ten minutes temporal

328 resolution over five consecutive days and interpreted with respect to agreement

329 between the observed and the predicted SF_6 to SF_5CF_3 concentration ratio. The

330 experiment was conducted under normal farming conditions (with cows etc.) to

331 cover the most relevant and challenging experimental settings. The standard

332 deviation of ten minutes and of daily average values are used as a measure for

333 the uncertainty in the observed SF_6 / SF_5CF_3 concentration ratios. Predicted

334 SF_6 to SF_5CF_3 concentration ratios are calculated from tracer gas

335 concentrations and flows taking into consideration manufacturer specification on

336 SF_6 impurities in the SF_5CF_3 tracer. The uncertainty of the predicted SF_6 to

337 SF_5CF_3 concentration ratios is estimated based on the given uncertainty

338 contributions using the laws of error propagation.

339 *2.4.2 Suitability of the tracer ratio method to quantify areal emission sources*

340 To test the suitability of the tracer ratio method to quantitatively assess areal

341 emission sources, SF_6 was used as a tracer, and SF_5CF_3 was dosed into the

342 same experimental section, simulating the areal emission source of a target

343 substance. For the primary tracer gas (SF_6), the permanently installed grid of

344 dosing orifices was applied, while the target substance (SF_5CF_3) was distributed

345 via a second, independent grid with 18 orifices (hole diameter 30 μm, Lenox

346 Laser Inc., USA) (Fig. 3). Flows of both tracer gases (SF_6, SF_5CF_3) were 100

347 mL min^{-1}. Photos indicating the position of the SF_5CF_3 grid are given in the

348 supplementary file (Fig. S1). The experiment was conducted in two variants,

349 each during three to four days, with open and closed curtains, to simulate

350   different ventilation situations. Predicted SF_6 / SF_5CF_3 concentration ratios and

351   uncertainties are calculated and interpreted as detailed in 2.4.1.

352   *2.4.3   Suitability of the tracer ratio method to quantify point emission sources*

353   The suitability of the tracer ratio method to quantify point emission sources is

354   tested in an experiment similar to 2.4.2, but the second tracer gas (SF_5CF_3),

355   used as a target substance to simulate the point emission source, is dosed into

356   the housing with just one tube equipped with five collocated orifices (hole

357   diameter 30 μm, Lenox Laser Inc., USA). Total flows of the two tracer gases

358   (SF_6, SF_5CF_3) were 100 mL min^{-1}. The SF_5CF_3 emission source was positioned

359   in the middle of the experimental section (Fig. 3), as indicated on a photo in the

360   supplementary file (Fig. S2). Predicted SF_6 / SF_5CF_3 concentration ratios and

361   uncertainties are calculated and interpreted as detailed in 2.4.1. Experiments

362   were conducted over three consecutive days.

363   *2.4.4   Accuracy of the tracer ratio method to quantify GHG emissions*

364   Prior to the experiments the housing was thoroughly cleaned to minimize diffuse

365   microbial CH_4 and N_2O release. Nonetheless, there were some remaining

366   activities from slurry storage. SF_6 was distributed homogeneously into one

367   experimental area using the permanently installed grid of critical orifices, the

368   target gas (CH_4 or N_2O) was dosed into the same section via a second,

369   independent grid equipped with 18 orifices (hole diameter 30 μm, Lenox Laser

370   Inc., USA) (Fig. 3). Concentrations and flows of target gases were: 1860 mL

371   min^{-1} (rel. uncertainty ±2%, primary flow meter DryCal DC-2, Bios International

372   Corp., USA) 49.66% CH_4 in N_2 (rel. uncertainty ±1%); 598 mL min^{-1} (rel.

373   uncertainty ±2%, primary flow meter DryCal DC-2, Bios International Corp.,

374   USA) 39.86% N_2O in N_2 (rel. uncertainty ±1%). Flows were normalized to

375   standard conditions (0°C, 1013 mbar).

376   Predicted CH_4 and N_2O emissions and the respective uncertainties are

377   calculated from the concentration and the volume flow of the target gas.

378   Experimentally determined CH_4 and N_2O emissions are calculated from

379   analysed SF_6 and target gas concentrations and the mass flow of SF_6 into the

380   section according to Eq. (1). The SF_6 mass flow is determined from the

381   concentration and the flow (100 mL min^{-1}) of the distributed tracer gas, divided

382   by the molar volume (V_m = 22.414 L mol^{-1}) and multiplied with its molecular

383   mass (146.05 g mol^{-1}). Uncertainties of the experimentally determined CH_4 and

384   N_2O mass flow emissions are estimated from uncertainties in the SF_6 mass flow

385   and the analytical uncertainties in SF_6, CH_4 and N_2O determination

386   *2.4.5 Sensitivity of the tracer ratio method*

387   The sensitivity of the tracer ratio method is assessed based on an experiment,

388   where tracer gas (SF_6) is dosed into an empty (without cattle) and carefully

389   cleaned experimental area using the permanently installed grid of critical

390   orifices (Fig. 3). Over four days gas is sampled from this section, SF_6 and target

391   gas (NH_3, CH_4, CO_2, N_2O) concentrations are analyzed, background corrected

392   and integrative emissions calculated according to Eq. (1). The detected target

393   gas emissions are caused by several parameters, including the analytical

394   precision, "non-perfect" background correction estimates introducing an offset in

395   emission estimates and residual emissions from the cleaned but previously

396   used shed. In this manuscript target gas emissions of the empty housing are

397   used as a practical approach to describe the sensitivity of the trace ratio method

398   in relation to emissions under normal operation of the housing (e.g. 20 cows).

399   Residual emissions from the shed, however, display baseline emissions and do

400   not impair the sensitivity of the chosen approach. In addition, NH_3 passive

401   sampler measurements were conducted from 3 to 8 July 2015 in the housing

402   prior to the first move-in with the cows (21.7.2015) to test the suitability of the

403   NH_3 background correction.

404   *2.4.6 Cross-contamination between experimental sections*

405   Cross-contamination between experimental sections is assessed with an

406   experiment dosing constant flows (100 mL min^{-1}) of both tracer gases (SF_6,

407   SF_5CF_3) in individual areas under normal operation of the housing. Over four

408   days, gas is sampled from both sections, and the tracer gas concentrations are

409   analyzed by GC-ECD and corrected for concentrations in background air. The

410   tracer gas concentrations in the respective other area, called cross-

411   contamination, are then interpreted with respect to experimental conditions, e.g.

412   milking time where cows were in the center section, wind speed, and wind

413   direction.

414

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

SF_6 and SF_5CF_3 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. SF_6 / SF_5CF_3 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 SF_6 / SF_5CF_3 ratios might be due to temporal fluctuations in the tracer gas flows or variations in tracer gas analysis. Experimentally determined SF_6 / SF_5CF_3 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.
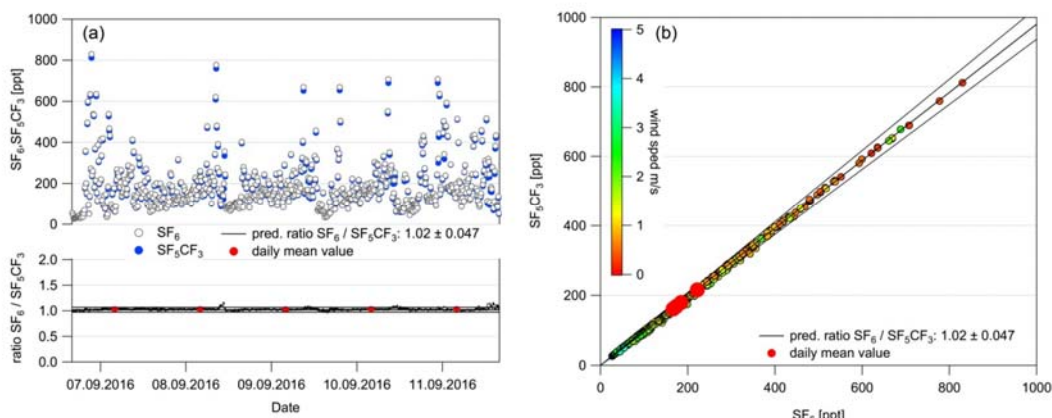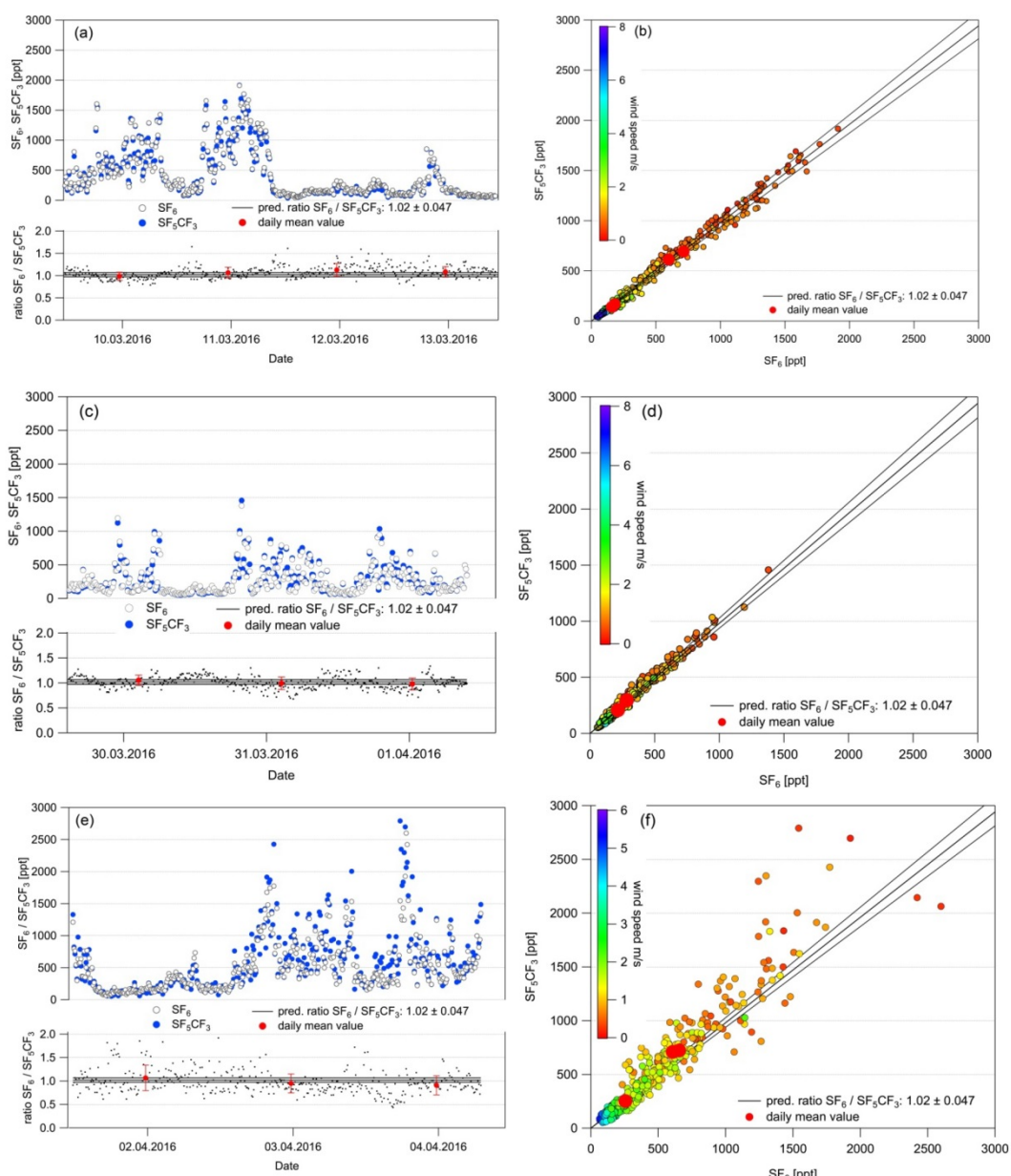
434   Fig. 4. SF_6 and SF_5CF_3 concentrations show a comparable temporal pattern when dosed through the
435   same tubing into one housing section of the experimental dairy housing. Daily averaged SF_6 / SF_5CF_3
436   ratios (red points, 1.03 ± 0.002) agree with predicted values (1.02 ± 0.05) within their uncertainties
437   indicating equivalence of both tracer gases (a). Plotting concentrations of SF_5CF_3 versus SF_6 indicates
438   equivalence of both tracer gases for all wind speeds (b). All indicated uncertainties are ±1 SD.

439   *3.2   Suitability of tracer ratio method to quantify areal and point emission*
440   *sources*

441   Dosing a second tracer gas (SF_5CF_3) via an additional, in-between grid of
442   orifices results in larger temporal variations of SF_6 / SF_5CF_3 concentration ratio
443   values (Fig. 5) than dosing through the same orifices. In addition, the temporal
444   variability of 10 minutes averaged values increased from areal dosing (closed
445   curtains: 0.13; open curtains: 0.12, 1 SD) to dosing as a point source (0.24).
446   Both effects can be rationalized by incomplete mixing (limited mimicking) of the
447   two tracer gases induced by spatial separation of the SF_6 and SF_5CF_3 dosing
448   orifices. This may be less severe for actual emission measurements where the
449   sources (e.g. NH_3) and the tracer gas dosing are less spatially separated. Daily
450   averaged SF_6 / SF_5CF_3 concentration ratios (areal source: closed curtains: 1.06
451   ± 0.05, Fig. 5 A - B, open curtains: 1.01 ± 0.03, Fig. 5 C - D, point source: 0.98

23

452 ± 0.07, Fig. 5 E - F), agree with the predicted ratio (1.02 ± 0.05) well within their

453 uncertainty limits. This indicates that the applied tracer ratio method is

454 appropriate to quantify daily averaged mass flow emissions of both areal and

455 point sources with low uncertainty. The experiment with point emission source

456 represents a worst case scenario, as the number of point sources, e.g. cows

457 emitting CH_4, in the housing under realistic operating is typically 20, much

458 higher than the five orifices employed in the test scenario.

459

460

Fig. 5. SF_6 and SF_5CF_3 concentrations as well as concentration ratios in the course of three or four measuring days. Daily averaged SF_6 / SF_5CF_3 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.

467

468   Our results agree with observations of Mendes et al. (2015), who reported

469   homogeneous mixing of an artificial tracer gas (SF_6) with two target gases

470   (CO_2, NH_3) above the animal occupied zone (> 2 m height). However, in

471   contrast to their experiments, which rely on individual bag and impinger

472   measurements (seven samples per height), our study is based on real-time

473   analyzers, which enables temporal averaging and allows interpretation of data

474   with respect to different ventilation conditions (e.g. wind speeds). Similar to our

475   results, the study of Demmers et al. (2001) displayed good pollutant recovery

476   (105 - 108 %), but only for low wind speeds. In contrast to our setup, the tracer

477   gas was distributed as a point or line source, and gas sampling was conducted

478   at individual spots rather than in a grid over the whole emitting area. This may

479   well explain that Demmers et al. (2001) observed substantial deviations of mass

480   flow emissions for high wind speeds (94-122 %), which they attributed to

481   inappropriate positioning of the sampling and tracer gas dosing points, as well

482   as to enhanced background concentrations. In summary, the presented areal

483   tracer gas dosing and multipoint sampling has proven to be a very robust

484   approach to quantify mass flow emissions of both point and areal emissions

485   sources from a naturally ventilated housing.

486   *3.3   Accuracy of the tracer ratio method to quantify GHG emissions*

487   Daily averaged CH_4 and N_2O mass flows determined with the tracer ratio

488   method (920 ± 51 g d^{-1} CH_4, 604 ± 44 g d^{-1} N_2O, ±1 SD) agree with the

489   predicted values (952 ± 20 g d^{-1} CH_4, 674 ± 14 g d^{-1} N_2O) within their expanded

490   uncertainty limits (Fig. 6). The temporal variability of daily average values and

491   individual 10 min measurements (920 ± 242 g d^{-1} CH_4, 604 ± 224 g d^{-1} N_2O) is

492 satisfactory, but higher than for SF_5CF_3 dosing. This indicates, that in addition

493 to differences in dosing schemes between tracer (SF_6) and target gas (CH_4,

494 N_2O, SF_5CF_3), target gas distribution and analysis of the two GHGs might be

495 impaired by additional parameters. The temporal variability of N_2O and CH_4

496 mass flow emissions, as compared to SF_5CF_3, might be enhanced due to

497 differences in gas density of the target components (N_2O: 2.0 g l^{-1}, CH_4: 0.7 g

498 l^{-1}) compared to air (1.3 g l^{-1}) or different response times of the analysers (GC –

499 ECD: SF_6, SF_5CF_3; QCLAS + Nafion dryer: N_2O; CRDS: CH_4). Both effects do

500 not apply for SF_5CF_3, which was analysed simultaneously with SF_6 in the

501 identical gas samples and highly diluted offering similar density than air. These

502 effects, however, cannot explain the observed systematic low recovery for CH_4

503 (-3 %) and N_2O (-10 %) mass flow emissions, compared to predicted values.

504 One plausible explanation for this might be that the gas specific correction

505 factors of the mass flow controllers used for CH_4 and N_2O addition, and

506 determined prior to the experiments with a primary flow meter, were not valid

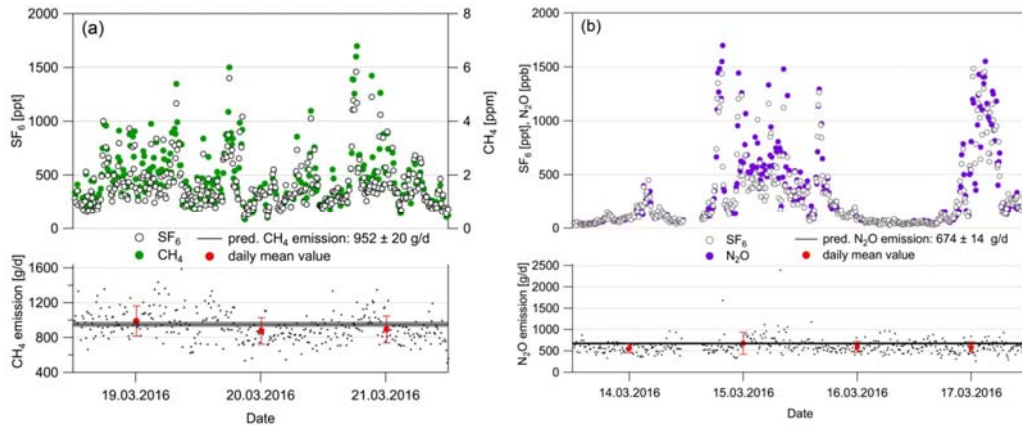507 under the experimental conditions (high outlet pressure).

508

509

Fig. 6. Concentration of SF_6, CH_4 and emission of CH_4 (a) as well as concentration of SF_6, N_2O and

emission of N_2O (b) during three measuring days. Daily mean CH_4 and N_2O 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.

514   In summary, the observed recovery (90 – 97%) for GHG mass emissions,

515   determined with the implemented tracer ratio method, is superior to the few

516   available validation studies published so far (Demmers et al., 2001; Calvet et

517   al., 2013; Ogink et al., 2013). The uncertainty for gas emissions from

518   mechanically ventilated livestock buildings, which are supposed to provide

519   highest data reliability, is expected to be at best 10 % of the measured value

520   (Calvet et al., 2013). For natural ventilated buildings the uncertainty for the

521   determination of the ventilation rate alone is estimated to be between 10 % for

522   tracer techniques and up to 40 or even 100 % for CO_2, heat or moisture

523   balances, CFD calculations or pressure difference methods. The selection of

524   gas sampling locations, effective dosing of tracers near emitting surfaces and

525   the detection of inlets and outlets were identified as most critical parameters for

526   improving measurement accuracy of the tracer gas approach (Calvet et al.,

527   2013; Ogink et al., 2013). The combination of areal tracer gas dosing and

528 multipoint sampling, background correction, and high precision analysis of

529 tracer and target substances in the present study significantly reduced the

530 uncertainty of the determined gas emissions. A further reduction in uncertainty

531 can be expected when calculating relative emissions of a treatment to a

532 reference area.

533 For NH_3 the above approach was not adapted, due to the high toxicity of the

534 gas and well known adsorption phenomena especially on wetted surfaces

535 (ground, walls, ceiling). Alternatively, quantitative transfer of NH_3 through the

536 sampling line was tested by purging the line with ultrapure water and analysis of

537 the effluent for NH_4^+ by ion chromatography. The residual NH_4^+ in the sample

538 line was always below 2 % of the cumulative NH_3. In addition, the accuracy of

539 the laser spectroscopic analytical technique for NH_3 was tested against the

540 manual reference method for emission measurements of NH_3 and gaseous

541 ammonium compounds (VDI, 2017), absorption in aqueous H_2SO_4 and NH_4^+

542 analysis by ion chromatography. Results by the reference method were 2 - 12

543 % higher, probably due to the inclusion of gaseous ammonium compounds

544 (data not shown).

545 *3.4   Sensitivity of the tracer ratio method*

546 For CO_2, background corrected emissions in the empty (without cattle) and

547 cleaned experimental dairy housing were -0.06 ± 1.5 kg d^{-1} (average daily value

548 ±1 SD), compared to 200 - 300 kg d^{-1} CO_2 under typical measurement

549 conditions, with 20 cows in the housing. As illustrated in Fig. 7, the sensitivity of

550 the tracer ratio method is mainly given by the capability for background

551 correction, i.e. to separate and subtract emissions in the close vicinity of the

552 housing. This is especially important for calm nights with CO_2 accumulation in

553 the nocturnal boundary layer, most probably due to emissions from soils in the

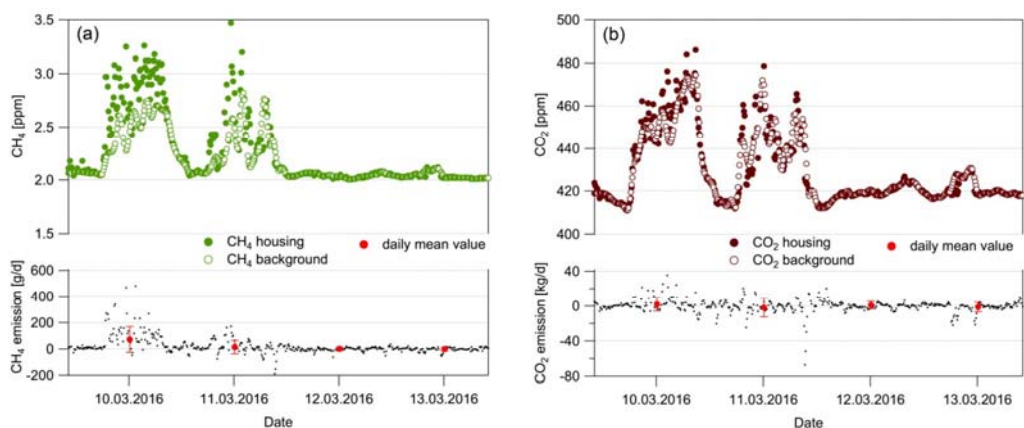554 surrounding of the housing (Mohn et al., 2008).

555

Fig. 7. Sensitivity of the tracer ratio method for CH_4 (a) and CO_2 (b) mass emissions in the cleaned
experimental dairy housing. The top graphs display the importance of appropriate background correction
to disentangle emissions in the housing and in the surrounding. The bottom graphs show CH_4 and CO_2
mass emissions after background correction indicating the high sensitivity of the implemented tracer ratio
method.

561 For CH_4, N_2O and NH_3, emissions in the empty housing were 21.0 ± 30.0 g d^{-1}

562 CH_4, 4.5 ± 1.3 g d^{-1} N_2O and 29.5 ± 4.3 g d^{-1} NH_3, indicating remaining

563 emissions in the building or in the close vicinity, which cannot be eliminated by

564 the background correction. This is visualized in Fig. 7, where the CH_4

565 concentration in the housing is clearly higher than at the background site.

566 Emissions in the housing might be due to residual soiling of surfaces (e.g. straw

567 mattresses) in the building, or remains of slurry in the channel or storage.

568 Therefore, in this specific setup, residual, i.e. baseline emissions rather than an

569　analytical detection limit given by the tracer ratio method itself dominate the

570　sensitivity of the analytical concept. Compared to emissions under typical

571　measurement conditions, with 20 cows in the housing (8000-9000 g d^{-1} CH_4,

572　600–900 g d^{-1} NH_3, 4-5 g d^{-1} N_2O), baseline emissions are below 1 % for CH_4,

573　3-5 % for NH_3 but up to 100 % for N_2O. Therefore, we conclude that the tracer

574　ratio method with background correction, as it was employed in this study, is

575　appropriate to determine CO_2, CH_4 and NH_3 mass emissions from the housing,

576　but N_2O emissions are rather small and dominated by miscellaneous sources

577　other than dairy cows and freshly polluted surfaces (Wolf et al., 2015). The

578　suitability of the background measurement site was monitored by the analysis of

579　SF_6 and SF_5CF_3, which would indicate the influence of housing emissions at the

580　background location.

581　*3.5　Cross-contamination between experimental sections*

582　One feature of the dual tracer approach is that cross-contaminations between

583　experimental areas are readily apparent by enhanced concentrations of the

584　tracer gas (SF_6, SF_5CF_3) in the respective other section. At wind speeds above

585　2 m s^{-1} tracer gas concentrations in the dosing area are around 100 – 400 ppt

586　and mostly below detection limit in the other section, while concentrations

587　increase for lower wind speeds above 1000 ppt for the dosing and 20-40 ppt in

588　the second experimental area (Fig. 8). From these observations it can be

589　concluded that cross-contamination between sections is in the lower percentage

590　range for both high and low wind speeds irrespective of the wind direction.

591　Moreover, this information is available by default as a quality control for every

592　future measuring campaign to assure the validity of the data. If cross-

593 contamination between both experimental sections exceeds a preset target

594 value (e.g. 10 %), the respective data could be flagged and either filtered out or
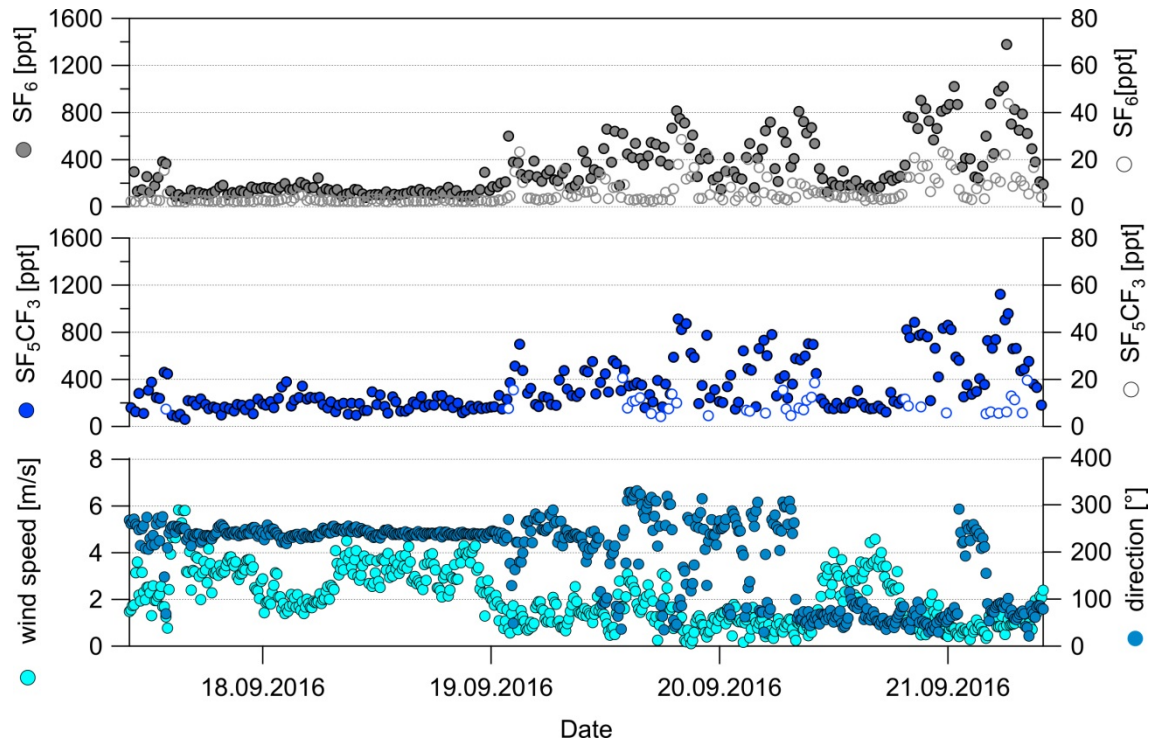
595 corrected.

596

597 Fig. 8. Tracer gas concentrations in the dosing section (filled symbols) and in the respective other housing

598 section (open symbols) indicating minimal cross-contamination between experimental areas. Dislocation of

599 tracer gases was only observed for low wind speeds irrespective of the wind direction.

600 **4.   Conclusion**

601 This manuscript describes the design and construction of a naturally ventilated

602 experimental dairy housing for the progressive development and testing of NH_3

603 and GHG reduction strategies. The building consists of two spatially separated

604 housing sections, a treatment and a reference area, which allows comparative

605 measurement conditions (e.g. climatic conditions) at practical scale. To quantify

606 mass emissions of NH_3, CH_4, CO_2, and N_2O a tracer ratio method with areal

607   dosing of tracer gases and multipoint sampling as well as real-time analysis of

608   tracer and target gases was implemented. Different, but equivalent tracer gases

609   (SF_6, SF_5CF_3) are used for the treatment and reference section to trace cross-

610   contamination. The areal tracer gas dosing was successfully validated for its

611   suitability to mimic areal and point emission sources, with the temporal

612   variability of the second being higher due to not completely congruent spatial

613   areas. The accuracy of the tracer ratio method was demonstrated by CH_4 and

614   N_2O addition experiments and the uncertainty of this approach shown to be in

615   the 3-10 % range superior to existing alternative approaches. The sensitivity of

616   the tracer ratio method was studied in the empty housing and shown to be

617   sufficiently high to determine NH_3, CH_4 and CO_2 mass flow emissions. Cross-

618   contamination between the experimental sections of the housing is monitored

619   on a routine basis but was shown to be below the detection limit or in the low

620   percentage range for the relevant meteorological conditions. In summary, the

621   experimental dairy housing provides a unique platform to reliably quantify mass

622   flow emissions of NH_3 and the GHGs from a naturally ventilated dairy housing

623   and quantify the reduction potential of mitigation options.

631 Luethi (Agroscope Tänikon) for technical assistance, and B. Kürsteiner and P.

632 Jenni for providing meteorological equipment. Martin Vollmer and Christoph

633 Zellweger (Empa Dübendorf) are acknowledged for support with the

634 development of the GC-ECD analytical technique and referencing of CH_4, CO_2

635 and N_2O measurements to the NOAA-GMD scales. In addition, we would like to

636 thank Stephan Henne (Empa Dübendorf) for his advice during data

637 interpretation.

638 **References**

639 Achermann, B., Bonjour, C., Kupper, T., Leuenberger, C., Menzi, H., Nyfeler-
640   Brunner, A., Rihm, B., Zaucker, F., 2009. Ammoniakemissionen in der
641   Schweiz: Neuberechnung 1990-2007, in: BAFU (Ed.), Fachtagung
642   Ammoniak- und Treibhausgasemissionen aus der Landwirtschaft:
643   Inventare und Programme zu deren Minderung. Bundesamt für Umwelt,
644   Zollikofen, p. 70.
645 Bai, M., Griffith, D.W.T., Phillips, F.A., Naylor, T., Muir, S.K., McGinn, S.M.,
646   Chen, D., 2016. Correlations of methane and carbon dioxide
647   concentrations from feedlot cattle as a predictor of methane emissions.
648   Ani. Prod. Sci. 56, 108-115. https://doi.org/10.1071/AN14550.
649 Berry, N.R., Zeyer, K., Emmenegger, L., Keck, M., 2005. Emissionen von Staub
650   (PM10) und Ammoniak (NH_3) aus traditionellen und neuen Stallsystemen
651   mit Untersuchungen im Bereich der Mastschweinehaltung. Agroscope
652   FAT Tänikon, Ettenhausen und Empa, Dübendorf, p. 108.
653 Bougouin, A., Leytem, A., Dijkstra, J., Dungan, R.S., Kebreab, E., 2016.
654   Nutritional and environmental effects on ammonia emissions from dairy
655   cattle housing: A meta-analysis. J. Environ. Qual. 45, 1123-1132.
656   https://doi.org/10.2134/jeq2015.07.0389.
657 Calvet, S., Gates, R.S., Zhang, G., Estellés, F., Ogink, N.W.M., Pedersen, S.,
658   Berckmans, D., 2013. Measuring gas emissions from livestock buildings:

659   A review on uncertainty analysis and error sources. Biosyst. Eng. 116,

660   221-231. https://doi.org/10.1016/j.biosystemseng.2012.11.004.

661 Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A.,

662   DeFries, R., Galloway, J., Heimann, M., Jones, C., Le Quéré, C., Myneni,

663   R.B., Piao, S., Thornton, P., 2013. Carbon and other biogeochemical

664   cycles, in: Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K.,

665   Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), Climate

666   Change 2013: The Physical Science Basis. Contribution of Working

667   Group I to the Fifth Assessment Report of the Intergovernmental Panel

668   on Climate Change. Cambridge University Press, Cambridge, United

669   Kingdom and New York, NY, USA, pp. 465-570.

670 CIGR, 2002. Climatization of animal houses - heat and moisture production at

671   animal and house level, in: Pedersen, S., Sällvik, K. (Eds.), 4th Report of

672   CIGR Working Group. Research Centre Bygholm, Danish Institute of

673   Agricultural Sciences, Horsens, Denmark, p. 45.

674 Demmers, T.G.M., Burgess, L.R., Short, J.L., Phillips, V.R., Clark, J.A., Wathes,

675   C.M., 1998. First experiences with methods to measure ammonia

676   emissions from naturally ventilated cattle buildings in the U.K. Atmos.

677   Environ. 32, 285-293. https://doi.org/10.1016/S1352-2310(97)00197-0.

678 Demmers, T.G.M., Phillips, V.R., Short, L.S., Burgess, L.R., Hoxey, R.P.,

679   Wathes, C.M., 2001. Validation of ventilation rate measurement methods

680   and the ammonia emission from naturally ventilated dairy and beef

681   buildings in the United Kingdom. J. Agr. Eng. Res. 79, 107-116.

682   https://doi.org/10.1006/jaer.2000.0678.

683 Edouard, N., Mosquera, J., van Dooren, H.J.C., Mendes, L.B., Ogink, N.W.M.,

684   2016. Comparison of CO_2 and SF_6 based tracer gas methods for the

685   estimation of ventilation rates in a naturally ventilated dairy barn. Biosyst.

686   Eng. 149, 11-23. http://dx.doi.org/10.1016/j.biosystemseng.2016.06.001.

687 Eyer, S., Tuzson, B., Popa, M.E., van der Veen, C., Röckmann, T., Brand,

688   W.A., Fisher, R., Lowry, D., Nisbet, E.G., Brennwald, M.S., Harris, E.,

689   Zellweger, C., Emmenegger, L., Fischer, H., Mohn, J., 2016. Real-time

690   analysis of $\delta^{13}C$- and $\delta D\text{-}CH_4$ in ambient methane with laser

691   spectroscopy: Method development and first inter-comparison results.

692   Atmos. Meas. Tech. 9, 263-280. https://doi.org/10.5194/amt-9-263-2016.

693 FOEN, 2016. Switzerland's Greenhouse Gas Inventory 1990–2014. Federal

694   Office for the Environment FOEN, Climate Division, Bern, p. 629.

695 Fowler, D., Coyle, M., Skiba, U., Sutton, M.A., Cape, J.N., Reis, S., Sheppard,

696   L.J., Jenkins, A., Grizzetti, B., Galloway, J.N., Vitousek, P., Leach, A.,

697   Bouwman, A.F., Butterbach-Bahl, K., Dentener, F., Stevenson, D.,

698   Amann, M., Voss, M., 2013. The global nitrogen cycle in the twenty-first

699   century. Philos. Trans. R. Soc. Lond., B, Biol. Sci. 368, 20130164.

700   https://doi.org/10.1098/rstb.2013.0164

701 Griffith, D.W.T., Bryant, G.R., Hsu, D., Reisinger, A.R., 2008. Methane

702   emissions from free-ranging cattle: Comparison of tracer and integrated

703   horizontal flux techniques. J. Environ. Qual. 37, 582-591.

704   https://doi.org/10.2134/jeq2006.0426.

705 Hiller, R.V., Bretscher, D., Delsontro, T., Diem, T., Eugster, W., Henneberger,

706   R., Hobi, S., Hodson, E., Imer, D., Kreuzer, M., Künzle, T., Merbold, L.,

707   Niklaus, P.A., Rihm, B., Schellenberger, A., Schroth, M.H., Schubert,

708   C.J., Siegrist, H., Stieger, J., Buchmann, N., Brunner, D., 2014.

709   Anthropogenic and natural methane fluxes in Switzerland synthesized

710   within a spatially explicit inventory. Biogeosciences 11, 1941-1960.

711   https://doi.org/10.5194/bg-11-1941-2014.

712 JCGM, 2008. Evaluation of measurement data — Guide to the expression of

713   uncertainty in measurement p. 120.

714 Keck, M., Schmidlin, A., Zeyer, K., Emmenegger, L., Schrade, S., 2011.

715   Geruchskonzentration und -emission von Milchviehställen mit Laufhof.

716   Agrarforschung 2, 114–119.

717 Kupper, T., Bonjour, C., Achermann, B., Rihm, B., Zaucker, F., Menzi, H., 2013.

718   Ammoniakemissionen in der Schweiz 1990-2010 und Prognose bis

719   2020. Hochschule für Agrar-, Forst- und Lebensmittelwissenschaften,

720   Bern, p. 110.

721 Mendes, L.B., Edouard, N., Ogink, N.W.M., van Dooren, H.J.C., Tinôco,

722   I.d.F.F., Mosquera, J., 2015. Spatial variability of mixing ratios of

723   ammonia and tracer gases in a naturally ventilated dairy cow barn.

Biosyst. Eng. 129, 360-369. http://dx.doi.org/10.1016/j.biosystemseng.2014.11.011.

Mohn, J., Forss, A.M., Brühlmann, S., Zeyer, K., Lüscher, R., Emmenegger, L., Novak, P., Heeb, N., 2004. Time-resolved ammonia measurement in vehicle exhaust. Int. J. Environ. Pollut. 22, 342-356. https://doi.org/10.1504/IJEP.2004.005548.

Mohn, J., Steinlin, C., Merbold, L., Emmenegger, L., Hagedorn, F., 2013. N_2O emissions and source processes in snow-covered soils in the Swiss Alps. Isot. Environ. Healt. S. 49, 520-531. http://dx.doi.org/10.1080/10256016.2013.826212.

Mohn, J., Tuzson, B., Manninen, A., Yoshida, N., Toyoda, S., Brand, W.A., Emmenegger, L., 2012. Site selective real-time measurements of atmospheric N_2O isotopomers by laser spectroscopy. Atmos. Meas. Tech. 5, 1601–1609. https://doi.org/10.5194/amt-5-1601-2012.

Mohn, J., Zeeman, M.J., Werner, R.A., Eugster, W., Emmenegger, L., 2008. Continuous field measurements of $\delta^{13}C$-CO_2 and trace gases by FTIR spectroscopy. Isot. Environ. Healt. S. 44, 241-251. http://doi.org/10.1080/10256010802309731.

Ogink, N.W.M., Mosquera, J., Calvet, S., Zhang, G., 2013. Methods for measuring gas emissions from naturally ventilated livestock buildings: Developments over the last decade and perspectives for improvement. Biosyst. Eng. 116, 297-308. https://doi.org/10.1016/j.biosystemseng.2012.10.005.

Pedersen, S., Blanes-Vidal, V., Joergensen, H., Chwalibog, A., Haeussermann, A., Heetkamp, M.J.W., Aarnink, A.J.A., 2008. Carbon dioxide production in animal houses: A literature review (Manuscript BC 08 008). Agricultural Engineering International: CIGR Ejournal X, 19.

Pedersen, S., Takai, H., Johnsen, J.O., Metz, J.H.M., Groot Koerkamp, P.W.G., Uenk, G.H., Phillips, V.R., Holden, M.R., Sneath, R.W., Short, J.L., White, R.P., Hartung, J., Seedorf, J., Schröder, M., Linkert, K.H., Wathes, C.M., 1998. A comparison of three balance methods for calculating ventilation rates in livestock buildings. J. Agr. Eng. Res. 70, 25-37. https://doi.org/10.1006/jaer.1997.0276.

757 Röckmann, T., Eyer, S., Van Der Veen, C., Popa, M.E., Tuzson, B., Monteil, G.,
758   Houweling, S., Harris, E., Brunner, D., Fischer, H., Zazzeri, G., Lowry,
759   D., Nisbet, E.G., Brand, W.A., Necki, J.M., Emmenegger, L., Mohn, J.,
760   2016. In situ observations of the isotopic composition of methane at the
761   Cabauw tall tower site. Atmos. Chem. Phys. 16, 10469-10487.
762   https://doi.org/10.5194/acp-16-10469-2016.

763 Schiefler, I., 2013. Greenhouse gas and ammonia emissions from dairy barns
764   (VDI-MEG Nr. 528). Bonn, University of Bonn, p. 84.

765 Schneider, F., Eichelser, R., Neser, S., 2006. Emissionspotenzial
766   landwirtschaftlicher Tierhaltungen: Milchvieh. Landtechnik 61, 218-219.
767   http://dx.doi.org/10.15150/lt.2006.1107.

768 Schrade, S., 2009. Ammoniak- und PM10-Emissionen im Laufstall für Milchvieh
769   mit freier Lüftung und Laufhof anhand einer Tracer-Ratio-Methode (VDI-
770   MEG Nr. 483), Agrar- und Ernährungswissenschaftliche Fakultät.
771   University of Kiel, Kiel, p. 131.

772 Schrade, S., Zähner, M., Poteko, J., Steiner, B., Keck, M., Sax, M., Herzog, D.,
773   Schick, M., 2015. Versuchsstall zur Entwicklung und Quantifizierung von
774   Massnahmen zur minderung von Emissionen, in: Kuratorium für Technik
775   und Bauwesen in der Landwirtschaft (Ed.), Bau, Technik und Umwelt in
776   der landwirtschaftlichen Nutztierhaltung, Freising, Germany, pp. 450-455.

777 Schrade, S., Zeyer, K., Emmenegger, L., Vollmer, M.K., Keck, M., Hartung, E.,
778   2007. Ammonia emissions in naturally ventilated cattle housing with an
779   excercise yard: requirements and measuring concept using two tracer
780   gases, in: Monteny, G.J., Hartung, E. (Eds.), International Conference on
781   Ammonia in Agriculture: Policy, Science, Control and Implementation.
782   Wageningen Academic Publishers, Ede, The Netherlands, pp. 345–346.

783 Schrade, S., Zeyer, K., Gygax, L., Emmenegger, L., Hartung, E., Keck, M.,
784   2012. Ammonia emissions and emission factors of naturally ventilated
785   dairy housing with solid floors and an outdoor exercise area in
786   Switzerland. Atmos. Environ. 47, 183-194.
787   https://doi.org/10.1016/j.atmosenv.2011.11.015.

788 Sherman, M.H., 1990. Tracer-gas techniques for measuring ventilation in a
789   single zone. Build. Environ. 25, 365-374. https://doi.org/10.1016/0360-
790   1323(90)90010-O.

791 Sturges, W.T., Oram, D.E., Laube, J.C., Reeves, C.E., Newland, M.J., Hogan,
792   C., Martinerie, P., Witrant, E., Brenninkmeijer, C.A.M., Schuck, T.J.,
793   Fraser, P.J., 2012. Emissions halted of the potent greenhouse gas
794   SF_5CF_3. Atmos. Chem. Phys. 12, 3653-3658.

795 Teye, F.K., Hautala, M., 2007. Measuring ventilation rates in dairy buildings. Int.
796   J. Vent. 6, 247-256. http://dx.doi.org/10.1080/14733315.2007.11683781.

797 VDI, 2017. VDI 3878: Stationary source emissions - Measurement of ammonia
798   (and gaseous ammonium compounds) - Manual method. Beuth Verlag
799   GmbH, Düsseldorf, p. 24.

800 Von Wachenfelt, E., Pedersen, S., Gustafsson, G., 2001. Release of heat,
801   moisture and carbon dioxide in an aviary system for laying hens. Brit.
802   Poultry Sci. 42, 171-179. http://dx.doi.org/10.1080/00071660120048401.

803 Wolf, B., Merbold, L., Decock, C., Tuzson, B., Harris, E., Six, J., Emmenegger,
804   L., Mohn, J., 2015. First on-line isotopic characterization of N_2O above
805   intensively managed grassland. Biogeosciences 12, 2517-2531.
806   https://doi.org/10.5194/bg-12-2517-2015.

807 Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M.,
808   Kozlova, E., Gerard Spain, T., Steinbacher, M., Van Der Schoot, M.V.,
809   Buchmann, B., 2016. Assessment of recent advances in measurement
810   techniques for atmospheric carbon dioxide and methane observations.
811   Atmos. Meas. Tech. 9, 4737-4757. https://doi.org/10.5194/amt-9-4737-
812   2016.

813 Zellweger, C., Steinbacher, M., Buchmann, B., 2012. Evaluation of new laser
814   spectrometer techniques for in-situ carbon monoxide measurements.
815   Atmos. Meas. Tech. 5, 2555-2567. https://doi.org/10.5194/amt-5-2555-
816   2012.

817