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1   **Photoacoustic measurement may significantly overestimate NH₃ emissions from cattle**

2   **houses due to VOC interferences**

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23   **Abstract**: Infrared photoacoustic spectroscopy (PAS) is a widely used method for measurement

24   of NH_3 and greenhouse gas emissions especially in agriculture, but non-targeted gases such as

25   volatile organic compounds (VOCs) from cattle barns may interfere with target gases causing

26   inaccurate results. This study made an estimation of NH_3 interference in PAS caused by selected

27   non-targeted VOCs which were simultaneously measured by a PAS and a PTR-MS (proton

28   transfer reaction mass spectrometry). Laboratory calibration were performed for NH_3

29   measurement and VOCs were selected based on a headspace test of the feeding material maize

30   silage. Various levels of interference of tested VOCs were observed on NH_3 and greenhouse

31   emissions measured by the PAS. Particularly, ethanol, methanol, 1-butanol, 1-propanol and

32   acetic acid were found to have highest interference on NH_3. A linear response was typically

33   obtained, with non-linear relation was however observed for VOCs on N_2O emissions. The

34   corrected online NH_3 concentrations measured by the PAS from a field study were confirmed

35   to be reasonably correlated to the NH_3 concentration measured simultaneously by the PTR-MS.

36   It was concluded that the correction factors could be used for possible data corrections when

37   the concentrations of VOCs could be obtained by using e.g. PTR-MS.

38

39   **1   Introduction**

40   Measurements of ammonia and greenhouse emissions are gaining increased research attention

41   in recent years due to stronger interests on global change and air pollution. Especially, ammonia

42   not only causes serious environmental problems such as soil acidification as well as pollution

43   of underground water and surface water with nitrogen eutrophication (van Breemen et al., 1983;

44   Pearson and Stewart, 1993; Erisman et al., 2007), but is also important for fine particle

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45   formation (Bouwman et al., 1997; Seinfeld and Pandis, 1997; Pinder et al., 2007). The

46   greenhouse gas emissions, on the other hand, are causing climate change (Thomas et al., 2004;

47   Chadwick et al., 2011). Livestock husbandry was estimated to be responsible for more than 80 %

48   of the ammonia emission in Western Europe (Hutchings et al., 2001; EMEP, 2013) and more

49   than 60% in China (Paulot et al., 2014). In the U.S., agriculture accounts for ~90 % of the total

50   ammonia emissions (Aneja et al., 2009). Meanwhile, agriculture accounts for 52 and 84 % of

51   global anthropogenic methane and nitrous oxide emissions (Smith et al., 2008). Accurate

52   measurements of ammonia and greenhouse emissions are therefore vital for reliable emission

53   estimation and thereby the possible reduction of these emissions through various efforts, such

54   as air cleaning with biotrickling filters and air scrubbers (Melse and Van der werf, 2005; De

55   Vries and Melse, 2017). For ammonia measurements, more than 30 % difference was observed

56   when various methods were compared (Scholtens et al., 2004).

57   Infrared photoacoustic spectroscopy (PAS) is a widely-used technique for studies of air

58   emissions especially within agriculture (Osada et al., 1998; Osada and Fukumoto, 2001;

59   Emmenegger et al., 2004; Schilt et al., 2004; Heber et al., 2006; Elia et al., 2006; Blanes-Vidal

60   et al., 2007; Hassouna et al., 2008; Rong et al., 2009; Ngwabie et al., 2011; Cortus et al., 2012;

61   Joo et al., 2013; Wang-Li et al., 2013; Iqbal et al., 2013; Zhao et al., 2016; Ni et al., 2017; Lin

62   et al., 2017). The PAS technique determines the gas concentrations through measuring acoustic

63   signals caused by cell pressure change when gas inside absorbs energy from infrared light at a

64   specific wavelength using the optical filter and expands (Iqbal et al., 2013). For example, the

65   Innova 1312 (AirTech Instruments, Ballerup, Denmark) uses the PAS method and was

66   previously verified by the US EPA and recommended by the Air Resources Board in California

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67   (CARB, 2000). Besides, PAS has the advantages of performing continuous measurement with

68   low maintenance and good selectivity and can simultaneously measure five compounds,

69   typically including NH_3, CH_4, CO_2 and N_2O for agricultural applications. The water vapor was

70   usually also included in order to make proper concentration corrections when necessary.

71   Nevertheless, since the infrared spectroscopic method is applied for measuring gas

72   concentrations in PAS, the overlapping of IR spectra with non-targeted gases can introduce

73   significant interferences due to the adsorption of infrared light at similar wavelengths, even

74   though the infrared bands selected by optical filters are relatively narrow. The interferences can

75   be corrected through cross-compensation for all target gases when the instrument is calibrated

76   (Lumasense, 2012), but understanding and estimation of interferences from possible non-

77   targeted gases is very important. This is especially important for field applications where the

78   manure or the animal feed may emit various types of gases depending on the management and

79   operations in the animal houses (Hafner et al., 2010; Moset et al., 2012). Until now, the PAS

80   interference of has not been well estimated and corrected for, although interferences were

81   previously suspected in livestock facilities (Phillips et al., 2001; Mathot et al., 2007; Ni & Heber,

82   2008). Flechard et al. (2005) suspected that the N_2O concentration from soil measured by PAS

83   (Innova 1312) was heavily influenced by CO_2 and temperature even when cross-interference

84   compensation was applied; they developed an alternative correction algorithm based on

85   controlled N_2O/CO_2/H_2O ratios under selected temperature. Zhao et al (2012) claimed that the

86   internal cross compensation could eliminate the interferences between target gases, and

87   quantified interferences of non-targeted gas of NH_3 on targeted gases of ethanol, methanol, N_2O,

88   CO_2, and CH_4, however, without giving specific correction factors. Iqbal et al. (2013) also

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89   demonstrated that a careful calibration could eliminate the internal cross interferences of high

90   water vapor and CO_2 concentrations on low concentrations of N_2O at the soil surface by

91   comparison to GC measurements. Nevertheless, tests on interferences by non-targeted VOCs

92   were not included in their study, likely due to the typical low concentrations of VOC in soil

93   (Insam and Seewald, 2010). Hassouna et al. (2013) presented a field study on dairy cow

94   buildings, where interferences on NH_3, CH_4 and N_2O were observed. The interferences were

95   suspected to be caused by volatile organic compounds (VOCs; acetic acid, ethanol and 1-

96   propanol) that they measured simultaneously; two PAS instruments were applied with one of

97   them allocated with optical filters of these VOCs (NH_3 optical filter was included for both PAS).

98   Still, no correction factors were given in terms of tested volatile organic compounds, which

99   were typically emitted from feeding materials such as maize silage (Howard et al., 2010;

100   Malkina et al., 2011). Opposite to what was claimed by some previous studies (e.g., Heyden et

101   al., 2016), the correction of interferences of non-targeted VOCs on NH_3 emission is also

102   essential for the evaluation of emission abatement technologies such as air scrubbers, especially

103   when the inlet VOC concentrations are relatively high. An overestimation of ammonia removal

104   efficiency could easily be obtained since less interference would be expected for the outlet

105   VOCs especially for water-soluble compounds such as the VOCs investigated in this study.

106   This study, therefore, performed an evaluation on ammonia measurements and interferences by

107   non-targeted gases of volatile organic compound on targeted NH_3 and greenhouse gases

108   measurement by PAS, with the interference on NH_3 simultaneously demonstrated by Proton-

109   transfer-reaction mass spectrometry (PTR-MS), Cavity Ring-Down Spectroscopy (CRDS) and

110   PAS. The experiments were as follows: (1) ammonia laboratory calibration by the three

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111   instruments of PAS, PTR-MS and CRDS; (2) VOC selection test for non-targeted interference

112   to ammonia by the PAS; (3) Effect of non-targeted VOCs on ammonia and greenhouse

113   emissions measured by the PAS; (4) Field confirmation of interferences of non-targeted VOCs

114   on ammonia measurement and data correction.

115

116   **2   Materials and methods**

117   **2.1   Instrumentation for gas concentrations measurement**

118   In this study, a PTR-MS, a CRDS NH_3 analyzer and a PAS gas analyzer were used to measure

119   gas concentrations. PTR-MS is a state-of-the-art and widely used CIMS (short for chemical-

120   ionization mass spectrometry) technique for highly sensitive online measurements of VOCs

121   (De Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017). PTR-MS can also measure

122   a few inorganic compounds such as ammonia (at m/z 18) since the proton affinity (204.0

123   kcal/mol) of ammonia is higher than that of water (165.0 kcal/mol). Due to the fact that intrinsic

124   ion at m/z 18 could be formed in the plasma ion source (Norman et al., 2007), ammonia

125   measurement by PTR-MS need to be evaluated carefully. For agricultural applications with

126   relative high ammonia concentrations (e.g., Rong et al., 2009), this high background is usually

127   not a big problem, since the typical background concentration is only a few hundred ppbv.

128   When total gas concentration measured by PTR-MS is higher than approximately 10 ppmv,

129   dilution is needed to keep the stable level of primary ion signals. A high-sensitivity PTR-MS

130   (Ionicon Analytik GmbH, Innsbruck, Austria) was applied for the test of ammonia calibration

131   in the laboratory, effects of non-targeted VOCs on ammonia measurement and field

132   confirmation of interferences of non-targeted VOCs on ammonia measurement. Standard

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133   conditions with a total voltage of 600 V in the drift tube were utilized for the PTR-MS. Pressure

134   and temperature in the drift tube were maintained in the range of 2.1-2.2 mbar and at 60 °C,

135   respectively, which gives an E/N ratio of ca. 135 Townsend. The inlet of the PTR-MS is PEEK

136   tubing of 1.2 m length with 0.64 mm inner diameter (ID) and 1.6 mm outer diameter (OD). The

137   inlet flow to the PTR-MS during calibration test and measurements was kept ~150 mL/min.

138   The inlet temperature was maintained at 60 °C. Mass calibration was performed before each

139   test, while transmission calibration was performed for every two weeks as suggested by the

140   manufacturer.

141   CRDS determines the gas concentration (e.g., NH_3) by measuring the acceleration of ring down

142   time of light in the cavity due to absorption by a targeted gas species, this is compared to the

143   'normal' ring down time of the light introduced by a laser with tunable wavelength (von

144   Bobrutzki et al., 2010; Picarro, 2017). The very long effective path length of the light in the

145   cavity (e.g., over 20 km for 25 cm cavity) (Picarro, 2017), enables a significantly higher

146   sensitivity compared to conventional absorption spectroscopy (Berden et al., 2000; von

147   Bobrutzki et al., 2010). A G2103 Analyzer (Picarro Inc., Sunnyvale, CA, USA) using CRDS

148   technique was applied in this study for the test of ammonia laboratory calibration and for the

149   effect of non-targeted VOCs on ammonia measurement. The manufacturer calibrated the CRDS

150   analyzer approximately 3 months before calibration tests and interference measurements. The

151   CRDS analyzer was equipped with two in-line, sub-micron polytetrafluoroethylene (PTFE)

152   particulate matter filters; one at the gas inlet at the back of the analyzer and one at the inlet of

153   the cavity to protect the highly reflective mirrors. The inlet of the CRDS is a Teflon (PTFE)

154   tubing of 1.5 m length with 6.4 mm outer diameter. Since molecular spectroscopy is

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155   fundamentally affected by temperature and pressure, the CRDS's optical cavities incorporate

156   precise temperature and pressure control systems, with the measurement cell temperature

157   controlled under precision of ± 0.005 °C, while the measurement cell pressure controlled

158   under precision of ± 0.0002 atm. In this study, both the temperature and pressure of the air

159   sample continuously flowing through the optical cavity are tightly controlled at all times to

160   constant values of 45 °C and 140 Torr, respectively. The measurement interval is around 3

161   seconds. The CRDS analyzer measured the water vapor simultaneously.

162   A photoacoustic multi-gas monitor 1312 (Innova, Lumasense Technology A/S, Denmark) using

163   PAS technique was compared with the PTR-MS and the CRDS for ammonia calibration and

164   non-targeted VOCs on ammonia measurement. The sample integration time to measure

165   ammonia by the PAS was 20 s. The PAS used 6 optical filters including NH_3, CH_4, CO_2, H_2O,

166   N_2O and SF_6. The specifications of the optical filters are shown in Table S1. Water vapor must

167   be included for PAS measurement, since the absorbance spectrum of water overlap with other

168   gases such as N_2O and CO_2 thus causing interferences. The supplier calibrated the PAS before

169   the conduction of the measurements for comparison in this study. The interferences between

170   the target gases were therefore supposed to be eliminated through internal cross compensation

171   (Lumasense, 2012; Zhao et al., 2012).

172   **2.2   Experiment 1：laboratory test on ammonia calibration**

173   The background measurement, calibration on selected ammonia concentrations, and reaction

174   time and decay time measurement were performed for ammonia measurement by PAS, PTR-

175   MS and CRDS. For the background measurement, zero air controlled by a mass flow controller

176   (Bronkhorst, Ruurlo, The Netherlands) was supplied, and measurement was performed

177   individually for each instrument. The selected ions measurement mode was used for the PTR-

178   MS with m/z 18 being used for ammonia measurement. For the calibration test, a factory-

179   calibrated gas cylinder (AGA A/S, Copenhagen, Denmark) containing 99.7 (± 10 %) ppmv

180   ammonia was used for the calibration test. Mass flow controllers (Bronkhorst, Ruurlo, The

181   Netherlands) were used to dilute the cylinder gas with zero air to achieve the desired NH_3

182   concentration levels. For the decay time test, zero air flow was supplied to the instruments at

183   first, then switched to a diluted flow (via 2-levels of mass flow controllers) with ammonia

184   concentration around 5.2 ppmv supplying to all three instruments simultaneously, afterwards

185   the ammonia supply flow was then set to zero to test the decay time. Four individual decay time

186   tests were performed for the PAS, in order to confirm the long decay time of the instrument

187   with low ammonia concentrations (5.2-8.8 ppmv) or high ammonia concentration (99.7 ppmv).

188   For the reaction time test for the PAS, two different levels of ammonia concentration were

189   introduced individually to the instrument, in order to test the dependence of the reaction time

190   on ammonia concentration.

191   **2.3   Experiment 2: VOCs selection test**

192   In order to prepare the interferences test of non-targeted VOCs on ammonia measured by the

193   PAS, a headspace test was performed and VOCs were selected through a PTR-MS measurement.

194   Maize silage is a typical feeding material to the cows. A sample of maize silage was collected

195   from the farm where the field confirmation experiment was performed (Skjern, Jutland,

196   Denmark, altitude: 55°59′36.6″, longitude: 8°29′53.52″). The silage was then transferred to the

197   laboratory immediately for the headspace test. A clean plastic container (58×38×43 cm) with

198   two oval holding holes on sides was used for the headspace test for VOCs selection. The

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199   container was half opened and the silage filled half of the container. A 1-meter 1/4-inch ID

200   PTFE tube was used for the test, with one end placed around 5 cm above the silage, and the

201   other side connected to a T-piece. One side of the T-piece was connected to a 1/8-inch ID PTFE

202   tube (around a half meter) which is connecting to the inlet of the PTR-MS. The flow rate of the

203   PTR-MS was kept at 150 mL/min. A zero-air dilution flow (75 mL/min) was supplied to the T-

204   piece in order to make 1:1 dilution to keep the total concentration below 10 ppmv. The

205   headspace measurement was performed by the PTR-MS on scan mode, and masses were

206   measured from 21 to 250 with 200 ms for each mass. The selection of VOCs was based on the

207   scan results and relevant literature for silage (Howard et al., 2010; Malkina et al., 2011).

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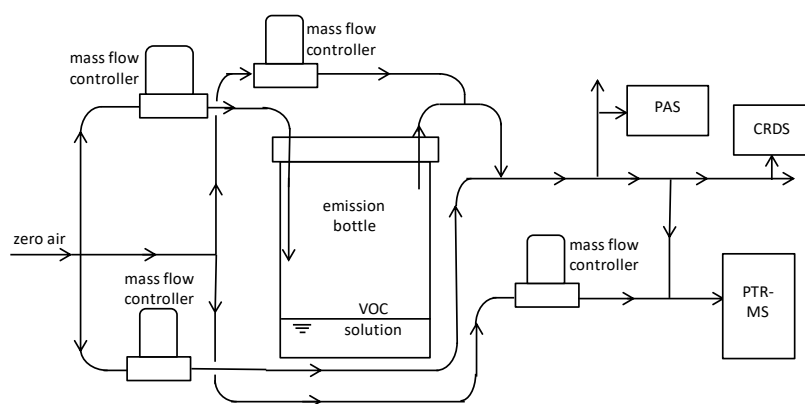
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210   **Figure 1.** The diagram of experimental set-up for ammonia interference calibration from VOCs.

211   **2.4   Experiment 3: Laboratory test for correction factors**

212   The diagram of the setup for the laboratory calibration test is shown in Figure 1. In the setup, a

213   pre-tested water solution containing the single VOC was purged from the headspace by zero air

214   (or nitrogen for one test on methanol), with flow controlled by a mass flow controller. The flow

215   was set with care, due to the relatively high sensitivity of VOC concentration on the purged gas

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216   flow rate. One-liter airtight glass bottles were used for holding the water solution containing

217   the VOC, and 1/4-inch ID PTFE tube was used for the pipelines in the setup. The purged air

218   flow in the PTFE tube containing a single VOC was diluted with air through a two-step dilution.

219   The flows were adjusted according to the purged VOC concentration and the desired final VOC

220   concentration. The pre-test for water solution preparation used a ratio of VOC:Water as 1:5,

221   and the ratio between VOC and water was adjusted if the purged concentration after dilution

222   (by zero air controlled by 2 mass flow controllers) measured by the PTR-MS was not within

223   the desired range (too low or too high). For the laboratory calibration test, the diluted VOC was

224   connected to the PAS, the CRDS and the PTR-MS for simultaneous measurements. In order to

225   maintain stable pressures in the PAS and the CRDS, specific ranges of excess flow rates were

226   required for these two instruments. Specific, the excess flow for the PAS was kept around 4 L

227   min^{-1}, while the excess flow for the CRDS was kept around 2 L min^{-1}. For the PTR-MS

228   measurement, a further dilution by zero air was typically used to keep the total concentrations

229   below 10 ppmv in order to avoid depletion of the primary ion, H_3O^+. Selected ion measurement

230   mode was applied for the PTR-MS, with an integration time of 2 seconds for the tested VOC

231   mass. During the experiments, the humidity was kept relatively low and stable, with dry zero

232   air used for dilution for all cases, except for one test on methanol, which was also tested under

233   nitrogen condition.

234   **2.5   Experiment 4: Field test for validation of correction factors**

235   The field demonstration test for non-targeted VOCs on ammonia measurement by the PAS was

236   performed in the dairy farm mentioned above (Skjern, Jutland, Denmark), where both the PTR-

237   MS and the PAS measured continuously. The dairy farm housed 360 cows with an average

238   weight of 650 kg. The ventilation system consisted of natural and mechanical partial pit

239   ventilation system.

240   For the field test, the PAS was combined with a Multiplexer 1309 to measure from several

241   sampling points. The PAS and the PTR-MS were placed in a movable trailer next to the dairy

242   farm. The manufacturer calibrated the PAS instrument before the field test. The sample

243   integration time was 5 s and the flushing time was 20 s. The air concentrations were measured

244   by the PAS sequentially among two selected locations inside the farm, one location in the pit

245   ventilation, one location outside the farm. Teflon tubes of 20 meters long and 8 mm OD were

246   used for the sampling of air. The sampling lines were connected with the channels of the PAS

247   multi-point sampler via continuously running Teflon membrane pumps to ensure constant

248   flushing. Selected VOCs, odorants and NH_3 were measured simultaneously by the high

249   sensitivity PTR-MS. Measurements were switched among the four measurement sampling lines

250   and the background at ca. 10 min intervals via a custom-built switching box. PTFE tubes were

251   used for the PTR-MS sampling lines, which were connected to Teflon sampling lines before the

252   Teflon membranes pumps. The switching box was equipped with a five-port channel selector

253   (Bio-Chem Valve Inc, USA) controlled automatically by 24V outputs from the PTR-MS. A

254   PTFE tube (ID 1 mm) was used to connect the switching box to the inlet sampling line (1-meter

255   PEEK tube with ID 0.64 mm) of the PTR-MS. For selected compounds, calibration was

256   performed for the PTR-MS before the field measurements using permeation tubes and reference

257   gas mixtures. Details regarding the calibration procedures could be found in our previous study

258   (Feilberg et al., 2010). Standard conditions as described previously was applied and maintained

259   for the PTR-MS. The mass discrimination was calibrated and adjusted weekly by using a

260   mixture of 14 aromatic compounds between m/z (mass to charge ratio) 79 and 181 (P/N 34423-

261   PI, Restek, Bellefonte, PA). Selected ions were monitored with dwell time between 200 and

262   2000 ms during each measurement cycle. Masses and dwell time selection was based on ion

263   abundance in full scan mode, relevant literature and experience regarding odorant compounds

264   from dairy buildings as well as from pig houses and pig slurry applications (Shaw et al., 2007;

265   Chung et al., 2009; Liu et al., 2014; Liu et al., 2018).
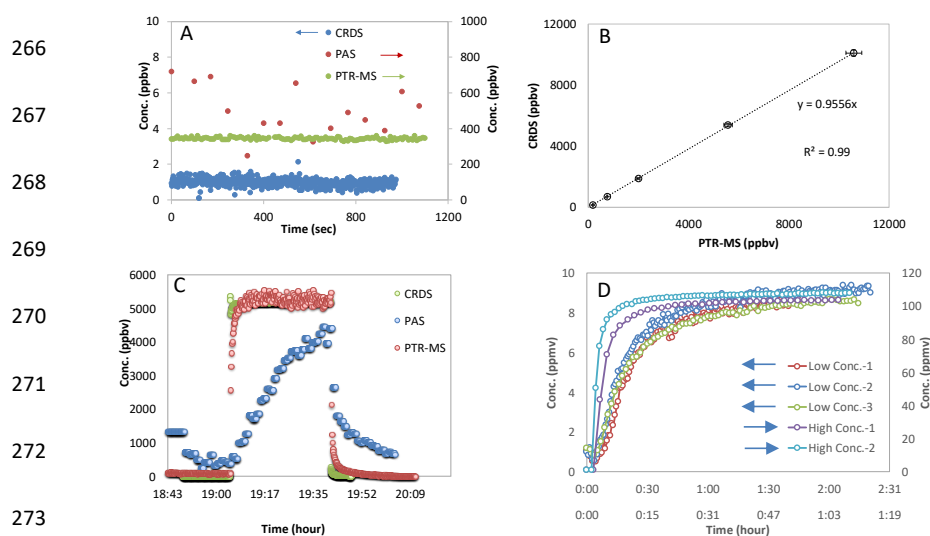
Figure 2. The calibration test of ammonia by the PAS, the PTR-MS and the CRDS. A: Background comparison for the CRDS, the PAS and the PTR-MS for ammonia measurement; B: The calibration of ammonia measured by the PTR-MS and by the CRDS; C: The instrument decay time of measured ammonia concentration by the PTR-MS, the PAS and the CRDS; D: The reaction time for ammonia for the PAS under low concentration (3 tests; ~8.9 ppmv) and high concentration (2 tests; 99.7 ppmv) conditions (Low Conc.-1, Low Conc.-2 and Low Conc.-3 point to the vertical axis on the left, and to the upper horizontal axis; High Conc.-1 and High Conc.-2 point to the vertical axis on the right, and to the lower horizontal axis; High Conc.-2 was tested without the multiplexer).

3   Results and discussion

3.1   Experiment 1：laboratory test on ammonia calibration

285   The background concentrations of ammonia measured by PAS, CRDS and PTR-MS,

286 respectively, are shown in Figure 2A, in which very low background concentration was

287 observed for the CRDS instrument (around 1 ppbv; 5 s) with detection limit around 0.67 ppbv

288 (3 times the standard deviation of the background). The PTR-MS, on the other hand, gave much

289 higher background with nearly 400 ppbv observed. The high background for ammonia

290 measured from the PTR-MS is caused by the intrinsic formation of NH_4^+ (m/z 18) in the ion

291 source (Norman et al., 2007). Nevertheless, the measured background signals for ammonia by

292 the PTR-MS was very stable and could be subtracted to give a detection limit of 21 ppbv (3

293 times the standard deviation of the background). Among the three instruments, the PAS gave

294 the highest background signal for ammonia (corresponding to 502 ± 140 ppb), with a detection

295 limit around 421 ppbv (3 times the standard deviation of the background).

296 For the calibration test of ammonia, the ammonia concentrations measured by the CRDS and

297 the PTR-MS is shown in Figure 2B, in which the linearity (k = 0.9556) and high correlation

298 (R^2=0.999) are satisfactory for both instruments. The measured ammonia concentrations also

299 agreed with expected ammonia concentrations from the ammonia gas cylinder diluted in zero

300 air.

301 **Table 1.** Instrumental decay time (in second).

Unit(s)	PTR-MS (5.2 ppm)	Picarro (5.2 ppm)	Innova (5.2-8.8 ppm)	Innova (100 ppm)
90% decay	70-80	4.5-4.7	1700-4000	450-550

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304 For the decay time test, the instrument decay times for ammonia measurements by the PAS, the

305 CRDS and the PTR-MS were measured simultaneously under a calibrated ammonia

306 concentration of 5.2 ppmv. As shown in Figure 2C, ammonia measured by the CRDS showed

307 the shortest decay time while the PAS gave the longest decay time. The estimated decay time

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308   is shown in Table 1, in which the 90% decay time for ammonia measured by the CRDS is

309   around 4.5 - 4.7 second, with the 90% decay time from the PTR-MS estimated to be 70 to 80

310   seconds. The decay time for ammonia measured by the PAS showed remarkably longer, with

311   estimated 90% decay time around 1700 to 4000 seconds (for four individual tests with ammonia

312   concentration ranged from 5.2 to 8.8 ppmv). When much higher ammonia concentration was

313   used (99.7 ppmv), the 90% decay times measured by the PAS were apparently shorter (450 to

314   550 seconds). This result is consistent with the reaction time tests under two levels of input

315   ammonia concentrations (~ 8.9 ppmv and 99.7 ppmv, respectively), with the reaction time

316   comparably much shorter when input ammonia concentration is higher, as shown in Figure 2D.

317   Besides, the multiplexer attached to the PAS seemed to increase the reaction time, as also shown

318   in Figure 2D. However, a very high concentration of about 100 ppm is not expected to be

319   commonly seen in agricultural applications.
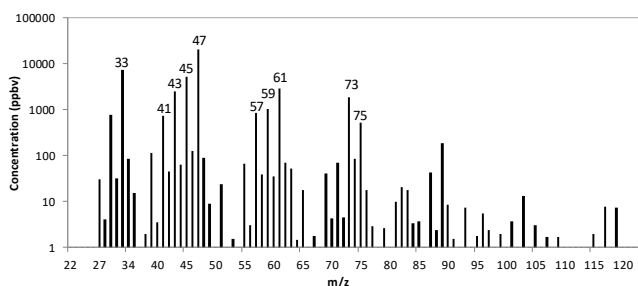
Figure 3. A scan example of the feeding material of silage by using headspace technique measured by
the PTR-MS. The m/z 47 is corrected for ethanol fragmentations formed in the PTR-MS through
calibration. Selected VOCs for the test in this study were ethanol, methanol, acetaldehyde, acetic acid,
2-butanone, acetone, propanol and butanol.

3.2   Experiment 2: VOCs selection test

327   The tested VOCs were selected according to a scan test of the headspace from the feeding

328   material of maize silage performed by the PTR-MS, as shown in Figure 3. The concentrations

329   shown in the figure were corrected for dilution, while the concentration of mass 47 was

330   corrected also from the calibration factor by assuming the mass 47 was assigned to ethanol.

331   Due to the fragmentation of ethanol in the PTR-MS measurement, only a fraction of ethanol

332   could be detected on mass 47 (Aprea et al., 2007). The highest peaks of the scan were at masses:

333   47, 33, 45, 61, 43, 73, 59, 75, 57 and 41. From the VOCs typically found in the highest

334   concentrations in barns and feeding material (Shaw et al., 2007; Chung et al., 2009; Howard

335   et al., 2010; Malkina et al., 2011; Hafner et al., 2013) and the scan results, a list of VOCs were

336   selected. The following VOCs were selected for the interferences tests of non-targeted VOC on

337   ammonia measurement by the PAS: ethanol, methanol, acetaldehyde, acetic acid, 2-butanone,

338   acetone, 1-propanol and 1-butanol. Compounds such as ethanol, methanol, acetic acid and 1-

339   propanol were typically found in cattle barns and feeding materials in high concentrations

340   (Shaw et al., 2007; Ngwabie et al., 2008; Howard et al., 2010; Hafner et al., 2013).

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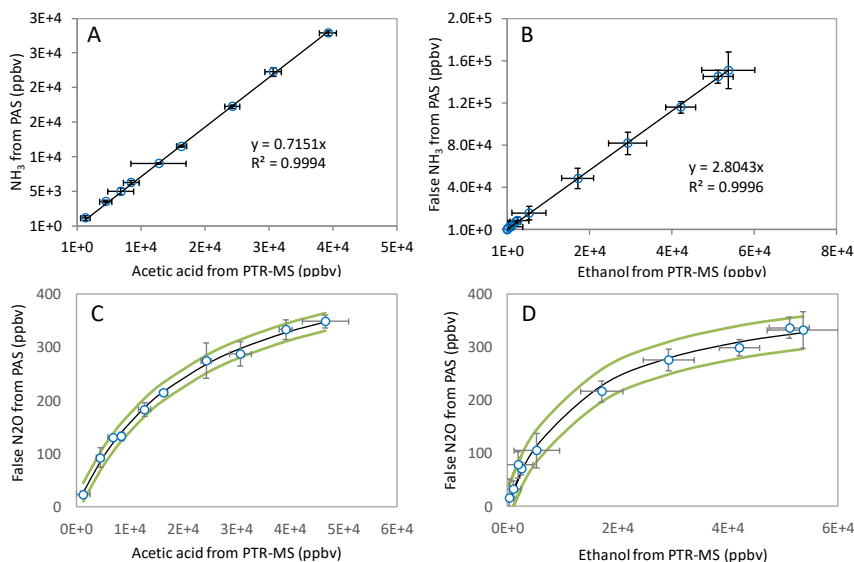
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360 **Figure 4.** Examples for the interference calibration from non-targeted VOC on NH_3 (A & B) and
361 N_2O (C & D) measured by the PAS. The VOC concentration on horizontal axis was measured by
362 the PTR-MS, while the NH_3 and N_2O concentrations on vertical axis were from false signals
363 measured meanwhile by the PAS. A: The interference calibration for acetic acid on NH_3; B: The
364 interference calibration for ethanol (corrected for fragments through calibration) on NH_3; C: The
365 interference calibration for ethanol (corrected for fragments through calibration) on N_2O; D: The
366 interference calibration for acetic acid on N_2O. In C & D, the red line indicated the fit curve by
367 equation $y=kx/(x+m)$, and the green and purple curves indicated 95% confidence range.

368 **3.3   Experiment 3: Laboratory test for correction factors**

369 The interference of non-targeted VOC on ammonia measurement by the PAS was investigated

370 through selected single VOC as the sole input measured simultaneously by PAS, PTR-MS and

371 CRDS, as shown in the setup in Figure 1. An example of the interference test can be seen in

372 Figure S1, where the three instruments measured acetic acid simultaneously under various

373 concentration levels. Concentration dependent interference was clear for acetic acid on PAS

374 ammonia measurements.

375 **Table 2.** Obtained correction factors (in equations) between tested non-targeted VOC and the false
376 signal measured by PAS. 'y' points to the false concentration measured by PAS, and 'x' points to
377 the VOC concentration. The value in the brackets indicated the correlation coefficient of the linear
378 fit. N is the number of VOC concentration levels tested for determination of correction factors.

Compound	N	NH_3 (y: ppbv; x: ppbv)	CH_4 (y: ppbv; x: ppbv)	N_2O (y: ppbv; x: ppmv)	CO_2 (y: ppbv; x: ppbv)	SF_6 (y: ppbv; x: ppbv)
ethanol	10	y=2.81x(1.00)	y=1.88x(1.00)	y=411x/(x+14)(0.93)	y=0.40x(0.99)	y=-0.014x(1.00)
methanol	9	y=3.29x(0.74)	y=3.81x(0.74)	y=99x/(x+9)(0.78)	y=0.45x(0.47)	y=-0.15x(0.73)
acetic acid	10	y=0.72x(1.00)	y=-3.14x(1.00)	y=514x/(x+22)(0.95)	y=0.39x(0.99)	y=0.31x(1.00)
acetaldehyde	4	(-)	y=-0.85x(0.61)	y=317x/(x+31)(0.98)	(-)	y=0.044x(0.58)
2-butanone	4	y=-0.13x(1.00)	y=-4.02x(1.00)	y=311x/(x+26)(1.00)	y=-0.61x(0.74)	y=0.23x(1.00)
acetone	6	y=0.02x(0.99)	y=2.10x(0.99)	y=104x/(x+4)(0.99)	(-)	y=0.015x(0.99)
1-propanol	5	y=2.41x(0.87)	y=2.95x(0.87)	y=3569x/(x+602)(1.00)	y=0.25x(0.51)	y=-0.064x(0.84)
1-butanol	7	y=2.66x(0.99)	y=3.07x(0.99)	y=807x/(x+73)(0.99)	(-)	y=-0.061x(0.97)
methanol(N_2)	4	y=1.03x(0.80)	y=1.46x(0.83)	(-)	y=0.35x(0.54)	y=-0.056x(0.86)

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381 In principle, establishing correction factors for each specific compound could eliminate the

382 interferences of VOCs on ammonia measurements on a specific instrument with the same filter

383 specifications. This requires, however, that VOC concentrations be measured simultaneously.

384   Figure 4A & B show two examples of the calibration lines for acetic acid and ethanol, from

385   which a correction factor (CF) between the false ammonia concentration and the tested

386   compound could be obtained (CF=0.72 for acetic acid and CF=2.81 for ethanol). A linear

387   response of the ammonia interference was observed for all the tested compounds and they had

388   high correlation coefficients. The correction factors for ammonia interference by other tested

389   VOCs can be found in Table 2, where ethanol, methanol, 1-propanol and 1-butanol give the

390   highest false signals on ammonia measured by the PAS, with correction factors of 2.81, 3.29,

391   2.41 and 2.66, respectively. Due to the fact that these compounds are often found in cattle barn

392   buildings and feed silage even in the level of ppmv especially for ethanol, methanol and 1-

393   propanol (Rabaud et al., 2003; Ngwabie et al., 2008; Howard et al., 2010; Hafner et al., 2013),

394   severe interference on ammonia measured by PAS could therefore exist. While acetic acid gave

395   significant false signals on ammonia (CF=0.72), acetone only showed little interference on

396   ammonia (CF=0.02). Meanwhile, negative false signals were observed for ammonia by 2-

397   butanone (CF=-0.13). Interestingly, the correction factor for false ammonia by methanol in

398   nitrogen matrix is significantly different from that by methanol presented in air matrix

399   (CF=1.03 vs 3.29). This observation is possibly related to the relatively rapid vibrational energy

400   transfer between the VOC and oxygen (Harren et al., 2000). While nitrogen has a vibrational

401   frequency around 2360 cm^{-1}, oxygen has a vibrational frequency of 1554 cm^{-1} with only 170

402   collisions needed to transfer energy to the vibrational mode of O_2 (Lambert, 1977).

403   Besides the interferences on ammonia by the non-targeted VOCs, other target gases also

404   showed various levels of interferences, as also indicated by previous studies (e.g., Zhao et al.,

405   2012; Hassouna et al., 2013). Because target gases may have more overlap for the infrared

406   spectrum, the primary interference on one target gas caused by the overlap with non-targeted

407   VOCs could therefore influence and cause secondary interference on other target gases (Zhao

408   et al., 2012). Still, in theory, correction factors could be obtained for the interfered gases by the

409   tested VOCs. Specifically, for the interference on methane by non-targeted methanol, 1-butanol,

410   1-propanol, acetone and ethanol showed positive false signals (CF=3.81, 3.07, 2.95, 2.10, 1.88,

411   respectively). 2-butanone, acetic acid and acetaldehyde showed negative false signals to

412   methane, with correction factors equal to -4.02, -3.14 and -0.85, respectively. All interferences

413   on methane are shown in Table 2. For methanol in nitrogen, the calibration again showed

414   significant difference compared to air (CF=1.46 vs. 3.81).

415   Meanwhile, the non-targeted VOC also caused false signals on nitrous oxide signals, with a

416   much lower level of interference. Further, the calibrations of the nitrous oxide interference by

417   the non-targeted VOCs seemed not to be following linear relationships. For examples, Figure

418   4C & D showed the false signals of nitrous oxide caused by ethanol and acetic acid. Clearly, a

419   non-linear relation exists between the nitrous oxide interference and VOC concentration. The

420   curves could be well fitted to the non-linear equation of $y=kx/(x+m)$, where k could represent

421   the maximum interference on nitrous oxide by the single VOC, m could represent the half-

422   saturation constant indicating the level higher than which of the VOC concentration could cause

423   half of the maximum interference on nitrous oxide. As shown in Table 2, all tested VOCs

424   showed positive non-linear interference to the nitrous oxide signals, and 1-butanol showed the

425   highest maximum interference on nitrous oxide. Interestingly, no interference was observed for

426   nitrous oxide when methanol was presented in nitrogen matrix, while a relatively lower level

427   of interference observed on nitrous oxide by methanol when presented in air matrix compared

428   to other tested VOC.

429   Furthermore, some of the tested non-targeted VOCs also caused interference on carbon dioxide

430   measured by the PAS. The background of carbon dioxide was considered as unchanged during

431   the interference tests. While methanol, ethanol, acetic acid and 1-propanol caused positive false

432   signals for carbon dioxide measured by the PAS (CF = 0.45, 0.40, 0.39, 0.25, respectively), 2-

433   butanone caused negative false signals with CF = -0.61 (Table 2). Other tested VOCs, including

434   acetone, acetaldehyde and 1-butanol, did not show interferences on carbon dioxide measured

435   by the PAS. This is likely because no overlap of the gas infrared adsorption spectra exists

436   between these VOCs and carbon dioxide. As expected, methanol in nitrogen also caused

437   interference on carbon dioxide (CF =0.35) slightly lower than methanol in air.

438   Besides, SF_6 measurements were interfered by the tested non-targeted VOC, with lower

439   correction factor obtained compared to NH_3, CH_4, N_2O and CO_2. Acetic acid and 2-butanone

440   caused the highest interferences on SF_6, with correction factors of 0.31 and 0.23, respectively.

441   Other tested VOCs caused significantly less interference on SF_6, among which methanol gave

442   the highest negative correction factor of -0.15. Again, the methanol in nitrogen gave a

443   significantly lower level of interference on SF_6 compared to methanol in air (CF = -0.056 vs -

444   0.15).

445   Overall, the tested non-target VOCs in this study caused significant interference on target gases,

446   where ammonia and methane showed the most interference. Even though less interference was

447   observed for nitrous oxide, this could still cause problems due to the typically low concentration

448   level of this compound in e.g. livestock facilities or soil (Iqbal et al., 2013; Rong et al., 2014).

449   Nevertheless, the correction factors obtained from this study offer a possibility for correcting

450   for the interferences caused by the tested non-targeted VOCs, if the specific VOC

451   concentrations are available from simultaneous measurements. For historical data this is apart

452   from a few exceptions never the case.

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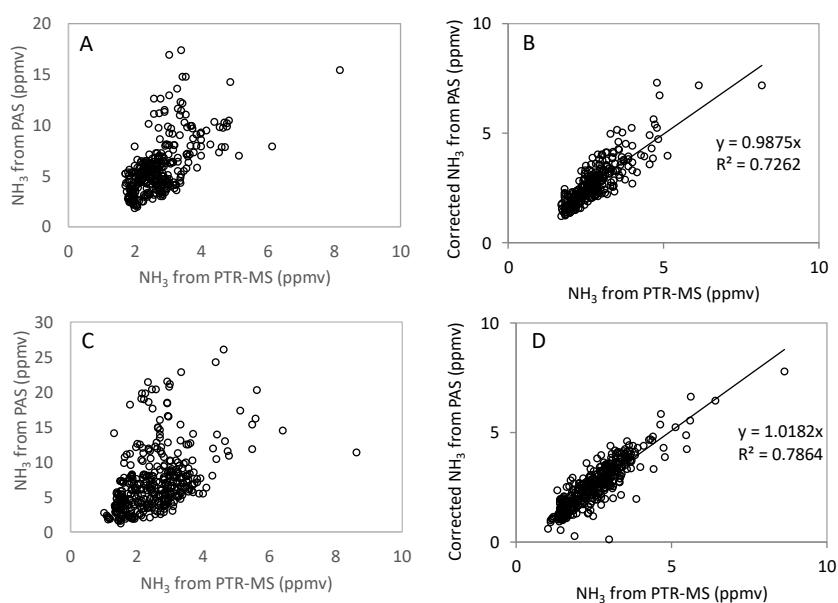
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475   **Figure 5.** NH_3 concentrations measured by the PAS (vertical axis) and by the PTR-MS (horizontal
476   axis) in the field measurement from Location One before the correction by the tested non-targeted
477   VOCs (A) and after the correction by the tested non-targeted VOCs (B), and from Location Two
478   before the correction by the tested non-targeted VOCs (C) and after the correction by the tested non-
479   targeted VOCs (D).

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481   **3.4   Experiment 4: Field test for validation of correction factors**

482   During the field test in the partially ventilated dairy barn, the ammonia measurements by PAS

483   and PTR-MS were compared between each other for one location in the pit and two locations

484   (Location One and Location Two) in the barn. Figure S2 showed the ammonia measured by

485   PAS and PTR-MS at the measurement point of the pit ventilation. In the pit ventilation, low

486   concentrations of VOCs were generally obtained and relatively high concentrations of ammonia

487   were observed for both instruments. Thus, no significant interferences were observed for

488   ammonia measured by the PAS, and ammonia measurements by PAS and PTR-MS showed a

489   good agreement as shown in Figure S2. However, for the two measurement points inside the

490   barn, significantly higher ammonia concentrations were obtained from PAS compared to the

491   concentrations measured by PTR-MS (Figure 5 A & C). The higher ammonia concentration

492   observed for the PAS measurement was most likely due to the interferences from VOCs, some

493   of which had high concentrations, especially for ethanol as shown in Table 3. In fact, the relation

494   between the ammonia concentrations measured by PAS and the ethanol concentrations

495   measured by PTR-MS, were highly correlated for both measurement locations, with slopes

496   close to 3 (2.97 and 3.12; see Figure S3). These two numbers are generally close to the

497   correction factor obtained for ethanol (CF = 2.81). The correction factors obtained in

498   'Experiment 3' were used for data correction of ammonia measurement by PAS since the

499   instrument configurations were kept the same. Thus, the interference of the VOCs on ammonia

500   measurement by PAS could be estimated from the correction factors obtained in 'Experiment

501   3' and used to correct the ammonia data. Figure 5B & D show the corrected ammonia

502   concentrations measured by PAS by using the correction factors, together with the measured

503   ammonia concentration by the PTR-MS for both measurement locations. The corrected

504   ammonia concentrations from the PAS are generally in good agreement with the ammonia

505   concentration measured by the PTR-MS, with slopes were close to 1 (0.99 and 1.02). This

506   experiment validated that with the correction from major VOCs, the interference on NH3

507 measured by PAS could be reasonable estimated in field applications. However, it should be

508 noted that a lot of redundant work is needed to make this correction if only NH_3 concentration

509 determination needed, since a number of VOCs concentrations need to be known in order to

510 achieve a right correction even though some minor VOCs within low range ppbv could be

511 omitted.

512

513 **Table 3.** Average concentrations (±standard deviation) of selected VOCs during the field test in the

514 dairy cattle barn for the two sampling locations 1 & 2, both of which are located inside the barn.

Compound	Concentrations (ppbv)	
	Location 1	Location 2
ethanol	1421±946	1622±1355
methanol	237±150	241±192
acetic acid	57±41	69±62
acetaldehyde	99±81	92±84
2-butanone	19±11	17±13
acetone	78±30	52±25
1-propanol	71±45	72±68
1-butanol	22±10	16±12
hydrogen sulfide	12±10	11±8
trimethylamine	8.6±3.5	5.7±3.1
dimethyl sulfide	15±9	14±10
4-methylphenol	5.2±2.1	3.8±2.2

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517 **4 Conclusions**

518 One must take special care when measuring NH_3 and greenhouse gas emissions by using PAS

519 techniques as Innova. Depending on the IR absorption spectra of different gases, non-targeted

520 gases such as VOCs may interfere significantly with the target gases causing inaccurate results.

521 In order to confirm and determine the correction factors regarding the interference on targeted

522 gases caused by selected VOCs, experiments were conducted by using simultaneously a PAS

523 and a PTR-MS, while also clarified by a CRDS. Results from these experiments provide useful

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524   guidelines with regards to interferences caused by non-targeted gases. The results on correction

525   factors revealed that the tested VOCs of ethanol, methanol, 1-butanol, 1-propanol and acetic

526   acid caused the most significant interference on NH_3 measured by PAS. Interestingly, non-linear

527   relations were obtained for interreferences on N_2O by test VOCs as non-targeted gases, while

528   linear response was obtained for interference on other targeted gases. The field test in the cattle

529   barn validated the interference caused by VOCs on NH_3 measurement by the PAS when

530   simultaneously measured by the PTR-MS. Therefore, the correction factors could be used for

531   potential data corrections when same type of PAS is used together with available VOCs data.

532   No validation was performed for greenhouse emissions correction due to lack of alternative

533   measurement.

534

535   *Code and data availability*. Data and code are available upon request to the corresponding

536   author.

537   *Supplement*. The supplementary information is available free of charge at DOI: .

538

539   *Author contributions*. DL, LR and AF designed the setup for the experiments performed; LR,

540   XK and AC contributed to setting up and conducting experiments and acquiring data; DL, AF,

541   JK, XK and APA contributed to section writing and analysis; LR, AF and JK assisted in data

542   analysis and manuscript editing.

543

544   *Competing interests*. The authors declare that they have no conflicts of interest.

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548

549   **References**

550   Aneja, V. P., Schlesinger, W. H., and Erisman, J. W.: Effects of agriculture upon the air quality

551   and climate: research, policy, and regulations, Environ. Sci. Technol., 43, 4234–4240,

552   https://doi.org/10.1021/es8024403, 2009.

553   Angela, E., Di, F. C., Mario, L. P., and Gaetano, S.: Photoacoustic Spectroscopy with Quantum

554   Cascade Lasers for Trace Gas Detection, Sensors-Basel, 6, 1411–1419,

555   https://doi.org/10.3390/s6101411, 2006.

556   Aprea E., Biasioli F., Mark T.D., and Gasperi F.: PTR-MS study of esters in water and

557   water/ethanol solutions: Fragmentation patterns and partition coefficients, Int. J. Mass

558   Spectrom., 262, 114–121, https://doi.org/10.1016/j.ijms.2006.10.016, 2007.

559   Berden, G., Peeters, R., and Meijer, G.: Cavity ring-down spectroscopy: Experimental schemes

560   and applications, Int. Rev. Phys. Chem., 19, 565–607,

561   https://doi.org/10.1080/014423500750040627, 2000.

562   Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-transfer reaction mass spectrometry, Chem.

563   Rev., 109, 861–896, https://doi.org/10.1002/chin.200923275, 2009.

564   Blanes-Vidal, V., Topper, P. A., and Wheeler, E. F.: Validation of ammonia emissions from dairy

565   cow manure estimated with a non-steady-state, recirculation flux chamber with whole-

566   building emissions, T. ASABE, 50, 633–640, https://doi.org/10.13031/2013.22652, 2007.

567   Bouwman, A. F., Lee, D. S., Asman, W. A. H., Dentener, F. J., Van, D. H. K. W., and Olivier, J.

Atmospheric
Measurement
Techniques
Discussions

568   G. J.: A global high-resolution emission inventory for ammonia, Global Biogeochem. Cy.,

569   11, 561–587, https://doi.org/10.1029/97GB02266, 1997.

570   California Air Resources Board (CARB).: Manufacturer Notification. Mail-Out #MSO 2000-

571   08,   CARB: Sacramento,   CA,   USA,   Available   online:

572   http://www.arb.ca.gov/msprog/mailouts/ mso0008/mso0008.pdf, 2000.

573   Chadwick, D., Sommer, S., Thorman, R., Fangueiro, D., Cardenas, L., Amon, B., and

574   Misselbrook, T.: Manure management: Implications for greenhouse gas emissions, Anim.

575   Feed Sci. Tech., 166-167, 514–531, https://doi.org/10.1016/j.anifeedsci.2011.04.036, 2011.

576   Chung, M.Y., Beene, M., Ashkan, S., Krauter, C., and Hasson, A.S.: Evaluation of non-enteric

577   sources of non-methane volatile organic compound (NMVOC) emissions from dairies,

578   Atmos. Environ., 44, 786–794, https://doi.org/10.1016/j.atmosenv.2009.11.033, 2009.

579   Cortus E.L., Jacobson L.D., Hetchler B.P., and Heber A.J.: Emission monitoring methodology

580   at a NAEMS dairy site, with an assessment of the uncertainty of measured ventilation rates,

581   ASABE   -   9th   International   Livestock   Environment   Symposium,   583-590,

582   https://doi.org/10.13031/2013.41578, 2012.

583   De Gouw J., and Warneke C.: Measurements of volatile organic compounds in the earth's

584   atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26,

585   223–257, https://doi.org/10.1002/mas.20119, 2007.

586   EMEP, Agency: EMEP/EEA air pollutant emission inventory guidebook - 2013. *Luxembourg:*

587   *Publications   Office   of   the   European   Union,*   3B: Manure   management,

588   https://www.eea.europa.eu/publications/emep-eea-guidebook-2013/part-b-sectoral-

589   guidance-chapters/4-agriculture/3-b-manure-management/view, 2013.

590   Emmenegger, L., Mohn J., Sigrist M., Marinov D., Steinemann U., Zumsteg F., and Meier M.:

591   Measurement of ammonia emissions using various techniques in a comparative tunnel study,

592   Int. J. Environ. Pollut., 22, 326–341, https://doi.org/10.1504/IJEP.2004.005547, 2004.

593   Erisman, J. W., Bleeker, A., Galloway, J., and Sutton, M. S.: Reduced nitrogen in ecology and

594   the   environment,   Environ.   Pollut.,   150,   140–149,

595   https://doi.org/10.1016/j.envpol.2007.06.033, 2007.

596   Feilberg A., Liu D., Adamsen A.P.S., Hansen M.J., and Jonassen K.E.N.: Odorant emissions

597   from intensive pig production measured by online proton-transfer-reaction mass

598   spectrometry, Environ. Sci. Technol., 44, 5894–5900, https://doi.org/10.1021/es100483s,

599   2010.

600   Fle´chard, C. R., Neftel, A., Jocher, M., Ammann, C., and Fuhrer, J.: Bi-directional

601   soil/atmosphere N2O exchange over two mown grassland systems with contrasting

602   management practices, Global Change Biol., 11, 2114–2127, https://doi.org/10.1111/j.1365-

603   2486.2005.01056.x, 2010.

604   Hafner S.D., Howard C., Muck R.E., Franco R.B., Montes F., Green P.G., Mitloehner F., Trabue,

605   S.L., and Rotz C.A.: Emission of volatile organic compounds from silage: Compounds,

606   sources,   and   implications,   Atmos.   Environ.,   77,   827–839,

607   https://doi.org/10.1016/j.atmosenv.2013.04.076, 2013.

608   Hafner, S. D., Montes, F., Rotz, C. A., and Mitloehner, F.: Ethanol emission from loose corn

609   silage   and   exposed   silage   particles.   Atmos.   Environ.,   44,   4172–4180,

610   https://doi.org/10.1016/j.atmosenv.2010.07.029, 2010.

611   Harren F.J.M., Cotti G., Oomens J., and Hekkert S.L.: Photoacoustic Spectroscopy in Trace Gas

Atmospheric
Measurement
Techniques
Discussions

612   Monitoring, in Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), 2203–2226,

613   ©JohnWiley & Sons Ltd, Chichester, 2000.

614   Hassouna, M., Espagnol, S., Robin, P., Paillat, J. M., Levasseur, P., and Li, Y.: Monitoring NH3,

615   N2O, CO2 and CH4 emissions during pig solid manure storage and effect of turning,

616   Compost Sci. Util., 16, 267–274, https://doi.org/10.1080/1065657X.2008.10702388, 2008.

617   Hassouna, M., Robin, P., Charpiot, A., Edouard, N., and Méda, B.: Infrared photoacoustic

618   spectroscopy in animal houses: Effect of non-compensated interferences on ammonia,

619   nitrous oxide and methane air concentrations, Biosyst. Eng., 114, 318–326,

620   https://doi.org/10.1016/j.biosystemseng.2012.12.011, 2013.

621   Heber A.J., Ni J.-Q., Lim T.T., Tao P.-C., Schmidt A.M., Koziel J.A., Beasley D.B., Hoff, S.J.,

622   Nicolai, R.E., Jacobson, L.D., and Zhang Y.: Quality assured measurements of animal

623   building emissions: Gas concentrations, J. Air Waste Manage., 56, 1472–1483,

624   https://doi.org/10.1080/10473289.2006.10465680, 2006.

625   Heyden, C. V. D., Brusselman, E., Volcke, E. I. P., and Demeyer, P.: Continuous measurements

626   of ammonia, nitrous oxide and methane from air scrubbers at pig housing facilities, J.

627   Environ. Manage., 181, 163–171, https://doi.org/10.1016/j.jenvman.2016.06.006, 2016.

628   Howard, C. J., Kumar, A., Malkina, I., Mitloehner, F., Green, P. G., Flocchini, R. G., and

629   Kleeman, M. J.: Reactive organic gas emissions from livestock feed contribute significantly

630   to ozone production in central California, Environ. Sci. Technol., 44, 2309–2314,

631   https://doi.org/ 10.1021/es902864u, 2010.

632   Hutchings, N. J., Sommer, S. G., Andersen, J. M., and Asman, W. A. H.: A detailed ammonia

633   emission inventory for Denmark, Atmos. Environ., 35, 1959–1968,

634   https://doi.org/10.1016/S1352-2310(00)00542-2, 2001.

635   Insam, H., and Seewald, M. S. A.: Volatile organic compounds (VOCs) in soils, Biol. Fert. Soils,

636   46, 199–213, https://doi.org/10.1007/s00374-010-0442-3, 2010.

637   Iqbal, J., Castellano, M.J., and Parkin, T.B.: Evaluation of photoacoustic infrared spectroscopy

638   for simultaneous measurement of N2O and CO2 gas concentrations and fluxes at the soil

639   surface, Global Change Biol., 19, 327–336, https://doi.org/10.1111/gcb.12021, 2013.

640   Jie, D. F., Wei, X., Zhou, H. L., Pan, J. M., and Ying, Y. B.: Research progress on interference

641   in the detection of pollutant gases and improving technology in livestock farms: A review,

642   Appl. Spectrosc. Rev., 52,101–122, https://doi.org/10.1080/05704928.2016.1208213, 2016.

643   Joo H.S., Ndegwa P.M., Neerackal G.M., Wang X., and Harrison J.H.: Effects of manure

644   managements on ammonia, hydrogen sulfide and greenhouse gases emissions from the

645   naturally   ventilated   dairy   barn,   ASABE,   2   ,   1302-1311,

646   https://doi.org/10.13031/aim.20131593447, 2013.

647   Lambert J.D.: Vibrational and Rotational Relaxation in Gases, Clarendon Press, Oxford, **1977**.

648   Lin, X., Zhang, R., Jiang, S., El-Mashad, H., and Xin, H.: Emissions of ammonia, carbon

649   dioxide and particulate matter from cage-free layer houses in California, Atmos. Environ.,

650   152, 246–255, https://doi.org/10.1016/j.atmosenv.2016.12.018, 2017.

651   Li, R., Nielsen, P. V., and Zhang, G. Q.: Effects of airflow and liquid temperature on ammonia

652   mass transfer above an emission surface: experimental study on emission rate, Bioresource

653   Technol., 100, 4654–4661, https://doi.org/10.1016/j.biortech.2009.05.003, 2009.

654   Liu D., Lokke M.M., Leegaard Riis A., Mortensen K., and Feilberg A.: Evaluation of clay

655   aggregate biotrickling filters for treatment of gaseous emissions from intensive pig

656   production, J. Environ. Manage., 136, 1–8, https://doi.org/10.1016/j.jenvman.2014.01.023,

657   2014.

658   Liu, D., Nyord, T., Rong, L., and Feilberg, A.: Real-time quantification of emissions of volatile

659   organic compounds from land spreading of pig slurry measured by PTR-MS and wind

660   tunnels,   Sci.   Total.   Environ.,   639,   1079–1087,

661   https://doi.org/10.1016/j.scitotenv.2018.05.149, 2018.

662   Lumasense.:   Photoacoustic   Gas   Monitor   -   INNOVA   1412i.

663   http://www.lumasenseinc.com/FR/produits/gas-sensing/gas-monitoring-

664   instruments/photoacoustic-spectroscopy-pas/photoacoustic-gas-monitor-innova-1412i/.

665   Accessed 18th November, 2018.

666   Malkina, I.L., Kumar, A., Green, P.G., and Mitloehner, F.M.: Identification and quantitation of

667   volatile organic compounds emitted from dairy silages and other feedstuffs, J. Environ. Qual.,

668   40, 28, https://doi.org/10.2134/jeq2010.0302, 2011.

669   Melse, R. W., and Werf, A. W. V. D.: Biofiltration for mitigation of methane emission from

670   animal husbandry, Environ. Sci. Technol., 39, 5460, https://doi.org/10.1021/es048048q,

671   2005.

672   Moset, V., Cambra-López, M., Estellés, F., Torres, A. G., and Cerisuelo, A.: Evolution of

673   chemical composition and gas emissions from aged pig slurry during outdoor storage with

674   and   without   prior   solid   separation,   Biosyst.   Eng.,   111,   2–10,

675   https://doi.org/10.1016/j.biosystemseng.2011.10.001, 2012.

676   Ngwabie, N. M., Jeppsson, K. H., Gustafsson, G., and Nimmermark, S.: Effects of animal

677   activity and air temperature on methane and ammonia emissions from a naturally ventilated

Atmospheric
Measurement
Techniques
Discussions

678   building   for   dairy   cows,   Atmos.   Environ.,   45,   6760–6768,

679   https://doi.org/10.1016/j.atmosenv.2011.08.027, 2011.

680   Ngwabie, N.M., Schade, G.W., Custer, T.G., Linke, S., and Hinz, T.: Abundances and flux

681   estimates of volatile organic compounds from a dairy cowshed in Germany, J. Environ. Qual.,

682   37, 565–573, https://doi.org/10.2134/jeq2006.0417, 2008.

683   Ni, J. Q., and Heber, A. J.: Sampling and Measurement of Ammonia at Animal Facilities, Adv.

684   Agron., 98, 201–269, https:// doi.org/10.1016/s0065-2113(08)00204-6, 2008.

685   Ni, J. Q., Diehl, C. A., Chai, L., Chen, Y., Heber, A. J., Lim, T. T., and Bogan, B. W.: Factors

686   and characteristics of ammonia, hydrogen sulfide, carbon dioxide, and particulate matter

687   emissions   from   two   manure-belt   layer   hen   houses,   Atmos.   Environ.,   156,

688   https://doi.org/10.1016/j.atmosenv.2017.02.033, 2017.

689   Norman, M., Hansel, A., and Wisthaler, A.: O_2^+ as reagent ion in the PTR-MS instrument:

690   Detection   of   gas-phase   ammonia,   Int.   J.   Mass   Spectrom.,   265,   382–387,

691   https://doi.org/10.1016/j.ijms.2007.06.010, 2007.

692   Osada, T., and Fukumoto, Y.: Development of a new dynamic chamber system for measuring

693   harmful gas emissions from composting livestock waste, Water Sci. Technol., 44, 79–86,

694   https://doi.org/10.2166/wst.2001.0513, 2001.

695   Osada, T., Rom H.B., and Dahl P.: Continuous measurement of nitrous oxide and methane

696   emission in pig units by infrared photoacoustic detection, T. ASAE, 41, 1109–1114,

697   https://doi.org/10.13031/2013.17256, 1998.

698   Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., and Henze, D. K.: Ammonia

699   emissions in the United States, European Union, and China derived by high‐resolution

Atmospheric
Measurement
Techniques
Discussions

700   inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions

701   inventory (MASAGE_NH3), J. Geophys. Res., 119, 4343–4364,

702   https://doi.org/10.1002/2013JD021130, 2015.

703   Pearson, J., and Stewart, G. R.: The deposition of atmospheric ammonia and its effects on plants,

704   New Phytol., 125, 283–305, https://doi.org/10.1111/j.1469-8137.1993.tb03882.x, 1993.

705   Picarro.: Technology: Cavity Ring-Down Spectroscopy (CRDS), Link:

706   https://www.picarro.com/technology/cavity_ring_down_spectroscopy. Accessed 12th May,

707   2018.

708   Phillips, V. R., Lee, D. S., Scholtens, R., Garland, J. A., and Sneath, R. W.: SE—Structures and

709   Environment : A Review of Methods for measuring Emission Rates of Ammonia from

710   Livestock Buildings and Slurry or Manure Stores, Part 2: monitoring Flux Rates,

711   Concentrations and Airflow Rates, J. Agr. Eng. Res., 78, 1–14,

712   https://doi.org/10.1006/jaer.2000.0618, 2001.

713   Pinder, R. W., Adams, P. J., and Pandis, S. N.: Ammonia emission controls as a cost-effective

714   strategy for reducing atmospheric particulate matter in the Eastern United States, Environ.

715   Sci. Technol., 41, 380–6, https://doi.org/10.1021/es060379a, 2007.

716   Rabaud, N.E., Ebeler, S.E., Ashbaugh, L.L., and Flocchini, R.G.: Characterization and

717   quantification of odorous and non-odorous volatile organic compounds near a commercial

718   dairy in California, Atmos. Environ., 37, 933–940, https://doi.org/10.1016/S1352-

719   2310(02)00970-6, 2003.

720   Rong L., Liu D., Pedersen E.F., and Zhang G.: Effect of climate parameters on air exchange

721   rate and ammonia and methane emissions from a hybrid ventilated dairy cow building, Energ.

722   Buildings, 82, 632–643, https://doi.org/10.1016/j.enbuild.2014.07.089, 2014.

723   Schilt, S., Thévenaz, L., Niklès, M., Emmenegger, L., and Hüglin, C.: Ammonia monitoring at

724   trace level using photoacoustic spectroscopy in industrial and environmental applications,

725   Spectrochim. Acta. A, 60, 3259–3268, https://doi.org/10.1016/j.saa.2003.11.032, 2004.

726   Scholtens, R., Jones, C. J. D. M., Lee, D. S., and Phillips, V. R.: Measuring ammonia emission

727   rates from livestock buildings and manure stores－part 1: development and validation of

728   external tracer ratio, internal tracer ratio and passive flux sampling methods, Atmos. Environ.,

729   38, 3003–3015, https://doi.org/10.1016/j.atmosenv.2004.02.030, 2004.

730   Seinfeld, J.H.; and Pandis, S.N.: Atmospheric Chemistry and Physics: From Air Pollution to

731   Climate Change, Wiley-VCH: New York. 1326 pp., ISBN 0-471-17815-2, 1997.

732   Shaw, S.L., Mitloehner, F.M., Jackson, W., Depeters, E.J., Fadel, J.G., Robinson, P.H.,

733   Holzinger, R., and Goldstein, A.H.: Volatile organic compound emissions from dairy cows

734   and their waste as measured by proton-transfer-reaction mass spectrometry, Environ. Sci.

735   Technol., 41, 1310–1316, https://doi.org/10.1021/es061475e, 2007.

736   Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., Mccarl, B., Ogle, S., O'Mara,

737   F., and Rice, C.: Greenhouse gas mitigation in agriculture, Philos. T. R. Soc. B, 363, 789–

738   813, https://doi.org/10.1098/rstb.2007.2184, 2008.

739   Thomas, C. D., Cameron, A., Green, R. E., Bakkenes, M., Beaumont, L. J., Collingham, Y. C.,

740   Erasmus, B. F., De Siqueira, M. F., Grainger, A., and Hannah, L.: Extinction risk from climate

741   change, Nat., 427, 145–148, https://doi.org/10.1038/nature02121, 2004.

742   Van Breemen, N., Mulder, J., and Driscoll, C. T.: Acidification and alkalinization of soils, Plant

743   Soil, 75, 283–308, https://doi.org/10.1007/BF02369968, 1983.

Atmospheric
Measurement
Techniques
Discussions

744   Von Bobrutzki, K., Braban, C.F., Famulari, D., Jones, S.K., Blackall, T., Smith, T.E.L., Blom,

745   M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M.R., Percival, C.J., Whitehead, J.D.,

746   Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M.A., and

747   Nemitz, E.: Field inter-comparison of eleven atmospheric ammonia measurement techniques,

748   Atmos. Meas. Tech+.,   3, 91–112, https://doi.org/10.5194/amt-3-91-2010, 2010.

749   Vries, J. W. D., and Melse, R. W.: Comparing environmental impact of air scrubbers for

750   ammonia abatement at pig houses: A life cycle assessment, Biosyst. Eng., 161, 53–61,

751   https://doi.org/10.1016/j.biosystemseng.2017.06.010, 2017.

752   Wang-Li L., Li Q.-F., Chai L., Cortus E.L., Wang K., Kilic I., Bogan B.W., Ni J.-Q., and Heber

753   A.J.: The national air emissions monitoring study's Southeast Layer Site: Part III. Ammonia

754   concentrations   and   emissions,   T.   ASABE,   56,   1185–1197,   https://

755   doi.org/10.13031/trans.56.9673, 2013.

756   Yuan, B., Koss, A.R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J.A.: Proton-

757   Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev.,

758   117, 13187–13229, https://doi.org/10.1021/acs.chemrev.7b00325, 2017.

759   Zhao, L., Hadlocon, L. J. S., Manuzon, R. B., Darr, M. J., Keener, H. M., Heber, A. J., and Ni,

760   J.: Ammonia concentrations and emission rates at a commercial poultry manure composting

761   facility, Biosyst. Eng., 150, 69–78, https://doi.org/10.1016/j.biosystemseng.2016.07.006,

762   2016.

763   Zhao, Y., Pan, Y., Rutherford, J., and Mitloehner, F. M.: Estimation of the Interference in Multi-

764   Gas Measurements Using Infrared Photoacoustic Analyzers, Atmos., 3, 246–265,

765   https://doi.org/10.3390/atmos3020246, 2012.