

Response to Minor revision:

The requested information in Table 1 on the accuracy of the NH₃ measurements by the three instruments is still missing. Please provide quantitative information.

Response: The accuracy of the NH₃ measurements by the three instruments are now given in Table 1. The accuracy was propagated from uncertainty of the calibration standard gas of ammonia (10%), uncertainty of mass flow controller (2%) used for gas dilution systems, and uncertainty of instrumental quantities of ammonia (12.8%, 1.6% and 0.2% for Innova, PTR-MS and Picarro, respectively). It should be noted that the uncertainty associated with the comparison to the standard gas did not take into account the interferences by other livestock gases on the Innova.

1 **Photoacoustic measurement with infrared band-pass filters significantly overestimate**

2 **NH₃ emissions from cattle houses due to VOCs interferences**

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23 **Abstract:** Infrared photoacoustic spectroscopy using band-pass filters (PAS) is a widely used
24 method for measurement of NH₃ and greenhouse gas emissions (CH₄, N₂O and CO₂) especially
25 in agriculture, but non-targeted gases such as volatile organic compounds (VOCs) from cattle
26 barns may interfere with target gases causing inaccurate results. This study made an estimation
27 of NH₃ interference in PAS caused by selected non-targeted VOCs which were simultaneously
28 measured by a PAS and a PTR-MS (proton transfer reaction mass spectrometry). Laboratory
29 calibrations were performed for NH₃ measurement and VOCs were selected based on a
30 headspace test of the feeding material (maize silage). Strong interferences of VOCs were
31 observed on NH₃ and greenhouse emissions measured by PAS. Particularly, ethanol, methanol,
32 1-butanol, 1-propanol and acetic acid were found to have the highest interferences on NH₃,
33 giving empirical relationships in the range of 0.7 to 3.3 ppmv NH₃ per ppmv VOC. A linear
34 response was typically obtained, except for a non-linear relation for VOCs on N₂O
35 concentration. The corrected online NH₃ concentrations measured by PAS in a dairy farm (with
36 empirical relationships 2.1 ± 0.8 and 2.9 ± 1.9 for Location One and Location Two, respectively)
37 were confirmed to be correlated ($R^2 = 0.73$ and 0.79) to the NH₃ concentration measured
38 simultaneously by the PTR-MS, when the empirical corrections obtained from single VOC tests
39 were applied.

40 **1 Introduction**

41 Measurements of ammonia and greenhouse gas (CH₄, N₂O and CO₂) emissions are gaining
42 increasing attention due to stronger interests on global change and air pollution. Ammonia not
43 only causes serious environmental problems such as soil acidification and pollution of
44 underground water and surface water (van Breemen et al., 1983; Pearson and Stewart, 1993;

45 Erisman et al., 2007), but is also important for fine particle formation (Bouwman et al., 1997;
46 Seinfeld and Pandis, 1997; Pinder et al., 2007). Greenhouse gas emissions, on the other hand,
47 are causing climate change (Thomas et al., 2004; Chadwick et al., 2011). Livestock husbandry
48 was estimated to be responsible for more than 80 % of the ammonia emission in Western Europe
49 (Hutchings et al., 2001; EMEP, 2013) and more than 60% in China (Paulot et al., 2014). In the
50 U.S.A, agriculture accounts for ~90 % of the total ammonia emissions (Aneja et al., 2009).
51 Meanwhile, agriculture accounts for 52 and 84 % of global anthropogenic methane and nitrous
52 oxide emissions (Smith et al., 2008). Accurate measurements of ammonia and greenhouse
53 emissions are therefore vital for reliable emission estimation and thereby the possible reduction
54 of these emissions through various efforts, such as air cleaning with biotrickling filters and air
55 scrubbers (Melse and Van der werf, 2005; De Vries and Melse, 2017). For ammonia
56 measurements, more than 30% difference between different methods has been reported
57 (Scholtens et al., 2004).

58 Infrared photoacoustic spectroscopy (PAS) is a widely-used technique for studies of air
59 emissions especially within agriculture (Osada et al., 1998; Osada and Fukumoto, 2001;
60 Emmenegger et al., 2004; Schilt et al., 2004; Heber et al., 2006; Elia et al., 2006; Blanes-Vidal
61 et al., 2007; Hassouna et al., 2008; Rong et al., 2009; Ngwabie et al., 2011; Cortus et al., 2012;
62 Joo et al., 2013; Wang-Li et al., 2013; Iqbal et al., 2013; Zhao et al., 2016; Ni et al., 2017; Lin
63 et al., 2017). The PAS technique determines the gas concentrations through measuring acoustic
64 signals caused by cell pressure changes when gas absorbs energy from infrared light at a
65 specific wavelength range using an optical filter and a chopper (Iqbal et al., 2013). For example,
66 the Innova 1312 and later versions (Lumasense Technologies, Ballerup, Denmark) uses the PAS

67 principle and was previously verified by the US EPA and recommended by the Air Resources
68 Board in California (CARB, 2000). In principle, this instrument "is capable of measuring
69 almost any gas that absorbs infrared light" (Innova, Lumasense Technology A/S, Denmark).
70 The method is based on nondispersive broadband spectroscopy and selectivity is achieved by
71 using appropriate wavelength filter, with one filter for each targeted trace gas. Innova 1312 and
72 1412 instruments have been used in a large number of tests to measure NH₃, CH₄, CO₂ and N₂O
73 for agricultural applications. Water vapor is also measured to account for the strong absorption
74 of water throughout the infrared spectrum (Christensen, 1990a). Nevertheless, since the infrared
75 spectroscopic method is applied for measuring gas concentrations in PAS, the overlapping of
76 IR spectra with non-targeted gases can introduce significant interferences due to the absorption
77 of infrared light at similar wavelengths. The specificity is limited by the bandwidth of the
78 optical filters. The interferences can be corrected by the instrument software through cross-
79 compensation for all target gases when the instrument is calibrated (Christensen, 1990a;
80 Lumasense, 2012), but understanding and estimation of interferences from non-targeted gases
81 needs to be considered in each specific measurement situation. This is especially important for
82 agricultural applications where the manure and the animal feed may emit various types of gases
83 depending on the management and operations in the animal houses (Hassouna et al., 2013;
84 Moset et al., 2012). Therefore, two key questions exist: (a) what is the magnitude of
85 interferences that can be expected in agricultural environments, and (b) is it possible to quantify
86 and correct interferences in a reasonable way? Until now, the PAS interference has not been
87 well estimated and corrected for, although interferences were previously suspected in livestock
88 facilities (Phillips et al., 2001; Mathot et al., 2007; Ni & Heber, 2008). Flechard et al. (2005)

89 suspected that the N₂O concentration from soil measured by PAS (Innova 1312) was heavily
90 influenced by CO₂ and temperature even when cross-interference compensation was applied;
91 they developed an alternative correction algorithm based on controlled N₂O/CO₂/H₂O ratios
92 under selected temperature. Zhao et al (2012) claimed that the internal cross compensation
93 could eliminate the interferences between target gases, and quantified interferences of non-
94 targeted gas of NH₃ on targeted gases of ethanol, methanol, N₂O, CO₂, and CH₄, however,
95 without giving specific relationships. Iqbal et al. (2013) also demonstrated that a careful
96 calibration could eliminate the internal cross interferences of high water vapor and CO₂
97 concentrations on low concentrations of N₂O at the soil surface by comparison to GC
98 measurements. Nevertheless, tests of interferences by non-targeted VOCs were not included in
99 their study, likely due to the typical low concentrations of VOC in soil (Insam and Seewald,
100 2010). Hassouna et al. (2013) presented a field study on dairy cow buildings, where
101 interferences on NH₃, CH₄ and N₂O were observed. The interferences were suspected to be
102 caused by VOCs (acetic acid, ethanol and 1-propanol) that they measured simultaneously. In
103 their study, two PAS instruments were applied with one of them allocated with optical filters of
104 these VOCs (NH₃ optical filter was included for both PAS). Still, no empirical relationships
105 were given in terms of tested volatile organic compounds, which were typically emitted from
106 feeding materials such as maize silage (Howard et al., 2010; Malkina et al., 2011). The
107 correction of interferences of non-targeted VOCs on NH₃ emission is also essential for the
108 evaluation of emission abatement technologies such as air scrubbers, especially when the inlet
109 VOC concentrations are relatively high. An overestimation of ammonia removal efficiency
110 could easily be obtained since less interference would be expected for the outlet VOCs

111 especially for water-soluble compounds such as the VOCs investigated in this study.
112 In this work, an evaluation of interferences by non-targeted VOCs on targeted NH₃ and
113 greenhouse gas measurements by PAS is presented. The interference on NH₃ was tested by
114 simultaneous application of Proton-transfer-reaction mass spectrometry (PTR-MS), Cavity
115 Ring-Down Spectroscopy (CRDS) and PAS. The experiments were as follows: (1) ammonia
116 laboratory calibration by PAS, PTR-MS and CRDS; (2) VOC selection for testing of
117 interference on ammonia measured by PAS; (3) Effect of VOCs on ammonia and greenhouse
118 emissions measured by the PAS; (4) Field confirmation of interferences of non-targeted VOCs
119 on ammonia measurement and test of potential for data correction.

120 **2 Materials and methods**

121 **2.1 Instrumentation for gas concentrations measurement**

122 In this study, a PTR-MS, a CRDS NH₃ analyzer and a PAS gas analyzer were used to measure
123 trace gas concentrations in air. PTR-MS is a state-of-the-art and widely used technique for
124 highly sensitive online measurements of VOCs (De Gouw and Warneke, 2007; Blake et al.,
125 2009; Yuan et al., 2017). PTR-MS can also measure a few inorganic compounds such as
126 ammonia (at m/z 18) since the proton affinity (204.0 kcal/mol) of ammonia is higher than that
127 of water (165.0 kcal/mol). Since the intrinsic ion at m/z 18 is always formed in the plasma ion
128 source (Norman et al., 2007), ammonia measurements by PTR-MS are routinely corrected for
129 instrumental background contribution. The typical m/z 18 background signal corresponds to a
130 few hundred ppbv of NH₃. The background signal is relatively stable and still allows for NH₃
131 detection limits of 20-50 ppb. For agricultural measurement conditions, concentrations are
132 typically from a few hundred ppb to >10 ppm (e.g., Rong et al., 2009). When total gas

133 concentration measured by PTR-MS is higher than approximately 10 ppmv, dilution is needed
134 to keep the primary ion signals stable. A high-sensitivity PTR-MS (Ionicon Analytik GmbH,
135 Innsbruck, Austria) was applied for the test of ammonia calibration in the laboratory, effects of
136 non-targeted VOCs on ammonia measurement and field confirmation of interferences of non-
137 targeted VOCs on ammonia measurement. Standard conditions with a total voltage of 600 V in
138 the drift tube were utilized for the PTR-MS. Pressure and temperature in the drift tube were
139 maintained in the range of 2.1-2.2 mbar and at 60 °C, respectively, which gives an E/N ratio of
140 ca. 135 Townsend. The inlet of the PTR-MS is PEEK tubing of 1.2 m length with 0.64 mm
141 inner diameter (ID) and 1.6 mm outer diameter (OD). The inlet flow to the PTR-MS during
142 calibration test and measurements was kept ~150 mL/min. The inlet temperature was
143 maintained at 60 °C. The instrument calibration was performed based on specific reaction rate
144 constants and mass discrimination factors (accuracy better than 12%), as described in our
145 previous study (Liu et al., 2018). Mass calibration was performed before each test, while mass
146 discrimination calibration was performed for every two weeks.

147 CRDS determines the gas concentration (e.g., NH₃) by measuring the ring-down time of light
148 in the cavity due to absorption by a targeted gas species, which is compared to the ring-down
149 time without any additional absorption due to a targeted gas species. The light source is a laser
150 with tunable wavelength (von Bobruzki et al., 2010; Picarro, 2017). The very long effective
151 path length of the light in the cavity (e.g., over 20 km for 25 cm cavity) (Picarro, 2017), enables
152 a significantly higher sensitivity compared to conventional absorption spectroscopy (Berden et
153 al., 2000; von Bobruzki et al., 2010). There is negligible interference from VOCs on CRDS
154 measurements, which makes CRDS ideal to measure NH₃ concentrations in this setting (Kamp

155 et al., 2019). A G2103 Analyzer (Picarro Inc., Sunnyvale, CA, USA) using CRDS technique
156 was applied in this study for the test of ammonia laboratory calibration and the effect of non-
157 targeted VOCs on ammonia measurement. The accuracy of the CRDS instrument is routinely
158 checked against a certified reference gas as described by Kamp et al (2019). The CRDS analyzer
159 was equipped with two in-line, sub-micron polytetrafluoroethylene (PTFE) particulate matter
160 filters; one at the gas inlet at the back of the analyzer and one at the inlet of the cavity to protect
161 the highly reflective mirrors. The inlet of the CRDS is a PTFE (PTFE) tubing of 1.5 m length
162 with 6.4 mm outer diameter. The optical cavities incorporate precise temperature (± 0.005 °C)
163 and pressure (± 0.0002 atm) control systems. In this study, both the temperature and pressure
164 of the air sample continuously flowing through the optical cavity are tightly controlled at all
165 times to constant values of 45 °C and 140 Torr, respectively. The measurement interval is
166 around 2 seconds. The CRDS analyzer measured the water vapor simultaneously.

167 A photoacoustic multi-gas monitor 1312 (Innova, Lumasense Technology A/S, Denmark) was
168 compared with the PTR-MS and the CRDS for ammonia calibration and non-targeted VOCs
169 on ammonia measurement. An infra-red-light source was used for the PAS instrument and the
170 principle for the measurement is as follows. The infrared radiation can interact with a molecule
171 and transfer energy to it if the frequency of the radiation is the same as the frequency of
172 vibration within the molecule. When the molecule absorbs IR light, it vibrates with greater
173 amplitude. This increased activity is short-lived, however, and the excited molecule very
174 quickly transfers its extra energy to other molecules in the vicinity by collision. The increased
175 kinetic energy leads to an increase in the measurement chamber temperature and pressure. A
176 microphone is used to detect the consequently fluctuating pressure. The sample integration time

177 to measure ammonia by PAS was 20 s. The instrument used 6 optical filters for NH₃, CH₄, CO₂,
178 H₂O, N₂O and SF₆. The specifications of the optical filters are shown in Table S1. Water vapor
179 must be included for PAS measurement since the absorbance spectrum of water overlap with
180 other gases such as N₂O and CO₂ thus causing interferences. According to the manufacturer,
181 the Innova 1312 has linear response over a wide dynamic range, with the possibility to make
182 self-calibration (Lumasense, 2012). Before the measurements presented in this study, the
183 supplier calibrated the instrument. During the study the instrument was calibrated based on a
184 certified gas cylinder containing 99.7 (\pm 10 %) ppmv ammonia (AGA A/S, Copenhagen,
185 Denmark). The interferences between the target gases were therefore supposed to be eliminated
186 through internal cross compensation (Christensen, 1990b; Zhao et al., 2012).

187 **2.2 Experiment 1: laboratory test on ammonia calibration**

188 Instrumental background signals, ammonia calibrations and instrumental response times were
189 characterized for the PAS, PTR-MS and CRDS instruments. For the background measurement,
190 zero air controlled by a mass flow controller (Bronkhorst, Ruurlo, The Netherlands) was
191 supplied, and measurement was performed individually for each instrument. The zero air was
192 supplied from a HiQ zero air station (Linde AG, Munich, Germany). The selected ion
193 measurement mode was used for the PTR-MS with m/z 18 being used for ammonia detection.
194 For the calibration test, a factory-calibrated gas cylinder (AGA A/S, Copenhagen, Denmark)
195 containing 99.7 (\pm 10 %) ppmv ammonia was used. Mass flow controllers (Bronkhorst, Ruurlo,
196 The Netherlands) were used to dilute the gas from the cylinder with zero air to achieve the
197 desired NH₃ concentration levels (0-11 ppmv). For the test of response decay time, zero air flow
198 was supplied to the instruments at first, then switched to a diluted flow (via 2-levels of mass

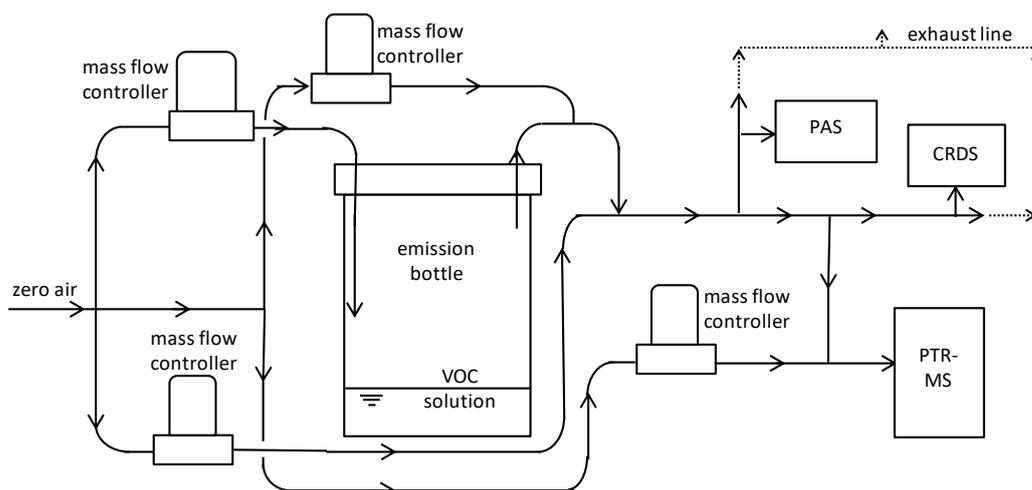
199 flow controllers) with ammonia concentration around 5.2 ppmv supplied to all three
200 instruments simultaneously. Subsequently, the ammonia supply was set to zero to test the decay
201 time. Four individual decay time tests were performed for the PAS, to confirm the long decay
202 time of the instrument with low ammonia concentrations (5.2-8.8 ppmv) or high ammonia
203 concentration (99.7 ppmv). For the test of response time for the PAS, two different levels of
204 ammonia concentration were introduced individually to the instrument, to test the dependence
205 of the response time on ammonia concentration.

206 **2.3 Experiment 2: VOCs selection test**

207 A headspace test was performed and VOCs were selected through a PTR-MS measurement as
208 preparation to the interference tests of VOCs on ammonia measured by the PAS. Maize silage
209 is typical feeding material to the cows and silage is generally considered an important source
210 of gaseous VOC in cattle barns. A sample of maize silage was collected from the farm where
211 the field experiment was performed (Skjern, Jutland, Denmark, altitude: 55°59'36.6", longitude:
212 8°29'53.52"). The silage was then transferred to the laboratory immediately for the headspace
213 test. A clean PTFE container (58×38×43 cm) with two oval holding holes (6×8 cm) on the
214 sides was used for the headspace test. The container was partly open and the silage filled half
215 of the container. A 1-meter 1/4-inch OD PTFE tube was used for the test, with one end placed
216 around 5 cm above the silage, and the other side connected to a T-piece. One side of the T-piece
217 was connected to a 1/8-inch OD PTFE tube (around a half meter) which was connected to the
218 inlet of the PTR-MS. The flow rate of the PTR-MS was kept at 150 mL/min. A zero-air dilution
219 flow (75 mL/min) was supplied to the T-piece to make 1:1 dilution to keep the total
220 concentration below 10 ppmv. The headspace measurement was performed by the PTR-MS in

221 scan mode, and masses were measured from m/z 21 to m/z 250 with 200 ms for each mass. The
 222 selection of VOCs was based on the scan results and relevant literature data on silage VOC,
 223 with the following VOCs being selected: ethanol, methanol, acetaldehyde, acetic acid, 2-
 224 butanone, acetone, 1-propanol and 1-butanol (Howard et al., 2010; Malkina et al., 2011; Hafner
 225 et al., 2013). These 8 selected VOCs were tested for empirical relationships (C_{NH_3obs}/C_{VOC}) with
 226 respect to contribution to measured NH_3 concentration (C_{NH_3obs}). All chemicals were purchased
 227 from Sigma-Aldrich with at least analytical grade purity.

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230 **Figure 1.** A diagram of the experimental set-up for test of ammonia interference due to VOC.

231 **2.4 Experiment 3: Laboratory test for empirical relationships**

232 The diagram of the setup for the laboratory calibration test is shown in Figure 1. In the setup, a
 233 water solution containing the single VOC was purged from the headspace by dry and clean air
 234 (or nitrogen for one test on methanol), with flow controlled by a mass flow controller. The air
 235 or nitrogen was supplied through a charcoal/silica gel filter. One-liter airtight glass bottles were
 236 used for the water solution containing the VOC, and 1/4-inch OD PTFE tube was used in the
 237 setup. The purged air flow was diluted with air through a two-step dilution. The flows were

238 adjusted according to the purged VOC concentration and the desired final VOC concentration.
239 The water solution was prepared by using a volume ratio of VOC:Water of 1:5, with purging
240 by clean air controlled by 2 mass flow controllers in order to reach a desired concentration
241 range. For the laboratory test, the diluted air containing VOC was connected to the PAS, the
242 CRDS and the PTR-MS for simultaneous measurements. The overall flow was maintained at a
243 level above the total maximum sampling flow of all three instruments and excess flow was
244 vented through a T-piece. For the PTR-MS measurement, a further dilution by zero air was
245 typically used to keep the total VOC concentrations below 10 ppmv to avoid depletion of the
246 primary ion, H_3O^+ . Selected ion measurement mode was applied for the PTR-MS, with an
247 integration time of 2 seconds for the tested VOC mass. During the experiments, the humidity
248 was kept relatively low and stable, with dry clean air used for dilution for all cases, except for
249 one test on methanol, which was also tested under nitrogen condition.

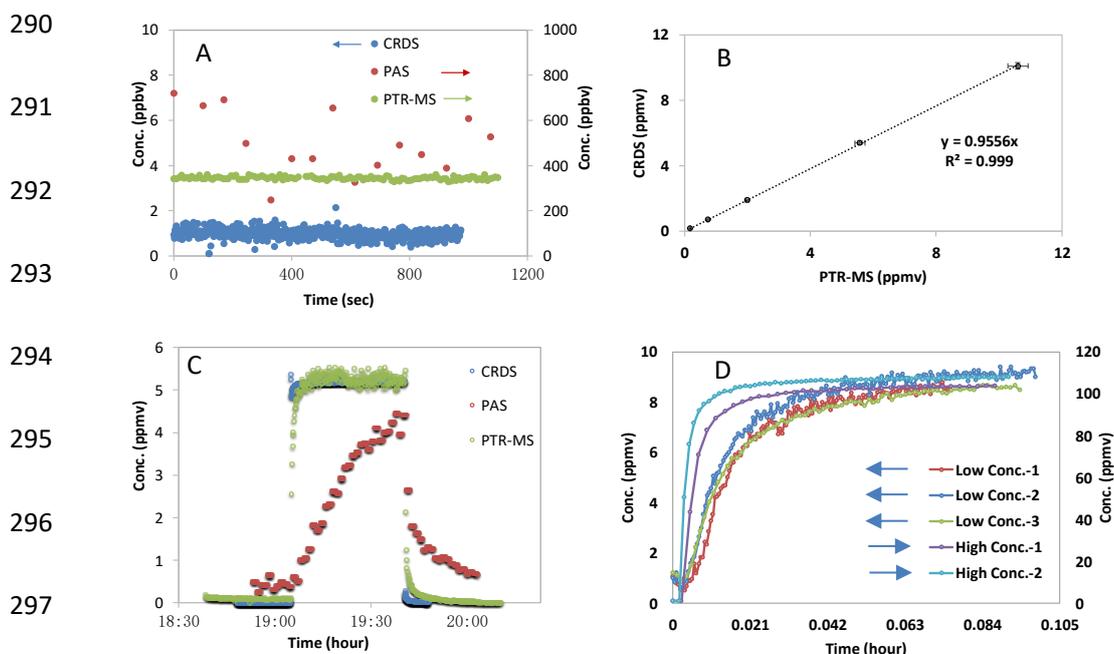
250 **2.5 Experiment 4: Field test for validation of empirical relationships**

251 The field demonstration test for non-targeted VOCs on ammonia measurement by the PAS was
252 performed in the dairy farm mentioned above (Skjern, Jutland, Denmark), where both the PTR-
253 MS and the PAS were measuring continuously over 20 days. The dairy farm housed 360 cows
254 with an average weight of 650 kg. The ventilation system consisted of natural and mechanical
255 partial pit ventilation system (Rong et al., 2015).

256 For the field test, the PAS was combined with a Multiplexer 1309 (Lumasense Technology A/S,
257 Denmark) to measure from several sampling points. The PAS and the PTR-MS were placed in
258 a trailer next to the dairy farm. The PAS sample integration time was 5 s and the flushing time
259 was 20 s. The air concentrations were measured by the PAS sequentially between two selected

260 locations inside the farm, one location in the pit ventilation, one location outside the farm. PTFE
261 tubes of 20 meters and 8 mm OD were used for the sampling of air. The sampling lines were
262 connected with the channels of the PAS multi-point sampler via continuously running PTFE
263 membrane pumps to ensure constant flushing. VOCs (all VOCs showed in section 2.3 were
264 included together with VOCs reported in previous studies (Malkina et al., 2011; Hafner et al.,
265 2013)) and NH₃ were measured simultaneously by PTR-MS. Measurements were switched
266 between the four measurement sampling lines (connecting to the four locations mentioned
267 above) and the background (outside air beside the trailer) at 8 min intervals via a custom-built
268 switching box. PTFE tubes were used for the PTR-MS sampling lines, which were connected
269 to PTFE sampling lines before the PTFE membranes pumps. The switching box was equipped
270 with a five-port channel selector (Bio-Chem Valve Inc, USA) controlled automatically by 24V
271 outputs from the PTR-MS. A PTFE tube (ID 1 mm) was used to connect the switching box to
272 the inlet sampling line (1-meter PEEK tube with ID 0.64 mm) of the PTR-MS. For selected
273 compounds, calibration was performed for the PTR-MS before the field measurements using
274 permeation tubes and reference gas mixtures. Permeation tubes (VICI Metronics, Inc., Houston,
275 TX, USA) included acetic acid, propanoic acid, butanoic acid, pentanoic acid and 4-
276 methylphenol. Gas mixtures (all 5 ppmv in nitrogen) included hydrogen sulfide (AGA,
277 Copenhagen, Denmark), methanethiol (AGA, Copenhagen, Denmark), and dimethyl sulfide
278 (Air Liquide, Horsens, Denmark). Details regarding the calibration procedures could be found
279 in our previous study, with accuracies within 12% error and in most cases within 8% (Liu et al.,
280 2018). VOC concentrations were determined directly by the PTR-MS, based on estimated
281 reaction rate constants as described by Liu et al. (2018). Standard conditions as described

282 previously was applied and maintained for the PTR-MS (Feilberg et al., 2010). The mass
 283 discrimination was calibrated and adjusted weekly by using a mixture of 14 aromatic
 284 compounds between m/z (mass to charge ratio) 79 and 181 (P/N 34423-PI, Restek, Bellefonte,
 285 PA). Selected ions were monitored with dwell time between 200 and 2000 ms during each
 286 measurement cycle. Masses and dwell time selection was based on ion abundance in full scan
 287 mode, relevant literature and experience regarding odorant compounds from dairy buildings as
 288 well as from pig houses and pig slurry applications (Shaw et al., 2007; Chung et al., 2009; Liu
 289 et al., 2014; Liu et al., 2018).



299 **Figure 2.** Ammonia test measurements by PAS, PTR-MS and CRDS. A: Background signals
 300 measured in ammonia-free air. B: Intercomparison of ammonia concentrations measured by PTR-
 301 MS and CRDS. C: Instrumental response of PTR-MS, PAS and CRDS instruments to a
 302 rectangular ammonia concentration pulse.; D: Instrumental response of PAS instrument to a
 303 stepwise increase in ammonia concentration (low concentration (3 tests; ~8.9 ppmv) and high
 304 concentration (2 tests; 99.7 ppmv); Low Conc.-1, Low Conc.-2 and Low Conc.-3 point to the
 305 vertical axis on the left, and to the upper horizontal axis; High Conc.-1 and High Conc.-2 point to
 306 the vertical axis on the right, and to the lower horizontal axis; High Conc.-2 was tested without the
 307 multiplexer). Data in B has been background-subtracted and the linear fits were least square fits
 308 without error weighting.

309 3 Results and discussion

310 3.1 Experiment 1: laboratory test on ammonia calibration

311 The instrumental baseline concentrations of ammonia-free zero air measured by PAS, CRDS
312 and PTR-MS, respectively, are shown in Figure 2A, in which a very low background signal was
313 observed for the CRDS instrument (around 1 ppbv) with a detection limit of 0.7 ppbv (3 times
314 the standard deviation of the background). The higher background for ammonia measured from
315 the PTR-MS is caused by the intrinsic formation of NH_4^+ (m/z 18) in the ion source (Norman
316 et al., 2007). Nevertheless, the measured background signals for ammonia by the PTR-MS was
317 very stable and could be subtracted to give a detection limit of 21 ppbv (3 times the standard
318 deviation of the background). Among the three instruments, the PAS gave the highest
319 background signal for ammonia (corresponding to 502 ± 140 ppb), with a detection limit of 421
320 ppbv (3 times the standard deviation of the background).

321 For the calibration test of ammonia, the ammonia concentrations simultaneously measured by
322 the CRDS and the PTR-MS is shown in Figure 2B, in which the linearity ($k = 0.96 \pm 0.005$)
323 and high correlation ($R^2=0.999$) are generally very satisfactory for both instruments. The
324 measured ammonia concentrations also agreed with expected ammonia concentrations from the
325 ammonia reference gas within the uncertainty of 10% provided by the gas supplier.

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331 **Table 1.** Instruments comparison regarding the specifications for ammonia measurements (SD =
 332 standard deviation).

	LOD(3×SD; ppbv)	Upper limit (ppmv)	90% decay time (s)	Measurement time	1σ Accuracy*	Possible Interferences
Innova	421(200 [*])	(-) ^A	1700-4000 (5.2-8.8 ppmv); 450-550 (100 ppmv)	Less than 2 min	16.4%	Non-targeted gases with IR spectra Overlapping
PTR-MS	21.5	10 [#]	70-80 (5.2 ppmv)	Less than 5 s	10.3%	intrinsic ion at m/z 18
Picarro	0.662	>20 ^{&}	4.5-4.7 (5.2 ppmv)	Less than 2 s	10.2%	Negligible ^{&}

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334 * - Accuracy propagated from uncertainty of the calibration standard gas of ammonia (10%),
 335 uncertainty of mass flow controller (2%) used for gas dilution systems, and uncertainty of
 336 instrumental quantities of ammonia (12.8%, 1.6% and 0.2% for Innova, PTR-MS and Picarro,
 337 respectively). It should be noted that the uncertainty associated with the comparison to the
 338 standard gas did not take into account the interferences by other livestock gases on the Innova.

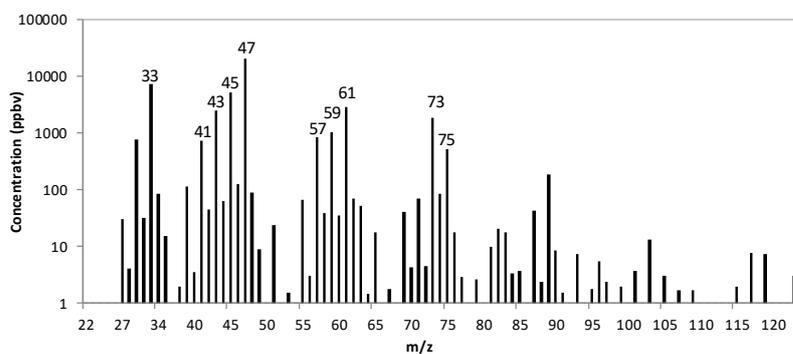
339 A - Not specified by the producer.

340 # - According to the concentration calculation assumption and producer suggestion, total gas
 341 concentration should be lower than 10 ppmv, otherwise dilution is needed.

342 &- According to Kamp et al., 2019.

343 For the signal decay test, the instrument decay times for ammonia measurements by PAS,
 344 CRDS and PTR-MS were measured simultaneously under a static ammonia concentration of
 345 5.2 ppmv. As shown in Figure 2C, ammonia measured by the CRDS showed the shortest decay
 346 time while the PAS gave by far the longest decay time. The estimated decay time is shown in
 347 Table 1, in which the 90% decay time (time for the concentration to decrease by 90%) for
 348 ammonia measured by the CRDS is around 4.5 - 4.7 second, with the 90% decay time from the
 349 PTR-MS estimated to be 70 to 80 seconds. The decay time for ammonia measured by the PAS
 350 was remarkably longer, with an estimated 90% decay time of around 30 minutes to more than
 351 an hour (for four individual tests with ammonia concentration ranged from 5.2 to 8.8 ppmv).
 352 When much higher ammonia concentration was used (99.7 ppmv), the 90% decay time
 353 measured by the PAS was shorter (450 to 550 seconds). This result is consistent with the
 354 response time tests under two levels of input ammonia concentrations (~ 8.9 ppmv and 99.7

355 ppmv, respectively), with the response time much shorter when the ammonia concentration is
356 higher, as shown in Figure 2D. Besides, the multiplexer attached to the PAS seemed to increase
357 the response time, as also shown in Figure 2D. However, a very high concentration of about
358 100 ppmv is not expected in agricultural applications.



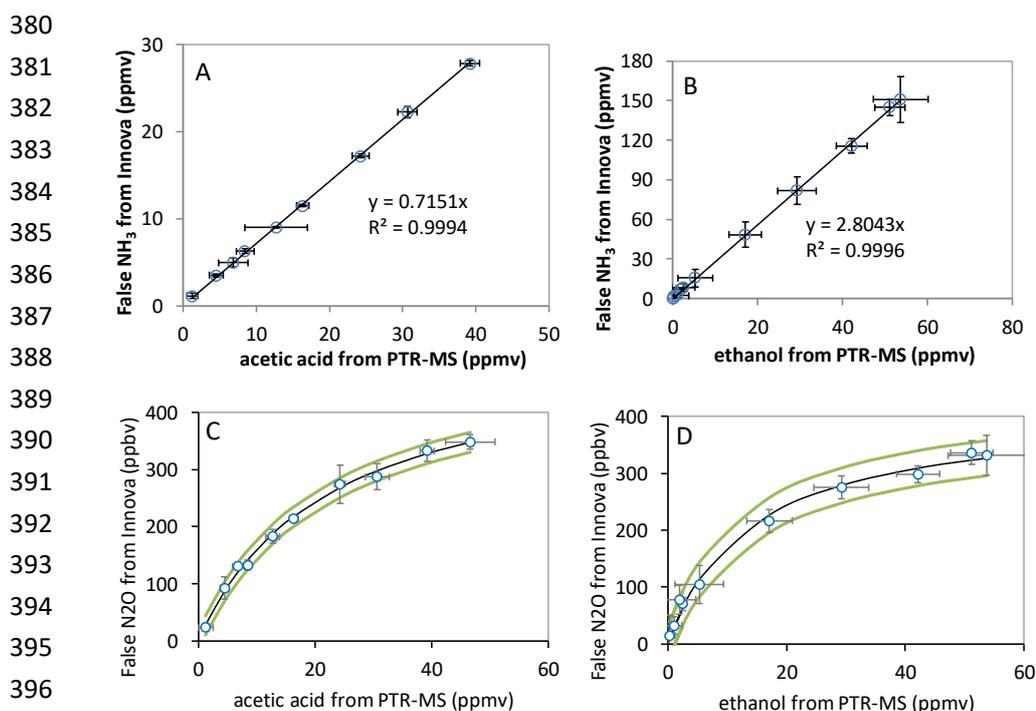
359 **Figure 3.** A scan example of the feeding material of silage by using headspace technique measured by
360 the PTR-MS. The m/z 47 is corrected for ethanol fragmentations formed in the PTR-MS through
361 calibration. Selected VOCs for the test in this study were ethanol, methanol, acetaldehyde, acetic acid,
362 2-butanone, acetone, propanol and butanol.
363

364

365 **3.2 Experiment 2: VOCs selection test**

366 The tested VOCs were selected according to a scan test of the headspace from the feeding
367 material of maize silage performed by the PTR-MS, as shown in Figure 3. Due to the
368 fragmentation of ethanol in the PTR-MS measurement (around 10%) (Inomata and Tanimoto,
369 2009), the concentration corresponding to mass 47 was corrected based on direct calibration
370 under the assumption that mass 47 is solely due to ethanol. The highest peaks of the scan were
371 at masses (m/z): 47, 33, 45, 61, 43, 73, 59, 75, 57 and 41. From the VOCs typically found in
372 the highest concentrations in barns and feeding material (Shaw et al., 2007; Chung et al.,
373 2009; Howard et al., 2010; Malkina et al., 2011; Hafner et al., 2013) and the scan results, a list
374 of VOCs were selected. The following VOCs were selected for the interference tests of non-
375 targeted VOC on ammonia measurement by the PAS: ethanol, methanol, acetaldehyde, acetic

376 acid, 2-butanone, acetone, 1-propanol and 1-butanol. Compounds such as ethanol, methanol,
 377 acetic acid and 1-propanol are typically measured in cattle barns and feeding materials in high
 378 concentrations (Shaw et al., 2007; Ngwabie et al., 2008; Howard et al., 2010; Hafner et al.,
 379 2013).



398 **Figure 4.** Examples for the interference calibration from non-targeted VOC on NH₃ (A & B) and
 399 N₂O (C & D) measured by the PAS. The VOC concentration on the horizontal axis was measured
 400 by the PTR-MS, while the NH₃ and N₂O concentrations on vertical axis were from false signals
 401 measured meanwhile by the PAS. A: The interference calibration for acetic acid on NH₃; B: The
 402 interference calibration for ethanol (corrected for fragments through calibration) on NH₃; C: The
 403 interference calibration for ethanol (corrected for fragments through calibration) on N₂O; D: The
 404 interference calibration for acetic acid on N₂O. In C & D, the red line indicated the fit curve by
 405 equation $y=kx/(x+m)$, and the green and purple curves indicated 95% confidence range. The plotted
 406 error bars represent the standard deviations for the measured VOC by the PTR-MS under a
 407 selected VOC level (x-axis) and for the measured NH₃/N₂O level by the PAS meanwhile (y-
 408 axis). Data were all background-subtracted and the linear fits were least square fits without error
 409 weighting.

410

411 3.3 Experiment 3: Laboratory test for empirical relationships

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

413 using single VOC-containing air as inlet measured simultaneously by PAS, PTR-MS and CRDS,
 414 as shown in the setup in Figure 1. An example of the interference test can be seen in Figure S1,
 415 where acetic acid was measured simultaneously by the three instruments under various
 416 concentration levels. Concentration dependent interference was clear for acetic acid on PAS
 417 ammonia measurements.

418 **Table 2.** Obtained empirical relationships (slope) describing the functional dependence of the
 419 interference in the measurement of the target compound (e.g., NH₃) by PAS on non-targeted VOC
 420 concentrations. The value in the brackets indicated the uncertainty (SD of the slope) of the linear fit,
 421 except for N₂O where correlation coefficient is shown. N is the number of VOC concentration levels
 422 tested for determination of empirical relationships. Nonlinear fit was given for N₂O, where 'x' is
 423 measured VOC concentration and 'y' is the false concentration measured by PAS. The concentration
 424 range covered for the tested VOC is as follows: ethanol (7 ppbv-58 ppmv); methanol (5 ppbv-45
 425 ppmv); acetic acid (3 ppbv - 48 ppmv); acetaldehyde (8 ppbv-38 ppmv); 2-butanone (3 ppbv - 60
 426 ppmv); acetone (4 ppbv - 48 ppmv); 1-propanol (5 ppbv - 55 ppmv); 1-butanol (6 ppbv - 52 ppmv).

Compound	N	NH ₃	CH ₄	N ₂ O (y: ppbv; x: ppmv)	CO ₂	SF ₆
ethanol	10	2.81(0.02)	1.88(0.01)	y=411x/(x+14) (0.93)	0.40(0.02)	-0.014(0.002)
methanol	9	3.29(0.72)	3.81(0.67)	y=99x/(x+9) (0.78)	0.45(0.17)	-0.15(0.02)
acetic acid	10	0.72x(0.01)	-3.14x(0.08)	y=514x/(x+22) (0.95)	0.39(0.03)	0.31(0.01)
acetaldehyde	4	(-)	-0.85(0.45)	y=317x/(x+31) (0.98)	(-)	0.044(0.021)
2-butanone	4	-0.13x(0.003)	-4.02(0.04)	y=311x/(x+26) (1.00)	-0.61(0.18)	0.23(0.005)
acetone	6	0.02(0.001)	2.10(0.13)	y=104x/(x+4) (0.99)	(-)	0.015(0.001)
1-propanol	5	2.41(0.21)	2.95(0.38)	y=3569x/(x+602) (1.00)	0.25(0.21)	-0.064(0.012)
1-butanol	7	2.66(0.05)	3.07(0.09)	y=807x/(x+73) (0.99)	(-)	-0.061(0.004)
methanol(N ₂)	4	1.03(0.31)	1.46(0.22)	(-)	0.35(0.24)	-0.056(0.010)

427

428 In principle, establishing empirical correction factors for each specific compound could be used
 429 to minimize the interferences of VOCs on the target gas measurements on a specific instrument
 430 with the same filter specifications. This requires, however, that VOC concentrations be
 431 measured simultaneously by expensive analyzers such as PTR-MS and will in any case result
 432 in higher uncertainties due to accumulated uncertainties from multiple interference
 433 relationships. Figure 4A & B show two examples of the calibration lines for acetic acid and

434 ethanol, from which an empirical relationship (ER) between the false ammonia concentration
435 and the tested compound could be obtained (ER=0.72 for acetic acid and ER=2.8 for ethanol).

436 A linear response of the ammonia interference was observed for all the tested compounds and
437 they had generally low SD for the slope the linear fits. The ER for ammonia interference by
438 other tested VOCs can be found in Table 2, where ethanol, methanol, 1-propanol and 1-butanol
439 give the highest false signals on ammonia measured by the PAS, with ER of 2.8, 3.3, 2.4 and
440 2.7, respectively. Due to the fact that these compounds are often found in cattle barns and feed
441 silage even in the level of ppmv, especially for ethanol, methanol and 1-propanol (Rabaud et
442 al., 2003; Ngwabie et al., 2008; Howard et al., 2010; Hafner et al., 2013), severe interference
443 on ammonia measured by PAS therefore will occur. While acetic acid gave significant false
444 signals on ammonia (ER=0.72), acetone only showed little interference on ammonia (ER=0.02).

445 Meanwhile, negative false signals were observed for ammonia by 2-butanone (ER=-0.13). Such
446 negative interferences can usually be explained by the internal cross compensation procedure
447 for one target filter (first target filter, such as NH₃ filter) on positive artifacts at another target
448 filter (second target filter, such as CH₄ filter) caused by non-target gas (such as VOC) on the
449 second target filter. This physical explanation was included in a few relevant references such
450 as Zhao et al. (2012). Interestingly, the empirical relationship for false ammonia by methanol
451 in nitrogen matrix is significantly different from that by methanol presented in air matrix
452 (ER=1.03 vs 3.29). This observation is possibly related to the relatively rapid vibrational energy
453 transfer between the VOC and oxygen (Harren et al., 2000). While nitrogen has a vibrational
454 frequency around 2360 cm⁻¹, oxygen has a vibrational frequency of 1554 cm⁻¹ with only 170
455 collisions needed to transfer energy to the vibrational mode of O₂ (Lambert, 1977).

456 Besides the interferences on ammonia by the non-targeted VOCs, other target gases also
457 showed various levels of interferences, as also indicated by previous studies (e.g., Zhao et al.,
458 2012; Hassouna et al., 2013). Because target gases may have more overlap for the infrared
459 spectrum, the primary interference on one target gas caused by the overlap with non-targeted
460 VOCs could therefore influence and cause secondary interference on other target gases (Zhao
461 et al., 2012; Adamsen, 2018). Still, in theory, empirical relationships could be obtained for the
462 interfered gases by the tested VOCs. Specifically, for the interference on methane by non-
463 targeted methanol, 1-butanol, 1-propanol, acetone and ethanol showed positive false signals
464 (ER=3.8, 3.1, 3.0, 2.1, 1.9, respectively). 2-butanone, acetic acid and acetaldehyde showed
465 negative false signals to methane, with ER equal to -4.02, -3.14 and -0.85, respectively. An
466 explanation for the negative false signals could be that absorption takes place in the band for
467 H₂O correction (Adamsen, 2018). All interferences on methane are shown in Table 2. For
468 methanol in nitrogen, the calibration showed a significant difference compared to air (ER=1.46
469 vs. 3.81).

470 Meanwhile, the non-targeted VOC also caused false signals on nitrous oxide signals, with a
471 much lower level of interference. Furthermore, the calibrations of the nitrous oxide interference
472 by the non-targeted VOCs seemed not to be following linear relationships. For examples, Figure
473 4C & D showed the false signals of nitrous oxide caused by ethanol and acetic acid. A non-
474 linear relationship exists between nitrous oxide interference and VOC concentration. The
475 curves could be well fitted to the non-linear equation of $y = \frac{kx}{x+m}$, where k represents the
476 maximum interference on nitrous oxide by the single VOC, m represents the half-saturation
477 constant indicating the level higher at which the VOC concentration could cause half of the

478 maximum interference on nitrous oxide. As shown in Table 2, all tested VOCs showed positive
479 non-linear interference to the nitrous oxide signals, and 1-butanol showed the highest maximum
480 interference on nitrous oxide. Interestingly, no interference was observed for nitrous oxide
481 when methanol was presented in a nitrogen matrix, while a relatively lower level of interference
482 by methanol was observed for nitrous oxide when presented in atmospheric air.

483 Furthermore, some of the tested VOCs also caused interference on carbon dioxide measured by
484 the PAS. The background of carbon dioxide was considered as unchanged during the
485 interference tests. While methanol, ethanol, acetic acid and 1-propanol caused positive false
486 signals for carbon dioxide measured by the PAS (ER = 0.45, 0.40, 0.39, 0.25, respectively), 2-
487 butanone caused negative false signals with ER = -0.61 (Table 2). Other tested VOCs, including
488 acetone, acetaldehyde and 1-butanol, did not show interferences on carbon dioxide measured
489 by the PAS. This is likely because no overlap of the gas infrared adsorption spectra exists
490 between these VOCs and carbon dioxide. As expected, methanol in nitrogen also caused
491 interference on carbon dioxide (ER = 0.35) slightly lower than methanol in air.

492 Besides, SF₆ measurements were interfered by the tested non-targeted VOC, with lower
493 empirical relationship obtained compared to NH₃, CH₄, N₂O and CO₂. Acetic acid and 2-
494 butanone caused the highest interferences on SF₆, with ER of 0.31 and 0.23, respectively. Other
495 tested VOCs caused significantly less interference on SF₆, among which methanol gave the
496 highest negative ER of -0.15. Again, the methanol in nitrogen gave a significantly lower level
497 of interference on SF₆ compared to methanol in air (ER = -0.056 vs -0.15).

498 Overall, the tested non-target VOCs in this study caused significant interference on target gases,
499 of which ammonia and methane were influenced to the largest degree. Even though less

500 interference was observed for nitrous oxide, this could still cause problems due to the typically
501 low concentration level of this compound in e.g. livestock facilities or soil (Iqbal et al., 2013;
502 Rong et al., 2014).

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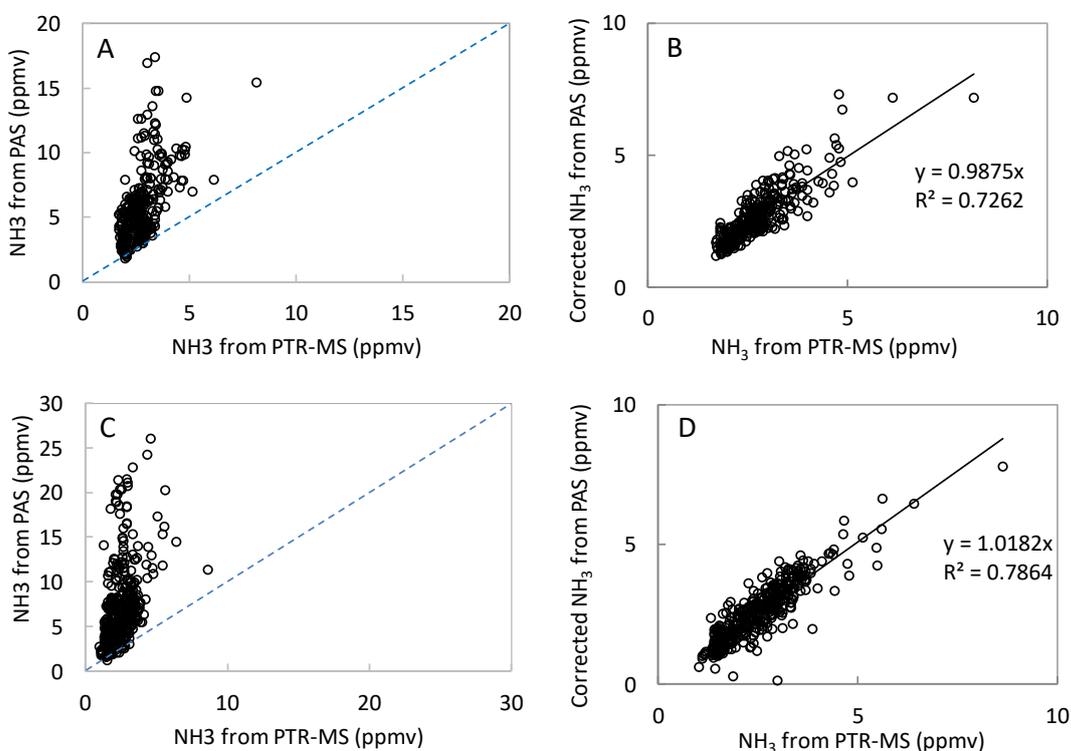
528

529 **Figure 5.** NH₃ concentrations measured by the PAS (vertical axis) and by the PTR-MS (horizontal
530 axis) in the field measurement from Location One before the correction by the tested non-targeted
531 VOCs (A) and after the correction by the tested non-targeted VOCs (B), and from Location Two
532 before the correction by the tested non-targeted VOCs (C) and after the correction by the tested non-
533 targeted VOCs (D). Data from B and D were background corrected and the linear fits were least
534 square fits without error weighting.

535

536 3.4 Experiment 4: Field test for validation of empirical relationships

537 During the field test in the dairy barn, the ammonia measurements by PAS and PTR-MS were



538 compared to each other for one location in the pit and two locations (Location One and Location
539 Two) in the barn. Figure S2 shows ammonia concentration measured by PAS and PTR-MS at
540 the pit ventilation. In the pit ventilation, low concentrations of VOCs were generally obtained
541 and relatively high concentrations of ammonia were observed for both instruments. Thus, no
542 significant interferences were observed for ammonia measured by the PAS, and ammonia
543 measurements by PAS and PTR-MS showed a good agreement as shown in Figure S2. However,
544 for the two measurement points inside the barn, significantly higher ammonia concentrations
545 were obtained from PAS compared to the concentrations measured by PTR-MS (Figure 5 A &
546 C). Table S2 showed the percentage for each range of ratio of PAS/PTR-MS concentrations for
547 the data shown in Figure 5 A & C, where ratio of PAS/PTR-MS concentrations mostly within
548 1-4. The higher ammonia concentration observed for the PAS measurement is ascribed to
549 interferences from VOCs, some of which had high concentrations, especially for ethanol as
550 shown in Table 3. The relation between the ammonia concentrations measured by PAS and the
551 ethanol concentrations measured by PTR-MS were highly correlated for both measurement
552 locations, with slopes close to 3 (3.0 and 3.1; see Figure S3). These two numbers are generally
553 close to the empirical relationship obtained for ethanol ($ER = 2.8$). The empirical relationships
554 obtained in 'Experiment 3' were used for data correction of ammonia measurement by PAS
555 since the instrument configurations were kept the same. Thus, the interference of the VOCs on
556 ammonia measurement by PAS could be estimated from the empirical relationships obtained in
557 'Experiment 3' and used to correct the ammonia data. Figure 5B & D show the corrected
558 ammonia concentrations measured by PAS by using the empirical relationships, together with
559 the measured ammonia concentration by the PTR-MS for both measurement locations. The

560 corrected ammonia concentrations from the PAS are generally in good agreement with the
561 ammonia concentration measured by the PTR-MS, with slopes close to 1 (0.99 and 1.02). It
562 should be noted that although the empirical relationships were obtained for single VOC
563 interferences on ammonia measurement by PAS, they were treated as being additive under field
564 conditions where multiple VOCs presented. Ethanol dominated the VOC composition in
565 general, but other types of VOC also contribute significantly. The average ratio of ethanol
566 concentration to the sum of the 8 VOCs (tested in the lab with obtained empirical relationships)
567 was 0.64 (± 0.11) for Location Two in the field study. This single application suggests that the
568 interference is close to additive, but further investigation is needed to confirm this finding. The
569 cattle barn experiment validated that correction from major VOCs is necessary for reliable PAS
570 measurements. In principle, it is possible to estimate the interference on NH₃ measured by PAS
571 measurements in field applications. However, it should be noted that a lot of redundant work is
572 needed to make this correction if only NH₃ concentration is measured since the concentrations
573 of several VOCs need to be known to achieve a proper correction.

574

575 **Table 3.** Average concentrations (\pm standard deviation) of selected VOCs during the field test in the
576 dairy cattle barn for the two sampling locations 1 & 2, both of which are located inside the barn. The
577 standard deviation applies to the mean values.

Compound	Concentrations (ppbv)	
	Location 1	Location 2
ethanol	1421±946	1622±1355
methanol	237.2±150.2	241.1±192.3
acetic acid	57.2±41.3	69.4±61.6
acetaldehyde	98.8±81.2	92.2±83.7
2-butanone	19.1±11.0	17.2±13.1
acetone	77.9±30.2	52.1±24.9
1-propanol	71.0±45.2	71.8±67.7
1-butanol	22.2±10.1	16.3±11.8
hydrogen sulfide	12.1±9.7	11.3±8.4
trimethylamine	8.6±3.5	5.7±3.1
dimethyl sulfide	15.1±9.2	14.3±9.8
4-methylphenol	5.2±2.1	3.8±2.2

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579

580 **4 Conclusions**

581 When measuring NH₃ and greenhouse gas emissions (CH₄, N₂O and CO₂) by PAS, non-target

582 VOCs may interfere significantly with the target gases causing inaccurate results. To confirm

583 and determine the magnitude of interferences, experiments have been conducted by

584 simultaneously using a PAS and a PTR-MS. Results from these experiments provide useful

585 guidelines concerning interferences caused by non-targeted VOCs. The results demonstrate that

586 ethanol, methanol, 1-butanol, 1-propanol and acetic acid are causing the most significant

587 interferences on NH₃ measured by PAS. A field test in a cattle barn validated the interference

588 caused by VOCs on NH₃ measurement by PAS by simultaneously measuring VOCs with PTR-

589 MS.

590

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

592 author.

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

594

595 *Author contributions.* DL, LR and AF designed the setup for the experiments performed; LR,
596 JK and AC contributed to setting up and conducting experiments and acquiring data; DL, AF,
597 JK, XK and APA contributed to writing the manuscript, data interpretation and data analysis;
598 LR, AF and JK assisted in data analysis and manuscript editing.

599

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

601

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