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# 1 **Characterization of particulate and gaseous pollutants from a** 2 **French dairy and sheep farm**

3

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## 24 **Abstract**

25 Agricultural activities highly contribute to atmospheric pollution, but the diversity and the  
26 magnitude of their emissions are still subject to large uncertainties. A field measurement  
27 campaign was conducted to characterize gaseous and particulate emissions from an experimental  
28 farm in France containing a sheep pen and a dairy stable. During the campaign, more than four  
29 hundred volatile organic compounds (VOCs) were characterized using an original combination of  
30 online and off-line measurements. Carbon dioxide (CO<sub>2</sub>) and ammonia (NH<sub>3</sub>) were the most  
31 concentrated compounds inside the buildings, followed by methanol, acetic acid and  
32 acetaldehyde. A CO<sub>2</sub> mass balance model was used to estimate NH<sub>3</sub> and VOC emission rates. To  
33 our knowledge, this study constitutes the first evaluation of emission rates for most of the  
34 identified VOCs. The measurements show that the dairy stable emitted more VOCs than the sheep  
35 pen. Despite strong VOC and NH<sub>3</sub> emissions, the chemical composition of particles indicates that  
36 gaseous farm emissions do not affect the loading of fine particles inside the farm and is mainly  
37 explained by the low residence time inside the buildings. The experimental dataset obtained in  
38 this work will help to improve emissions inventories for agricultural activities.

39 **Keywords:** VOC emissions, Ammonia, Agriculture, Air quality, PTR-Qi-TOF-MS

## 40 **Highlights**

- 41 • More than 400 VOCs have been identified in a dairy and sheep farm in France
- 42 • Dairy and sheep VOC tracers have been proposed
- 43 • The dairy stable emitted more VOCs than the sheep pen
- 44 • The chemical composition of fine aerosols was not affected by gaseous farm emissions

## 45 **1. Introduction**

46 Agricultural activities are one of the major sources of pollutants in the atmosphere. Agricultural  
47 emissions comprise both particulate and gaseous pollutants which can affect air quality as well as  
48 climate. For example, at the global scale, agriculture is the main source of ammonia (NH<sub>3</sub>) in the  
49 atmosphere; a gaseous compound which plays a central role in atmospheric particle formation and  
50 chemistry (Behera et al., 2013; Massad and Loubet, 2015; Yao et al., 2018). Among all  
51 agricultural activities, livestock management is recognized as a significant source of NH<sub>3</sub>, and  
52 estimated to contribute 34-40% of global NH<sub>3</sub> emissions (Behera et al., 2013; Schmithausen et al.,  
53 2018). Livestock is also a strong emitter of greenhouse gases such as methane (CH<sub>4</sub>) and carbon  
54 dioxide (CO<sub>2</sub>) (Hempel et al., 2016; Huang et al., 2015; Maldaner et al., 2018; Ngwabie et al.,  
55 2014). Other studies have shown that farm buildings emitting numerous volatile organic  
56 compounds (VOCs) may be as important as traffic road contributions (Ciganek and Neca, 2008;  
57 Yuan et al., 2017). VOCs are also key species for atmospheric chemistry and climate that are able  
58 to produce secondary pollutants, such as ozone and aerosols (Atkinson and Arey, 2003; Curci et  
59 al., 2009; Hallquist et al., 2009). The chemical reactivity of VOCs strongly affects their ability to  
60 generate ozone and aerosols (Seinfeld and Pandis, 2006) and it is therefore essential to identify  
61 the chemical nature of the VOCs emitted by farm buildings and evaluate the magnitude of their  
62 emissions. Several studies have shown that oxygenated VOCs, such as methanol, ethanol, acetone  
63 and acetic acid, dominate dairy cattle VOC emissions (Ngwabie et al., 2008; Sun et al., 2008).  
64 Emissions of odorant compounds are also frequently reported, for example dimethylsulfide  
65 (C<sub>2</sub>H<sub>6</sub>S), cresols (methyl phenol, C<sub>7</sub>H<sub>8</sub>) and trimethylamine (C<sub>3</sub>H<sub>9</sub>N) (Feilberg et al., 2010).

66 To achieve a complete screening of VOCs, it is recommended to conduct studies combining both  
67 on-line, e.g. proton transfer reaction mass spectrometry (PTR-MS), and off-line, e.g. gas/liquid  
68 chromatography, techniques (Ni et al., 2012). However, studies combining both methodologies  
69 remain scarce, and only a limited number of investigations have provided emission factors, which

70 are crucial parameters for evaluating environmental impacts of livestock management at various  
71 scales. For example, Feilberg et al. (2010) combined on-line and off-line techniques to estimate  
72 VOC emissions from intensive pig production, but the range of compounds was limited due to the  
73 use of a quadrupole PTR-MS. Only a few studies have proposed a complete VOC identification  
74 list (Ciganek and Neca, 2008; Schiffman et al., 2001; Yuan et al., 2017) and there are also  
75 insufficient studies of VOC emission rates from farm buildings. Indeed, a review focused on  
76 swine facilities by Ni et al. (2012) pointed out that there have been only three studies of emission  
77 factors, which also showed variations of up to three orders of magnitude for some compounds.  
78 Similarly, emission rates of VOCs from dairies can vary greatly from one study to another. For  
79 example, Shaw et al. (2007b) calculated a methanol emission factor of  $0.4 \text{ kg year}^{-1} \text{ animal}^{-1}$ ,  
80 whereas Sun et al (2008), in a comparable study, reported a methanol emission rate of  $61 \text{ kg year}^{-1}$   
81  $\text{animal}^{-1}$ .

82 Most of the reported studies to date have dealt with pig, dairy or poultry farming, but little is  
83 known about other livestock. Yet, according to the Food and Agriculture Organization of the  
84 United Nations, sheep livestock is one of the most important in the world. It is estimated that  
85 sheep livestock in 2017 was 224M of LSU (livestock units, sheep and goats), very close to pig  
86 livestock at 239M LSU (<http://www.fao.org/faostat/en/#data/EK>). Whereas Ni et al (2012) reviewed  
87 ca. 100 studies of VOC emissions at swine facilities, there are only two studies dealing with VOC  
88 emissions from sheep farming (Ngwabie et al., 2007; Yuan et al., 2017). More investigations into  
89 VOC emissions from farm buildings, and especially sheep farming, are needed to better constrain  
90 VOC emission inventories.

91 Animal husbandries are also reported to be a source of atmospheric particles (Cambra Lopez,  
92 2010). It is well established that coarse particles are mainly primary biologic particles related to  
93 the animal activity. But little is known about the origin of the fine particles and especially PM1

94 (particles with an aerodynamic diameter below 1  $\mu\text{m}$ ). Whether PM1 are of secondary or primary  
95 origin is still unclear (Lammel et al 2004). The strong emissions of ammonia and VOCs could  
96 potentially lead to strong secondary particle formation. Thus, online chemical characterization of  
97 the sub-micron aerosol using an aerosol chemical speciation monitor (ACSM) could greatly help  
98 to identify the origin of fine particles in animal husbandries.

99 In this context, a field campaign was carried out at an experimental farm in the western region of  
100 Paris (France). The aim of the study was first to characterize the VOC fingerprint inside a dairy  
101 stable and a sheep pen, which were both naturally ventilated buildings. On-line (Proton Transfer  
102 Reaction – Quadrupole ion guide – Time Of Flight – Mass Spectrometry, PTR-Qi-TOF-MS) and  
103 off-line (Thermal Desorption-Gas Chromatography – Mass Spectrometry, GC-MS and Gas  
104 Chromatography – Flame Ionization Detector, GC-FID) measurements were conducted outside  
105 and inside both buildings. Then, fine aerosol chemical composition (using an ACSM) was  
106 measured to characterize the contribution of livestock to the PM1 loading. Finally, a CO<sub>2</sub> mass  
107 balance model was used to estimate NH<sub>3</sub> and VOC emission rates and emission factors from both  
108 buildings.

109 **2. Materials and methods**

110 **2.1. Experimental set up**

111 A field measurement campaign was conducted in an experimental farm located at Grignon,  
112 France (35 km west of Paris, 48°50'28.89" N, 1°56'56.03" E, altitude: 131 m above sea level). The  
113 experimental set up consisted of a mobile laboratory van, where the instruments were placed.  
114 Three different locations were investigated: inside a dairy stable, inside a sheep pen, and  
115 outdoors, in the vicinity of the two buildings (Figure S1). The agricultural practices performed at  
116 the Grignon farm and the building sizes were representative of national standards. The PTR-Qi-  
117 TOF-MS (used to measure VOCs) and the ACSM (used to measure the PM1 chemical

118 composition) were not available at the same time (only one day in common, during the outdoor  
119 measurement period). As a result, the field campaign was divided in two main parts: the first one,  
120 when only the PTR-Qi-TOFMS was available, and the second part when the ACSM was  
121 available. The number of animals and the feeding were kept constant through the whole  
122 experiment, thus we can suppose that results from both periods could be extended to the whole  
123 experiment. A detailed time window describing the availability of the instruments during the  
124 campaign is provided in Figure S2. All the other instruments described below were available  
125 throughout the field campaign. The dairy stable was investigated during 16<sup>th</sup> -20<sup>th</sup> November 2017  
126 (with the PTR-Qi-TOF-MS) and also 28<sup>th</sup> November to 1<sup>st</sup> December 2017 (with the ACSM). The  
127 van was located in a corner of the stable, which was naturally ventilated (Figure S1). A total of  
128 205 animals were kept inside the stable during the campaign: 173 dairy cows and 32 calves, with  
129 a mean weight of about 550 kg per animal. For dairy cows, the milk yield per animal was 30 kg.  
130 The sheep pen was investigate between 20<sup>th</sup> and 22<sup>nd</sup> November 2017 (with the PTR-Qi-TOF-  
131 MS) and also 24<sup>th</sup> - 28<sup>th</sup> November 2017 (with the ACSM). As for the stable, the sheep pen was a  
132 naturally ventilated building. However, the openings in the sheep pen were smaller and a lower  
133 air exchange rate is thus expected in the sheep pen than the dairy stable. A total of 1041 sheep  
134 were in the building during the measurement period, 488 ewes, 534 lambs (males and females)  
135 and 19 rams. The mean body weight was estimated to be about 80 kg per animal. Finally, we  
136 moved the mobile laboratory outside to a location close to both the sheep pen and the dairy stable  
137 for the period 22<sup>nd</sup> - 24<sup>th</sup> November 2017 (with the PTR-Qi-TOF-MS, then the ACSM). At this  
138 outdoor location, there was a manure digester and some storage areas for animal feed and manure  
139 (Figure S1). All of these can be important sources of VOCs and ammonia (Blunden and Aneja,  
140 2008; Yuan et al., 2017). Tractors were moving outdoors and inside the farm buildings which  
141 could also have influenced our measurements.

## 2.2. Sampling and instrumentation

### 2.2.1. Ancillary measurements

Wind speed and direction were measured inside the buildings and outside using a 3-dimension sonic anemometer (R3, Gill instruments). CO<sub>2</sub> was measured with an open path infrared gas analyser (LI-7500, LI-COR biosciences). The mobile laboratory van used in this study was designed for atmospheric studies, with air conditioning and tubing dedicated to sampling of gases and aerosols. All measurements were performed at heights between 1.5 and 2 m above ground level. Nitrogen oxides (NO<sub>x</sub>, being the sum of NO and NO<sub>2</sub>) were monitored with a chemiluminescent gas analyser (model 42C, Thermo Fischer scientific). The NO<sub>x</sub> analyser sampled the air through a 1.5 m Teflon non-heated inlet at 2 L min<sup>-1</sup> and was calibrated before the campaign. A Teflon filter (Ø = 0.45 µM, Pall Life Sciences 4785 Ion Chromatography (IC) Acrodisc Syringe Filters) placed at the inlet prevented particles from entering the instrument.

NH<sub>3</sub> measurements were performed every 2 minutes using a commercial laser photoacoustic-based analyser (LSE Monitors B.V., the Netherlands). The inlet was 1.2 m Teflon tubing (1/8 inch diameter) heated at 40-45 °C; the inlet flow inside the analyzer was 0.040 L min<sup>-1</sup>. A Teflon filter was added at the inlet of the tubing to prevent particles from entering the instrument. The NH<sub>3</sub> analyzer was calibrated before the campaign by the manufacturer and had a detection limit of 1-2 ppb.

### 2.2.2. Online VOC analysis

VOCs were measured online using a proton transfer reaction - quadrupole ion guide - time of flight - mass spectrometer (PTR-Qi-TOF-MS, Ionicon analytik GmbH), that has been fully described by Abis et al. (2018). Air was sampled using 1.5 m long Teflon tubing with 1/8 inch diameter. The inlet airflow was set at 0.2 L min<sup>-1</sup>, and the inlet was heated at 80°C to avoid condensation of semi volatile compounds inside the tubing. A Teflon filter (Ø = 0.45 µM, Pall Life Sciences 4785 Ion Chromatography (IC) Acrodisc Syringe Filters) was placed at the entry of

167 the sampling line to remove particles from the air. The PTR-Qi-TOF-MS operated in standard  
168 conditions, with a drift pressure set between 3 mbar (in the sheep pen and outside) and 3.5 mbar  
169 (in the stable), a drift temperature of 80 °C and a drift voltage close to 751 V (in the sheep pen  
170 and outside) and 878 V (in the stable). These conditions were set to ensure a constant E/N ratio  
171 (where E is the electric field strength and N the gas number density) about 133 Td ( $1 \text{ Td} = 10^{-17} \text{ V}$   
172  $\text{cm}^{-2}$ ). This value for the E/N ratio limits fragmentation and lowers the sensitivity of the  
173 protonation rate to variations in relative humidity (Pang, 2015; Tani et al., 2003). Blanks were  
174 performed daily with high purity zero air (Alphagaz 1, zero air: 80% nitrogen, 20% oxygen,  
175 purity: 99.9999%, Air Liquide) to check instrument background signal, and calibrations were  
176 frequently performed with a toluene gas standard ( $102 \pm 10$  ppb, Messer) diluted in zero air.  
177 Methanol and ethanol can sometimes be subject to high fragmentation, leading to underestimation  
178 (especially because fragments produced are not measured by the PTR-Qi-TOF-MS). We further  
179 tested the instrument sensitivity to methanol and ethanol after the field campaign. The tests  
180 showed that, under the conditions of the experiment (i.e.  $E/N = 133 \text{ Td}$ ), the sensitivity for  
181 methanol and ethanol is 3.25 and 35 times less elevated than the sensitivity for toluene. It was  
182 thus decided to correct the mixing ratios of both alcohols with their respective correction factors.  
183 For all the other compounds, the sensitivity calculated using the toluene standard was used.  
184 Fragmentation of several compounds (especially acetic acid at  $m/z$  43, monoterpenes at  $m/z$  81  
185 was taken into account by considering the sum of the molecular mass ion and the fragmented ions  
186 to contribute to the total concentration). During the measurements, mass spectra up to  $m/z$  510  
187 were recorded every second.

### 188 **2.2.3. Offline VOC analysis**

189 Off-line analysis was also performed to obtain a more complete picture of the VOC emissions.  
190 For TD-GC-MS measurements, VOCs were trapped on cartridges using two different adsorbents  
191 (Tenax TA and carbotrap 300). Before the campaign, the tubes were pre-conditioned by heating at

192 80 °C under a helium stream of 60 L min<sup>-1</sup> for 6 hours. Then, ambient air was sampled during 3 to  
193 5 hours at 0.5 L min<sup>-1</sup> and regulated with a mass flow controller (Bronkhorst) (Table S1). After  
194 exposure, cartridges were stored in the dark at a temperature of 4°C until analysis. Tubes were  
195 desorbed using a thermo-desorption unit (TDU) from Gerstel, which was programmed to desorb  
196 the tubes from 50 to 260 °C for 10 min at a rate of 60 °C/min. VOCs were cryo-focused in the  
197 Programmable Temperature Vaporization (PTV) injector at -20 °C using a carbotrap liner.  
198 Following the desorption step, the PTV was programmed from -20°C to 280°C (held for 2 min)  
199 at 12 °C/s<sup>-1</sup> to inject the trapped compounds into the chromatographic column. Separation of the  
200 VOCs was achieved using an Agilent 7890B gas chromatograph fitted with a capillary column  
201 (30 m length, 0.25 mm inner diameter, 0.25 µm df, DB624 column, Restek). The oven  
202 temperature was initially set at 40 °C for 5 min, heated at a rate of 11 °C/min to 60 °C, then heated  
203 at a rate of 20°C/min to 220°C and maintained for 2 minutes. Helium was used as carrier gas.  
204 Detection of the VOCs was performed with an Agilent 5977A mass spectrometric detector. The  
205 Electronic Impact (EI) mode was at +70 eV; the monitoring was from m/z 36 to 300. The ion  
206 source and Quadrupole analyser temperature were respectively set at 230 and 150 °C.

207 Canister sampling was also performed by sampling the air for 15 minutes every 4 hours (Table  
208 S1). Air sampled by canisters was analysed by GC-FID (HP 6890) equipped with a CP-Al<sub>2</sub>O<sub>3</sub>  
209 Na<sub>2</sub>SO<sub>4</sub> column, providing a complementary analysis of small hydrocarbons. A pre-concentrator  
210 (Entech 7200) was placed at the inlet of the instrument to allow automatic injections. A standard  
211 cylinder with 5 non methane hydrocarbons (NMHC, Messer) was used to check that the  
212 instrument was functioning correctly and an international reference standard containing 32  
213 NMHC from C<sub>2</sub> to C<sub>10</sub> (NPL, National Physics Laboratory, Teddington, UK) was used for  
214 calibrations.

#### 2.2.4. Chemical composition of particles

In order to characterise the aerosol composition inside the farm buildings, an Aerosol Chemical Speciation Monitor (ACSM) was used during the field campaign, providing near real time concentrations of submicron organic matter (OM), nitrate ( $\text{NO}_3^-$ ); sulphate ( $\text{SO}_4^{2-}$ ), ammonium ( $\text{NH}_4^+$ ) and chloride ( $\text{Cl}^-$ ). The measurement principle of the ACSM has been extensively described elsewhere (Ng et al., 2011). Briefly, submicron particles are successively sampled at 3 L  $\text{min}^{-1}$ , sub-sampled at 85 mL  $\text{min}^{-1}$ , focused through an aerodynamic lens, and eventually flash-vaporized over a 600°C-heated tungsten vaporizer, followed by ionization by EI at 70 keV. Fragments are separated by quadrupole, and a fragmentation table is applied to retrieve the concentrations of the above-listed components. The ACSM has been calibrated from the injection of 300 nm ammonium nitrate particles, as described in Ng et al. (2011). Comparison with filter samples (filter sampling and analysis are described below) allowed for validation of the obtained calibration values (Figure S3). A slope of 1.16 has been obtained when comparing ACSM concentrations with filter sampling. This value was slightly higher than what was observed for long-term published ACSM datasets (e.g. Budisulistiorini et al., 2014; Petit et al., 2015). Still, this value was considered as satisfactory given i) the few number of data point ( $n=10$ ); ii) the relatively low observed concentrations, always below 3  $\mu\text{g}/\text{m}^3$ ; iii) the associated uncertainties for  $\text{NO}_3$  with ACSM (15%, Cretn et al., 2015) and filter sampling (5-10%, Bressi et al., 2013). Aerosols composition was also recorded at the same time at the SIRTA measurement station located 20 km south-east from the farm (48°42'32.0"N, 2°08'55.5"E) (<https://sirta.ipsl.fr/>).

The following water-soluble major ions were analysed by Ion Chromatographs (IC): chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium and calcium. A low volume sampler (Leckel) sampling device was used with Quartz filter (Tissuquartz 2500 QAT-UP, 47 mm, conditioned at 673 K for 24 h), with PM1 inlet size cut-off and with denuder (ChemComb3500 Thermo Scientific, for remove VOCs from inlet air), at a flow rate of 2.3  $\text{m}^3/\text{h}$ . The sampling time

240 was 2 hours. For analysis, half of the filter sample was extracted in 10 ml of Milli-Q Water (18.2  
241 MOhm) for 45 min in an ultrasonic bath. The extracts were then filtered using Acrodisc filters  
242 (Pall Life Sciences, Bulk IC Acrodisc 25 mm) with a porosity of 0.2  $\mu\text{m}$  to remove particles. To  
243 prevent bacteria activity, 6  $\mu\text{L}$  of chloroform was added to each vial. Cations were analysed on a  
244 CS16 pre-column (2 mm diameter) and column with an IC (Dionex, Model DX-600). Anions  
245 were analysed on a AS11HC pre-column (2 mm diameter) and column with an IC (Dionex,  
246 Model ICS2000). Annual laboratory EMEP IC inter-comparison studies were performed and  
247 showed errors lower than 10% for every cited ion (accessible at  
248 <https://projects.nilu.no//ccc/intercomparison/DQO-G-36.pdf>, Lab 50).

### 249 **3. Methodology**

#### 250 **3.1. Identification of emitted VOCs**

251 PTR-Qi-TOF mass spectra were all analysed using PTR-Viewer 3.2.8.0 (Ionicon analytik GmbH).  
252 To identify the emitted VOCs, we determined a separate peak table for each location (dairy stable,  
253 sheep pen, outdoor). For that purpose, we used 30 minutes averaged mass spectra to be  
254 statistically relevant. To exclude impurities from our analysis, the mass spectra obtained with pure  
255 zero air was subtracted from ambient mass spectra. In the case of the sheep pen dataset, we  
256 determined the peak table by scanning several 30 minutes mean mass spectra selected during  
257 different hours of the day and night. For the stable, we determined the peak table by analysing  
258 mass spectra corresponding to contrasting situations. We considered that  $\text{CO}_2$  may be a good  
259 tracer for animal activity and  $\text{NH}_3$  a good tracer for litter emissions. We hence kept the four  
260 following situations: high  $\text{CO}_2$ /high  $\text{NH}_3$ , high  $\text{CO}_2$ /low  $\text{NH}_3$ , low  $\text{CO}_2$ /high  $\text{NH}_3$  and low  
261  $\text{CO}_2$ /low  $\text{NH}_3$ . Mass spectra from these 4 regimes were successively inspected, to cover all  
262 possible cases. For the outdoor measurements, we chose mass spectra at different times of the day  
263 and determined peak tables from these spectra. For each of the 3 locations, we excluded periods

264 when NO and/or NO<sub>2</sub> mixing ratios were too high, to avoid situations where anthropogenic  
265 combustion sources (*e.g.* tractor passing by) could have biased our analysis. Once the peak tables  
266 were determined, the counts per second for each peak were integrated over each one-second mass  
267 spectra using PTR-Viewer 3.2.8.0. We then averaged over 5 min the obtained data. For PTR-Qi-  
268 TOF-MS, molecular formulae were proposed based on *i*) the exact *m/z* value, *ii*) the theoretical  
269 isotopic distribution of the associated molecular formula, and *iii*) the coherence of the atoms  
270 included in the compound, with respect to chemical rules such as valence of atoms, etc.

271 TD-GC-MS data were processed by MassHunter (B.07.04.5560) software (Agilent Technologies  
272 Inc.). Automatic peak detection and mass spectrum deconvolution were performed using  
273 Unknowns Analysis (B.06.00) software. Each compound was accompanied by a deconvoluted  
274 spectrum, which was compared to the NIST (National Institute of Standards and Technology,  
275 2011) Mass Spectrum database to allow its identification. A minimum match factor of 70 %  
276 between the observed and reference mass spectra was required. Each compound was then  
277 manually scrutinized to confirm the proposed formula. For each proposed compound, the  
278 retention time was analysed regarding the its physico-chemical properties, (*e.g.* boiling point). For  
279 example, we compared the retention time of compounds from the same chemical group, to ensure  
280 that compounds with low boiling points were not eluted later than compounds with high boiling  
281 points. An example of a total ion chromatogram is shown in Figure S4, highlighting compounds  
282 identified by both TD-GC-MS and PTR-Qi-TOF-MS, or only by TD-GS-MS.

### 283 **3.2. Calculation of emission rates**

284 Emission rates were calculated using a mass balance model (Pedersen et al., 1998; Schmithausen  
285 et al., 2018), based on the following equation:

$$286 \quad E_{(i)} = Q * (C_{indoor (i)} - C_{outdoor (i)}) \quad (1)$$

287 Where  $E$  (in  $\text{g h}^{-1}$ ) is the emission rate of the compound  $i$ ,  $Q$  (in  $\text{m}^3 \text{h}^{-1}$ ) is the ventilation flow rate  
 288 of the building,  $C_{indoor(i)}$  and  $C_{outdoor(i)}$  (in  $\text{g m}^{-3}$ ) are the concentrations of compound  $i$  inside  
 289 and outside the buildings. In equation (1),  $C_{indoor(i)}$  was averaged at 30 min time steps, while  
 290  $C_{outdoor(i)}$  was averaged over the entire outside experimental period. The difference in sampling  
 291 times between the concentrations inside and outside the buildings led to an uncertainty in the  
 292 emissions calculations. Nevertheless, emission rates were estimated only for compounds  
 293 significantly more concentrated inside the buildings than outside (see section 3.3). Uncertainties  
 294 due to the different sampling time were thus supposed to moderately affect emission rate  
 295 estimations.

296 The ventilation flow rate, which was considered the same for all gases, was estimated from  $\text{CO}_2$   
 297 as (Hassouna et al., 2015; Pedersen et al., 2008):

$$298 \quad Q = \frac{CO_{2HPU} \times A_{animals} \times HPU}{(CO_{2indoor} - CO_{2outdoor}) \times 10^{-6}} \quad (2)$$

299 Where  $CO_{2HPU}$  (in  $\text{g h}^{-1} \text{hpu}^{-1}$ ) is the  $\text{CO}_2$  production rate by heat production unit,  $A_{animals}$   
 300 (unitless) is the relative animal activity,  $HPU$  is the number of heat production units (1 heat  
 301 production unit = 1000 W),  $CO_{2indoor}$  and  $CO_{2outdoor}$  (in  $\text{g m}^{-3}$ ) are the  $\text{CO}_2$  concentrations  
 302 inside and outside the building, respectively. As recommended in the literature,  $CO_{2HPU}$  for the  
 303 dairy stable and sheep pen were set to  $393 \text{ g h}^{-1} \text{hpu}^{-1}$  and  $344 \text{ g h}^{-1} \text{hpu}^{-1}$ , respectively (Hassouna  
 304 et al., 2015; Pedersen et al., 2008; Schmithausen et al., 2018). These values are specifically  
 305 recommended for farm buildings and take into account both animal respiration and  $\text{CO}_2$   
 306 contributions from manure.  $A_{animals}$  was estimated using equation 3 (Pederson et al., 2002):

$$307 \quad A_{animals} = 1 - a \times \sin\left(2 \times \frac{\pi}{24}\right) \times (h + 6 - h_{min}) \quad (3)$$

308 Where  $a$  is a constant expressing the relative amplitude of the animal activity during the day (0.2  
309 for dairy cows),  $h$  is the hour of the day and  $h_{min}$  is the time of the day with minimal activity  
310 (02:10 for dairy cows).

311 The coefficients for animal activity concerning the sheep pen were not available in the literature.  
312 Thus, for sheep pen the CO<sub>2</sub> production was not corrected for animal activity, and the ventilation  
313 flow rate equation for sheep pen was estimated with  $A_{animals} = 1$ .

314 For both buildings,  $HPU$  were calculated by normalizing by 1000 the total heat produced by each  
315 building. The latter is obtained from the heat produced ( $Hp$ , in W) by an animal in a building  
316 multiplied by the total number of animals.  $Hp$  has been calculated as following (Pederson et al.,  
317 2002; Schmithausen et al., 2018):

$$318 \quad Hp = \alpha \times BW^{0.75} + \beta \times Y \quad (4)$$

319 Where  $Hp$  is the heat produced by one cow (in W)  $BW$  is the mean body weight of animals (in kg)  
320 and  $Y$  is the milking yield of a cow or an ewe (30 and 0.25 kg per day, respectively) and represent  
321 the weight daily gain in the case of a lamb,  $\alpha$  and  $\beta$  are coefficient from the literature (Pedersen et  
322 al., 2008, 1998; Pederson et al., 2002; Schmithausen et al., 2018). For a cow,  $\alpha$  is 5.6 and  $\beta$  is 2.  
323 For sheep (ewe or lamb)  $\alpha$  is 6.4 and  $\beta$  is 145.

324 Finally, VOC emission rates can be calculated using the estimated ventilation rate and equation 1.

### 325 **3.3. Statistical analysis**

326 All statistics were performed with R software (Rstudio version 1.0.153). First, the normality of  
327 each VOC measured with the PTR-Qi-TOF-MS was tested using a Shapiro-Wilk test. Then, we  
328 computed the correlation between each VOC for the sheep pen, the stable, and outside. As the  
329 distribution for each compound was not normal according to the Shapiro-Wilk tests (they are  
330 mostly right skewed), correlations were calculated using Kendall correlation test. The  $p$  values  
331 lower than 0.005 were rejected and not considered as significant for correlation analysis in Figure

332 4. The optimal number of groups as represented on Figure 4 was determined by a *k*-means  
333 analysis, which allows determination of the optimum number of clusters for a given dataset  
334 (number of clusters that best explain variance). Then, the classification of VOCs inside the 4  
335 respective groups has been performed using a classical hierarchical clustering.

336 Dairy stable and sheep pen emission rates were calculated only for compounds whose mixing  
337 ratios were statistically different inside the building compared to outdoors. In the case of  
338 compounds only measured inside the buildings, we only considered compounds with mixing  
339 ratios statistically higher than the mixing ratio of the same compound in the zero air. Differences  
340 between ambient air and the outdoor/zero air were computed using a welsh t-test, as our samples  
341 were independents with different variances. If the obtained p-values were above 0.005, we  
342 considered that the samples were not significantly different.

## 343 **4. Results**

### 344 **4.1. Time series**

345 Figure 1 presents the time series of CO<sub>2</sub> and NH<sub>3</sub> mixing ratios for the entire measurement  
346 campaign (dairy stable, sheep pen and outdoor), as well as two VOCs (trimethylamine and  
347 dimethylsulfide) previously reported in the literature as emitted by farm buildings (Feilberg et al.,  
348 2010; Ngwabie et al., 2008, 2007; Shaw et al., 2007; Sun et al., 2008). NH<sub>4</sub><sup>+</sup> concentrations (in  
349 the particle phase) inside the farm and at SIRTA are also presented in Figure 1. Firstly, CO<sub>2</sub> and  
350 NH<sub>3</sub> mixing ratios were much higher in both buildings than outdoor. Both compounds also  
351 roughly followed similar trends which showed concentrations were higher in the sheep pen than  
352 in the dairy stable. In addition, CO<sub>2</sub> and NH<sub>3</sub> mixing ratios were quite similar during the two  
353 periods (The PTR-Qi-TOF-MS and the ACSM periods). Concentrations are similar for the two  
354 stable periods (orange area at the beginning and the end of the campaign in Figure 1) as well as  
355 for the two sheep pen periods. This result confirmed that the PTR-Qi-TOF-MS and ACSM

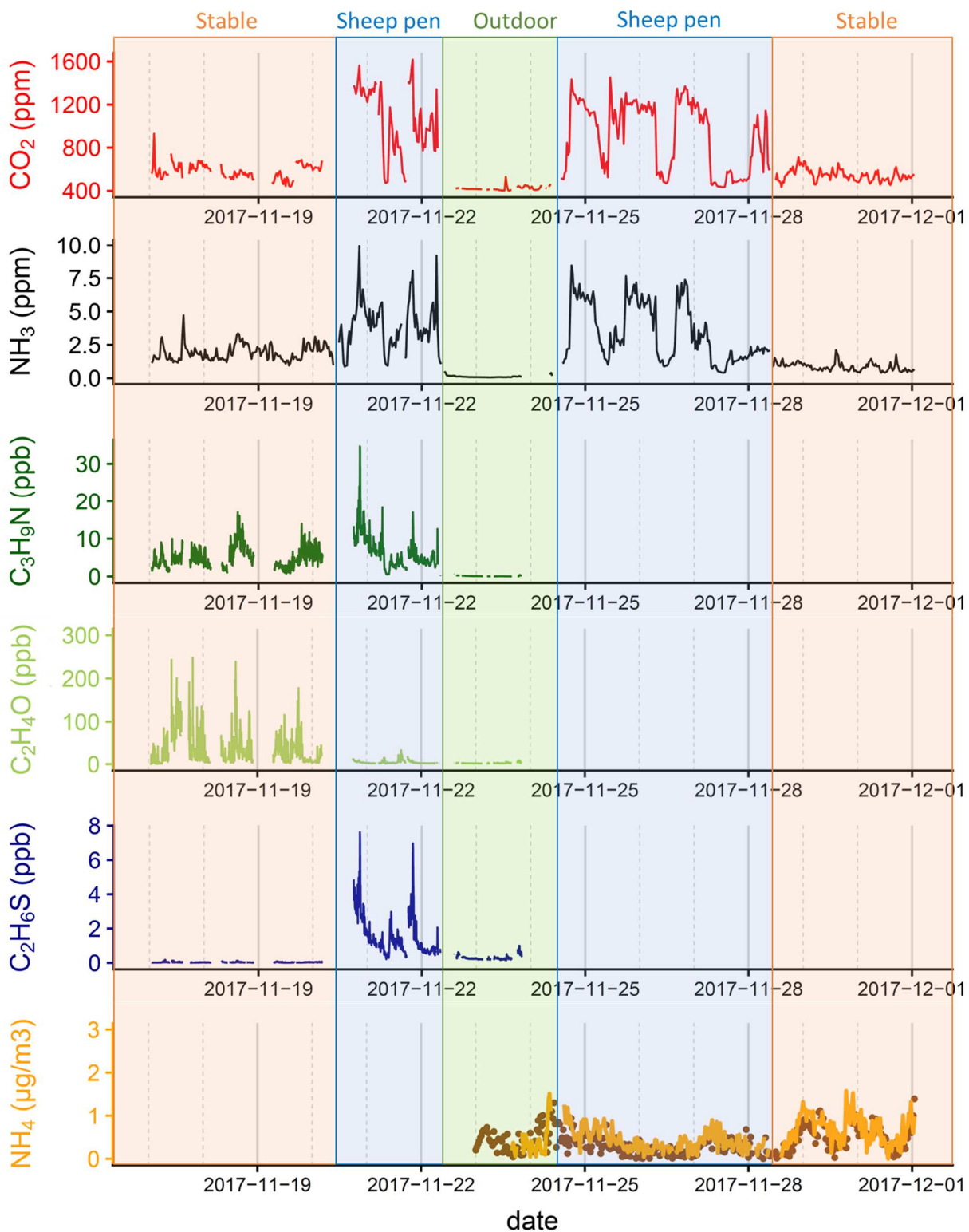
356 measurement periods are comparable as supposed above. We thus consider that conclusions  
357 deduced from the PTR-Qi-TOF-MS or ACSM periods can apply for all the campaign.

358 In the sheep pen (delimited by the blue fonts in Figure 1), clear and reproducible diurnal cycles of  
359 gas concentrations can be observed and easily explained by the ventilation variability. Indeed, in  
360 the evening, the large lateral doors of the sheep pen were closed, leading to accumulation of  
361 pollutants in the building during the night. As soon as the doors were opened in the early  
362 morning, the concentration of pollutants dropped due to increased dilution with external air. In the  
363 stable, no specific diurnal variations were observed. Variations in  $\text{NH}_3$  and  $\text{CO}_2$  concentrations  
364 were thus probably due to other parameters, notably the magnitude of the sources.

365 Regarding VOCs, trimethylamine ( $\text{C}_3\text{H}_9\text{N}$ ) was also higher in the farm buildings than outside. Its  
366 temporal evolution seems to be highly correlated to  $\text{NH}_3$ , rather than  $\text{CO}_2$ . This may indicate a  
367 common source of  $\text{NH}_3$  and trimethylamine. It has been shown that  $\text{NH}_3$  and trimethylamine are  
368 co-emitted in animal husbandries. It was first suggested that the rumen could be the main source  
369 of trimethylamine and  $\text{NH}_3$  in dairy barns (Kuhn et al., 2011). But Sintermann et al. (2014)  
370 showed that there is no correlation between methane (tracer of rumen emissions) and  
371 trimethylamine (also no correlation with  $\text{NH}_3$ ). Very recently, using real time VOC  
372 measurements, Gierschner et al. (2019) did not observe direct trimethylamine emissions from  
373 dairies. Thus, it is clear that dairy excreta (urine + feces) are the main source of both  $\text{NH}_3$  and  
374 trimethylamine in dairy farming (Sinterman et al. 2014). The correlations between compounds  
375 will be further investigated below in an effort to identify common sources of VOCs (section 4.5).  
376 Two VOCs that were identified as potential tracers for the dairy stable and the sheep pen are also  
377 represented on Figure 1. Acetaldehyde was found at higher mixing ratios inside the stable than in  
378 the sheep pen or outdoor. As a result, acetaldehyde may be used as a tracer of the dairy stable  
379 emissions. Dimethylsulfide (DMS,  $\text{C}_2\text{H}_6\text{S}$ ) mixing ratios in the dairy stable were similar to the

380 outside. Thus, it seems that the sheep pen was the main source of DMS in the farm, and that the  
381 dairy stable did not emit DMS. The absence of DMS emissions from the dairy stable differs from  
382 previous studies on dairy farm emissions, where DMS was often reported (Filipy et al., 2006;  
383 Ngwabie et al., 2007).  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  are available during the second part of the  
384 campaign. While  $\text{NH}_3$  was more concentrated inside the building, it was somewhat surprising to  
385 find that  $\text{NH}_4^+$  was present at similar levels in both farm buildings as outside. We also compared  
386  $\text{NH}_4^+$  concentrations measured at the farm with those observed at the SIRTA station.  
387 Concentrations were in the same range and followed the same temporal trend, suggesting that  
388  $\text{NH}_3$  is mostly present in the gas phase. This result is in agreement with a previous study  
389 conducted at a dairy feedlot (Hiranuma et al., 2010) which showed that  $\text{NH}_3$  is mostly gaseous  
390 and does not affect aerosol loading 3.5 km downwind of the feedlot. These observations may be  
391 explained by a timescale for transport that is shorter than the gas/particle partitioning process, or  
392 limited by the amount of species that chemically react with ammonia via a condensation reaction  
393 (e.g., nitric acid to form ammonium nitrate, sulfuric acid leading to ammonium sulfate, etc. )  
394 (Seinfeld and Pandis, 2006). The same reasoning can be applied for the other components of the  
395 aerosol composition (see Figure S4). Only 3 peaks of organic matter were higher at the farm than  
396 at the SIRTA station and these could be attributed to a tractor passing close to the mobile  
397 laboratory. Thus, we can conclude that farm building emissions did not lead to significant  
398 modification to the chemical composition of sub-micron aerosols. This will be further discussed  
399 in relation to gaseous emissions and residence time inside both buildings.

400



**Figure 1:** Time series of carbon dioxide (CO<sub>2</sub> in ppm), ammonia (NH<sub>3</sub> in ppm), trimethylamine (C<sub>3</sub>H<sub>9</sub>N in ppb), acetaldehyde (C<sub>2</sub>H<sub>4</sub>O in ppb), dimethylsulfide (DMS, C<sub>2</sub>H<sub>6</sub>S in ppb), and ammonium (NH<sub>4</sub><sup>+</sup>, in µg m<sup>-3</sup>) for the experimental farm (light brown line) and the SIRTA station (brown points) during the whole experiment. Time periods highlighted in orange correspond to measurements in the dairy stable, in blue to measurements in the sheep pen and in green to measurements outdoor. Each vertical bar (solid and dashed) represents a new day, at 00:00 local time.

402

## 403 **4.2. Identification of VOCs**

404 Combining the three techniques (GC-FID, TD-GC-MS and PTR-Qi-TOF-MS), more than 400  
405 compounds were detected during the whole measurement period. All the identified compounds  
406 are listed in the associated data file, and the number of identified compounds by each technique  
407 can be found in Table S2. Information about the parameters used for identification, such as PTR-  
408 Qi-TOF-MS mass resolution, or GC retention time can be found in the supplementary data file.  
409 Using the PTR-Qi-TOF-MS, 387 molecular formulas were successfully attributed. 62 molecular  
410 formulas among the 387 detected by the PTR-Qi-TOF-MS were also identified using off-line TD-  
411 GC-MS, and 8 using GC-FID (Table S2). Considering that these measurement techniques are  
412 independent, the number of common compounds underlines the consistency of the identification  
413 process. Only three compounds were identified in all measurement techniques: benzene, toluene  
414 and C<sub>7</sub>H<sub>14</sub> isomers. This is not surprising given that the range of VOCs detected by each  
415 technique was very different. The GC-FID detected C<sub>2</sub>-C<sub>8</sub> hydrocarbons (alkane, alkene or  
416 alkyne), whereas the TD-GC-MS was not set up to measure small hydrocarbons (the first  
417 hydrocarbon detected by TD-GC-MS was benzene), and the PTR-Qi-TOF-MS cannot measure  
418 linear alkanes. The only alkanes detected using the PTR-Qi-TOF-MS were cyclic alkanes. For  
419 example, C<sub>7</sub>H<sub>14</sub> and C<sub>5</sub>H<sub>10</sub> could be identified as cyclic alkanes rather than alkenes, based on the  
420 chromatographic analysis (see the associated data file). Nevertheless, the possibility that a  
421 corresponding alkene, isomeric to the cyclic alkane, was detected by the PTR-Qi-TOF-MS and  
422 not detected by GC-FID cannot be fully excluded. A similar conclusion was drawn for TD-GC-  
423 MS and PTR-Qi-TOF-MS: only cyclic alkanes were measured by the PTR-Qi-TOF-MS (*e.g.*  
424 cyclopentane or cyclobutane). Thus, the PTR-Qi-TOF-MS did not detect any linear alkane, except  
425 methane. Methane indeed provided a significant signal at *m/z* 17.038 (corresponding to  
426 protonated methane, CH<sub>4</sub>H<sup>+</sup>) despite its low proton affinity (118 kcal mol<sup>-1</sup>) probably due to very

427 high mixing ratios inside the farm buildings (Chupka and Berkowitz, 1971; Haque et al., 2017;  
428 Hempel et al., 2016; Schmithausen et al., 2018). But it cannot be considered as quantitative as  
429 methane proton affinity was lower than water proton affinity. We can hypothesize that methane  
430 was protonated in the lenses region of the PTR-Qi-TOF-M, as suggested for CO<sub>2</sub> by Herbig et al.  
431 (2009).

432 More compounds were found in the dairy stable than in the sheep pen and outdoor (Figure 1).  
433 About half of the compounds were oxygenated compounds, around a third were hydrocarbons,  
434 followed by nitrogen (N containing compounds) and sulfur containing compounds (S containing  
435 compounds), at 13% and 3% respectively. A few halogenated compounds (1% of the identified  
436 molecular formulas) were also detected.

437 Note that according to off-line analysis (GC-FID and/or TD-GC-MS), some of the molecular  
438 formulas identified with the PTR-Qi-TOF-MS correspond to several compounds (see associated  
439 data file). For example, the protonated ion corresponding to m/z 113.1325 was identified as C<sub>8</sub>H<sub>16</sub>  
440 using PTR-Qi-TOF-MS. TD-GC-MS analysis identified 3 cyclic alkanes with this formula (ethyl-  
441 cyclohexane; 1,2,3-trimethyl-cyclopentane; 1,3-dimethyl-cyclohexane). Thus, there were  
442 certainly more compounds than the number of molecular formulas identified with the PTR-Qi-  
443 TOF-MS.

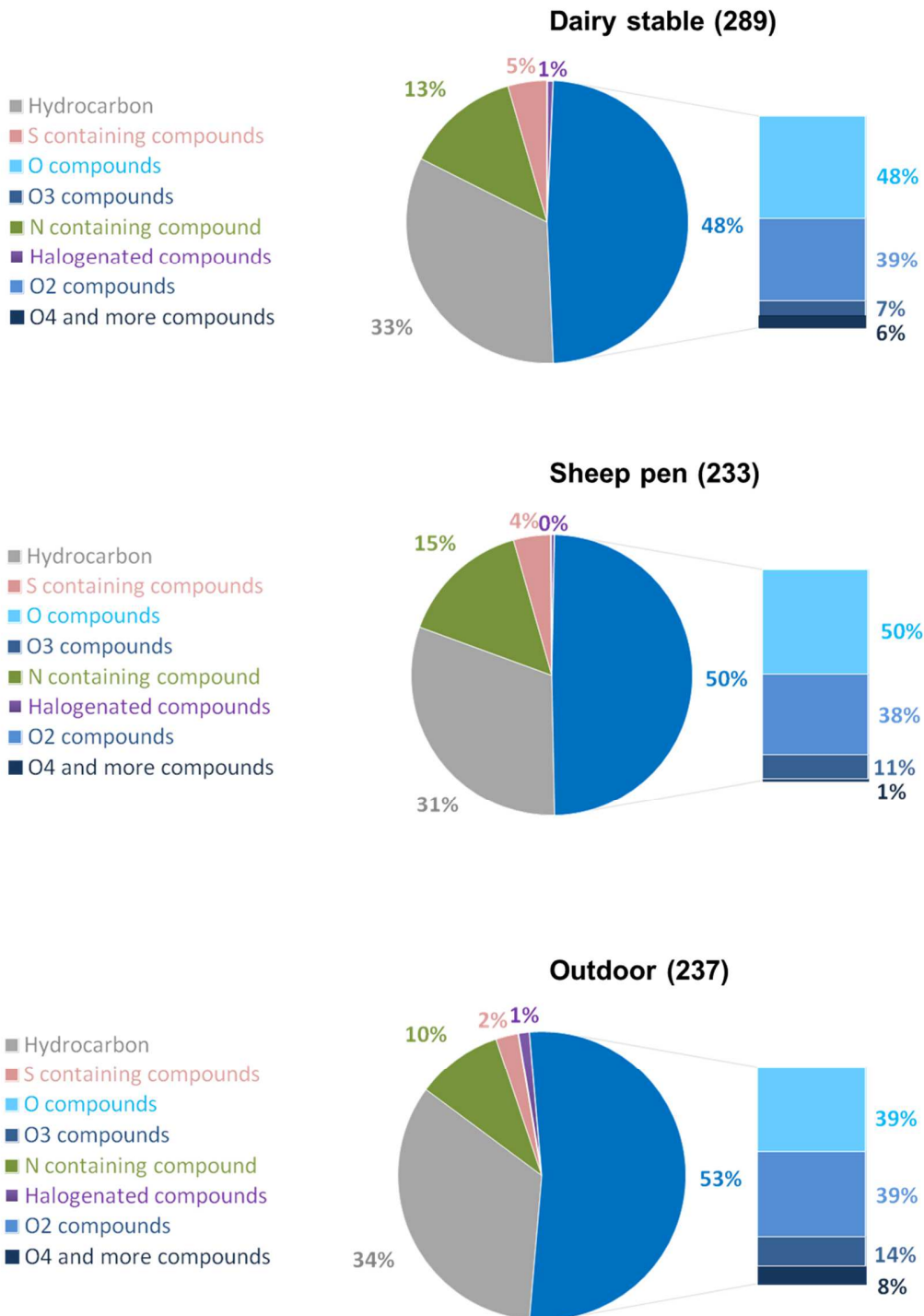
### 444 **4.3. Investigation of VOCs in the dairy stable, the sheep pen and outdoor**

445 Figure 2 shows the speciation of VOCs by functional groups in the stable, the sheep pen and  
446 outdoor. We first observed that the distributions of the chemical families (Figure 2) were roughly  
447 similar in the dairy stable and the sheep pen, and slightly different from outside. Thus, only a  
448 detailed VOC identification made it possible to clearly separate the chemical fingerprint of each  
449 building. This is possible by combining analytical techniques, as performed in this study. Such  
450 identification may help to identify tracers for emissions from each building.

451 In the stable, 33% of the molecular formulas identified corresponded to hydrocarbons. Most of  
452 them were alkenes; many aromatic hydrocarbons were detected, such as BTEX (benzene, toluene,  
453 ethylbenzene and xylenes) and some polycyclic aromatic hydrocarbons (PAHs), as naphthalene or  
454 acenaphthene derivatives for example. Typical hydrocarbons frequently attributed to biogenic  
455 origin (isoprene, monoterpenes and sesquiterpenes) were also reported in the dairy stable  
456 (Schiffman et al., 2001). It is interesting to note that many molecular formulas identified had the  
457 same number of carbon atoms (from 1 to 20 carbon atoms), with the number of hydrogen atoms  
458 that increase by 2 (for example, from  $C_{12}H_{10}$ ,  $C_{12}H_{12}$ ,  $C_{12}H_{14}$ , to  $C_{12}H_{22}$ ). A useful observation is  
459 that isopentane, 1-butene and 2,2,4-trimethyl-pentane were detected only in the stable. These  
460 compounds may hence be specific tracers for dairy stable emissions. About half of the compounds  
461 (49%) were oxygenated with molecular formulas  $C_xH_yO_z$ . Most of them contained between one  
462 and three oxygen atoms, as shown in Figure 2. Only 6% of oxygenated compounds contained 4 or  
463 more oxygen atoms. Thus, most of the oxygenated compounds in the stable were not highly  
464 oxidized VOCs. As for hydrocarbons, oxygenated compounds with the same number of carbon  
465 atoms and the same number of oxygen atoms were detected. The number of carbon atoms ranged  
466 from 1 to 16. Most of the hydrocarbons had the same number of carbon atoms as the oxygenated  
467 compounds (except for those with 17 carbon atoms). We can hypothesize that, in addition to the  
468 classical microbial degradation pathways, some oxygenated compounds may have been produced  
469 by gas phase or heterogeneous (reaction occurring at surfaces) oxidation of hydrocarbons (with  
470 OH radical or ozone). Based on the results from the 3 instruments, we observed many  
471 characteristic groups of oxygenated compounds in significant proportions inside the stable:  
472 alcohols, carboxylic acids, ketones, ethers, aldehydes and even esters. We noticed that oxygenated  
473 VOCs with the highest masses were mostly ester compounds with a few long chain aldehydes  
474 (e.g. nonanal, decanal, pentadecanal). Nitrogen compounds represented 13% of the identified  
475 molecular formulas. Most of them were small amines or amide compounds, such as

476 dimethylamine ( $C_2H_7N$ ), formamide ( $CH_3NO$ ), triazine ( $C_3H_3N_3$ ) or  $C_4H_5N$ . The observation of  
477 triazine is interesting as it was only measured inside the stable. We observed short-chain sulfur  
478 compounds, also known to be strongly odorant such as methanethiol ( $CH_4S$ ), dimethyl sulfide  
479 ( $C_2H_6S$ ) and dimethylsulfoxide ( $C_2H_6OS$ ) (Feilberg et al., 2010; Schiffman et al., 2001). TD-GC-  
480 MS analysis confirmed the presence of benzothiazole ( $C_7H_5NS$ ) in emissions from the stable and  
481 allowed identification of  $C_5H_7NS$  as 2,4-dimethyl-thiazole. Two chlorinated compounds were  
482 also measured: chloramide and dichloromethane. Dichloromethane was previously reported in  
483 emissions from pig and cattle buildings (Ciganek and Neca, 2008; Schiffman et al., 2001). But, to  
484 the best of our knowledge, chloramide is reported here for the first time in dairy stable emissions.

485



486 **Figure 2:** Classification of compounds detected inside the stable, the sheep pen and outdoor. The  
 487 oxygenated compounds are further classified by the number of oxygen atoms (in the right part of  
 488 each graph). The total number of identified molecular formulas identified in the different  
 489 measurement locations is given in parentheses.

490 In the sheep pen, hydrocarbons constituted 31% of the 233 identified molecular formulas, while  
491 they represented around 33% in the dairy stable. Most of the hydrocarbons identified were cyclic  
492 alkanes (Supplementary data file). The presence of several aromatic compounds was also  
493 observed and could have important implications for atmospheric chemistry, due to their reactivity  
494 and their ability to form secondary organic aerosols (Atkinson and Arey, 2007; Tomaz et al.,  
495 2017). We also noticed that isoprene was emitted inside the sheep pen, and no specific  
496 monoterpene was identified using TD-GC-MS, as in the stable. Octane, a C<sub>8</sub>H<sub>18</sub> compound, was  
497 only identified in the sheep pen, whereas the same molecular formula corresponded to 2,2,4-  
498 trimethyl-pentane in the stable. Oxygenated compounds represented 50% of the identified  
499 molecular formulas, practically the same proportion as in the stable (Figure 2). Oxygenated  
500 compounds contained less O atoms than in the stable, as less molecular formulas contained more  
501 than three oxygen atoms (1% in the sheep pen compared to 6% in the stable). Our identification  
502 highlights that oxygenated VOCs were mostly carboxylic acids, ketones, or alcohols, and a few  
503 aldehydes. As in the stable, few long-chain aldehydes were identified in the sheep pen, but some  
504 of these oxygenated compounds, such as 6-methyl-1-octanol (C<sub>9</sub>H<sub>20</sub>O) were not reported in the  
505 sheep pen. That means that the fingerprints of oxygenated compounds in the sheep pen and dairy  
506 stable were different. Exactly as in the stable, we observed that for oxygenated compounds and  
507 hydrocarbons, many molecular formulas identified had the same number of carbon atoms. Again,  
508 it suggests that oxygenated compounds may partly originate from reaction of hydrocarbons with  
509 the oxidants. In the sheep pen, the proportion of nitrogen compounds was slightly higher than in  
510 the stable (15% against 13%). Odorant compounds such as trimethylamine or pyridine derivatives  
511 were notably observed. Pyridine (C<sub>5</sub>H<sub>5</sub>N), methylpiperidine (C<sub>6</sub>H<sub>13</sub>N), dimethylpyridine (C<sub>7</sub>H<sub>9</sub>N),  
512 and benzenepropanenitrile (C<sub>9</sub>H<sub>9</sub>N) were specific to the sheep pen (*i.e.* not detected elsewhere)  
513 and could hence be used as tracers of sheep pen emissions. Seven S-containing compounds were  
514 measured inside the sheep pen. Among them, methanethiol (CH<sub>4</sub>S), dimethylsulfide (C<sub>2</sub>H<sub>6</sub>S),

515 dimethylsulfoxide ( $C_2H_6Os$ ) and dimethylsulfone ( $C_2H_6O_2S$ ) were reported to be strongly odorant  
516 compounds (Hansen et al., 2016; Schiffman et al., 2001). The two other sulfur compounds were  
517 thiazole compounds. We observed one halogenated compound, dichlorobenzene ( $C_6H_4Cl_2$ ), which  
518 was not reported in the stable nor outdoor.

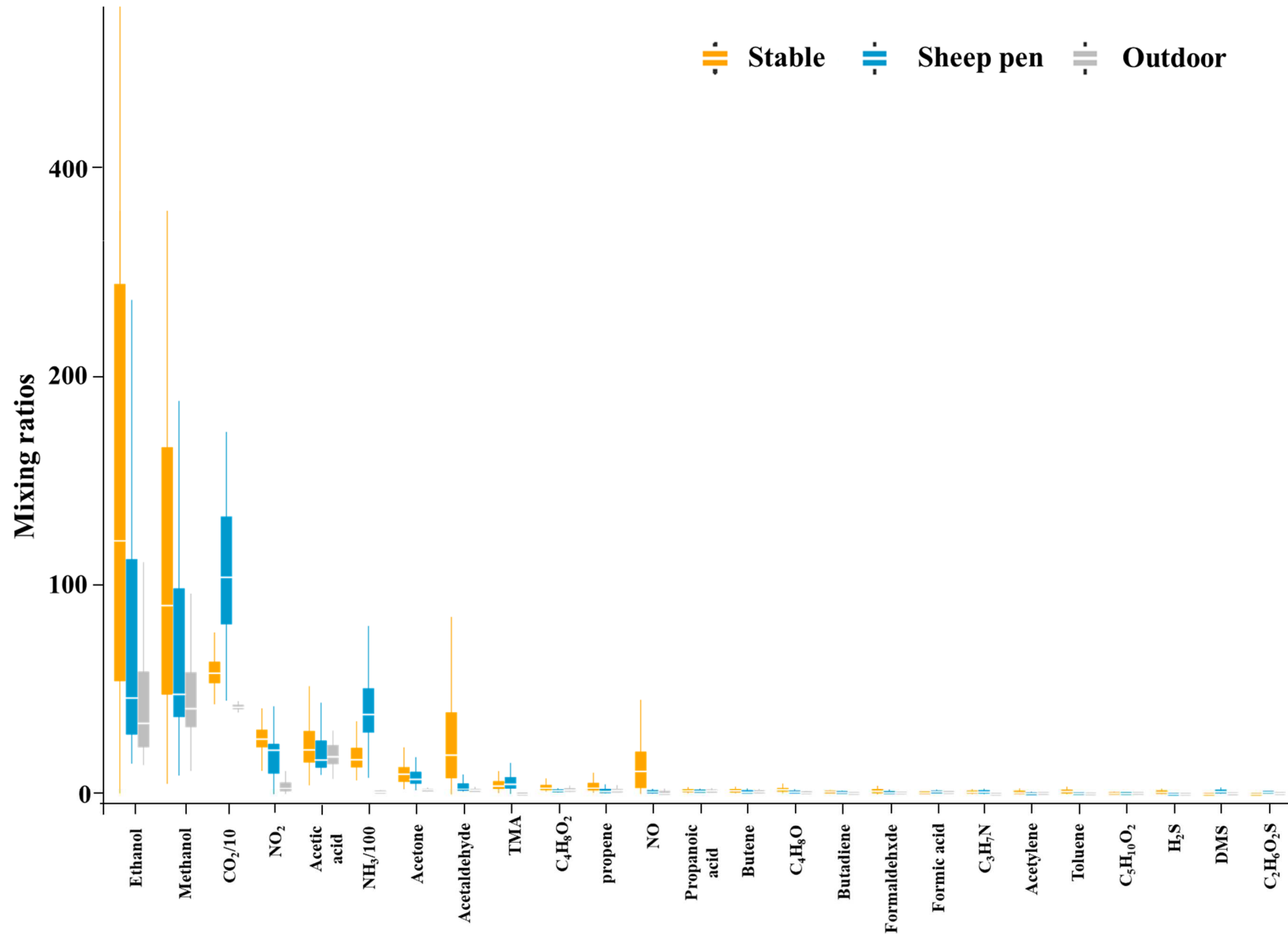
519 237 molecular formulas were identified during the outdoor experiment. This number is very close  
520 to that in the sheep pen, and lower than in the stable. This is logical considering that the location  
521 of the mobile van outside was closer to the sheep pen (Figure S1). Hydrocarbons represented 34%  
522 of the identified molecular formulas, which is a little higher than in both buildings (Figure 2).  
523 Alkenes, alkynes, cyclic alkanes were identified, and some aromatic compounds. As in the  
524 buildings, we noticed that many hydrocarbons had the same number of carbon atoms, ranging  
525 from 1 to 22. The proportion of oxygenated compounds was slightly higher outdoor than in both  
526 buildings (53% outdoor, and 49% inside both buildings). Another difference compared to the  
527 chemical fingerprint inside the buildings was the lower proportion of oxygenated compounds that  
528 contained 1 or 2 oxygen atoms (Figure 2). This means that oxygenated compounds were more  
529 oxidized outside than inside the two buildings. This was expected considering that measurement  
530 inside the buildings were closer to the VOC sources, and supports the hypothesis that some of the  
531 oxygenated compounds resulted from the oxidation of hydrocarbons. N-containing compounds  
532 represented only 10% of the identified molecular formulas (Figure 2), which was a lower fraction  
533 than inside the buildings. The same observation applied for S-containing compounds, which only  
534 represented 2%. Acetamide ( $C_2H_5NO$ ) was identified outside but was not observed in the  
535 buildings, suggesting that it may come from other sources such as the nearby animal feed store or  
536 manure digester (Figure S1). Three halogenated compounds were identified outdoor. Among  
537 them chloramide and dichloromethane were also found in the stable, but not in the sheep pen.

#### 4.4. Most abundant compounds inside the building and outside

Figure 3 presents the median mixing ratios and percentiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) of the 20 most abundant compounds in the stable, in the sheep pen and outdoor. In the three locations, the most abundant compounds were CO<sub>2</sub> and NH<sub>3</sub>. CO<sub>2</sub> median concentrations exceeded 1000 ppm in the sheep pen. The mixing ratios of NH<sub>3</sub> measured inside the buildings were in the same range as previous studies, exceeding the ppm level (Hensen et al., 2009; Huang and Guo, 2018; Ngwabie et al., 2008, 2007; Ni et al., 2012). For NH<sub>3</sub>, median mixing ratios in the sheep pen and the stable were about 40 and 18 times higher than outside, respectively. In the sheep pen and the stable, CO<sub>2</sub> median levels were about 2.5 times and 1.5 times higher than the outdoor mixing ratios, respectively. Thus, NH<sub>3</sub> enrichment inside both buildings was higher than CO<sub>2</sub> enrichment, as already observed in naturally ventilated buildings (Ngwabie et al., 2014, 2007). Both CO<sub>2</sub> and NH<sub>3</sub> levels were higher in the sheep pen than in the stable, in agreement with the study of Ngwabie et al. (2007).

The most concentrated VOCs were mainly small-oxygenated compounds. In both buildings, ethanol (C<sub>2</sub>H<sub>6</sub>O) was the most abundant VOC whereas methanol was the most emitted VOC outdoor. Our results are quite similar to other studies, where ethanol was more concentrated than methanol (Ngwabie et al., 2008, 2007). Ethanol median mixing ratios were around 130 ppb, 48 ppb and 42 ppb in the stable, the sheep pen and outdoor, respectively. These mixing ratios were in the range of previous studies in various farm buildings (Blunden et al., 2005; Ni et al., 2012; Yuan et al., 2017). In our study, ethanol and methanol mixing ratios were very close (Figure 3). However, ethanol was usually one order of magnitude higher than methanol. This difference may arise from different feedings, as it is supposed to be the main source of ethanol in farm buildings (Yuan et al., 2017). For example, in the study of Ngwabie et al. (2008), cows were fed with a mix of corn silage, grass silage, rape expeller, pressed beet pulp, and barley straw. In

562 our study, dairy cows and sheep were mainly fed with corn and alfalfa silage, completed with  
563 press beet pulp ground ear corn and potato.



564

**Figure 2 :** Median mixing ratios and percentiles (25<sup>th</sup> and 75<sup>th</sup> as end of boxes) of the 20 most concentrated compounds inside the dairy stable, the sheep pen, and outside. All the means and the percentiles are given in ppb, except for CO<sub>2</sub> in ppm. Not that NH<sub>3</sub> was divided by 100 for scaling reasons. TMA: trimethylamine (C<sub>3</sub>H<sub>9</sub>N); DMS : dimethylsulfide (C<sub>2</sub>H<sub>6</sub>S)

565 The small differences in animal feeding operations may thus be the reason of the higher methanol  
566 levels observed. Acetic acid ( $C_2H_4O_2$ ) mean mixing ratios were found to be similar in the sheep  
567 pen, the stable and outdoor. It was the 3<sup>rd</sup> most concentrated VOC in the dairy stable, sheep pen  
568 and outdoor.

569 In the stable, acetaldehyde ( $C_2H_4O$ ) is the 4<sup>th</sup> most abundant VOC, with mixing ratios close to that  
570 of acetic acid (Figure 3). Acetaldehyde was ranked only in sixth position in the sheep pen and  
571 outside, and median mixing ratios were one order of magnitude lower than in the stable. This was  
572 the case for most of the VOCs that were more concentrated in the stable than in the sheep pen and  
573 outside (Figure 3). Only a few hydrocarbons ( $C_xH_y$ ) were among the most concentrated  
574 compounds. Toluene was one of the most concentrated compounds only in the stable. For butene,  
575 the mixing ratios were comparable inside and outside the farm buildings. This means that both  
576 buildings were not strong sources of butene.

577 Figure 3 shows that nitrogen oxides ( $NO_x$ ) mixing ratios were higher in the buildings than  
578 outside, meaning that both buildings can be considered as a source of  $NO_x$ . Both NO and  $NO_2$   
579 were more concentrated inside the stable than outdoor. However, in the sheep pen, only  $NO_2$  was  
580 higher than outside (NO mixing ratios were very close in the sheep pen and outside, see Figure 3).

581 Trimethylamine ( $C_3H_9N$ ) was the most abundant N-containing compound after  $NH_3$ , in both  
582 buildings (Figure 3). Trimethylamine was one of the few compounds listed in Figure 3 that was  
583 more concentrated in the sheep pen than in the stable. For both buildings, mixing ratios were in  
584 agreement with previous studies in dairy or sheep farms (Ngwabie et al., 2008, 2007). We  
585 observed that there was more N- and S-containing compounds among the 20 most concentrated  
586 compounds in the sheep pen than in the stable and outdoor (Figure 3).  $H_2S$  was one of the most  
587 concentrated S containing compounds inside the stable but was not detected in the sheep pen or  
588 outdoor.  $H_2S$  may hence be used as a tracer for stable emissions within the whole farm (Figure 3).

589  $H_2S$  was already reported inside farm buildings, and is known to be co-emitted with  $NH_3$  and

amines (Blunden and Aneja, 2008; Feilberg et al., 2017). H<sub>2</sub>S levels measured in our study were close to that measured in dairy cattle stables, but at least one order of magnitude below reported values in pig farms (Feilberg et al., 2017, 2010). In the sheep pen, the two S-containing compounds that were among the most abundant VOCs were DMS (dimethylsulfide, C<sub>2</sub>H<sub>6</sub>S) and dimethylsulfone (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>S), which were in the same range as reported by previous studies (Ngwabie et al., 2008, 2007; Trabue et al., 2010). For the outdoor measurement there was only one S-containing compound and no N-containing compounds (except NH<sub>3</sub>). Finally, NH<sub>3</sub>, NO<sub>x</sub> and VOCs levels inside the building greatly exceeded the levels outside. Higher concentrations lead to a higher exposure levels for animals and farmers inside the buildings. The effect of such exposure on animal and human health should be further investigated.

#### 4.5. Correlation between different compounds

We performed a correlation analysis between VOCs with a mean mixing ratio above 0.1 ppb (to keep only the most significant VOCs). This criterion lead to a subset of 50 VOCs for the stable and 42 for the sheep pen. The correlation was based on the temporal evolution of each compound. The aim of such correlation analysis is to see which VOCs correlated to each other, and with other physico-chemical parameters such as NO<sub>x</sub>, CO<sub>2</sub>, NH<sub>3</sub>, temperature and wind speed. Hence, a high temporal correlation between compounds may underline similar emission processes or species involved in a same chemical process, as evidenced by Sinterman et al. (2004) to differentiate between animal and excreta emissions. The aim of the correlation analysis was to determine whether all the VOCs originated from one or several sources. The correlations obtained in the sheep pen and the stable are represented in Figures 4a, and 4b.

As indicated in Figure 4a, VOCs in the stable were anti-correlated with wind speed, indicating that VOCs were emitted inside the stable and did not come from external sources. *k*-means analysis revealed that four groups can be identified on the correlation heat-map. A first group of 14 compounds included hydrocarbons and oxygenated compounds, in addition to NO<sub>x</sub> and CO<sub>2</sub>

615 (group 2 in the Figure 4.a). Markers of anthropogenic combustion sources, such as BTEX,  
616 trimethyl benzene, propyl benzene, and NO<sub>x</sub> were found in this group. CO<sub>2</sub> could be emitted by  
617 combustion sources, in addition to animal respiration, explaining why it was in this group but  
618 with low correlation. As all the compounds were anti-correlated with wind speed, the  
619 anthropogenic source should be inside the stable. This suggests that farming activities implying a  
620 tractor (performing mulching for example) may be the source of the compounds in this group.  
621 This was also confirmed by the onsite personnel, as they frequently used tractors for some  
622 activities in the stable. However, they do not have a detailed report of activities that allowed to  
623 exactly assign the concentration peaks to these activities.

624 The second group of 21 compounds (group 1 in Figure 4.a) was mainly composed of  
625 hydrocarbons and oxygenated compounds. There were also 3 N-containing compounds, 1 S-  
626 containing compound and air temperature. Ethanol and methanol, the two most concentrated  
627 VOCs were in this group and were strongly correlated with the other VOCs in this group. As  
628 explained above, feeding operations are supposed to be the main source of these alcohols (Yuan  
629 et al., 2017). We thus supposed that the feeding operations are the source the VOCs included in  
630 the group 2. Six compounds and wind speed comprised the third group: 2 N-containing  
631 compounds, 2 S-containing compounds, cresols and NH<sub>3</sub>. Most of these compounds have a strong  
632 unpleasant odor. The presence of NH<sub>3</sub> and small S-containing compounds suggests that the main  
633 source for this group was dairy cattle excreta. This is strengthened by the presence of cresols in  
634 this group, well known to be associated with urea and feces (Mackie et al., 1998; Shaw et al.,  
635 2007; Sun et al., 2008). Mackie et al. (1998) explained that cresols are produced during the  
636 microbial degradation of tyrosine and associated with the production of phenol. Logically, phenol  
637 and cresols were positively correlated, even if phenol was in another group (Figure 4a). The last  
638 group contained 13 compounds: 4 hydrocarbons, 6 oxygenated compounds, 2 N-containing  
639 compounds, 1 S-containing compounds. Considering that acetone was mainly emitted by animals,

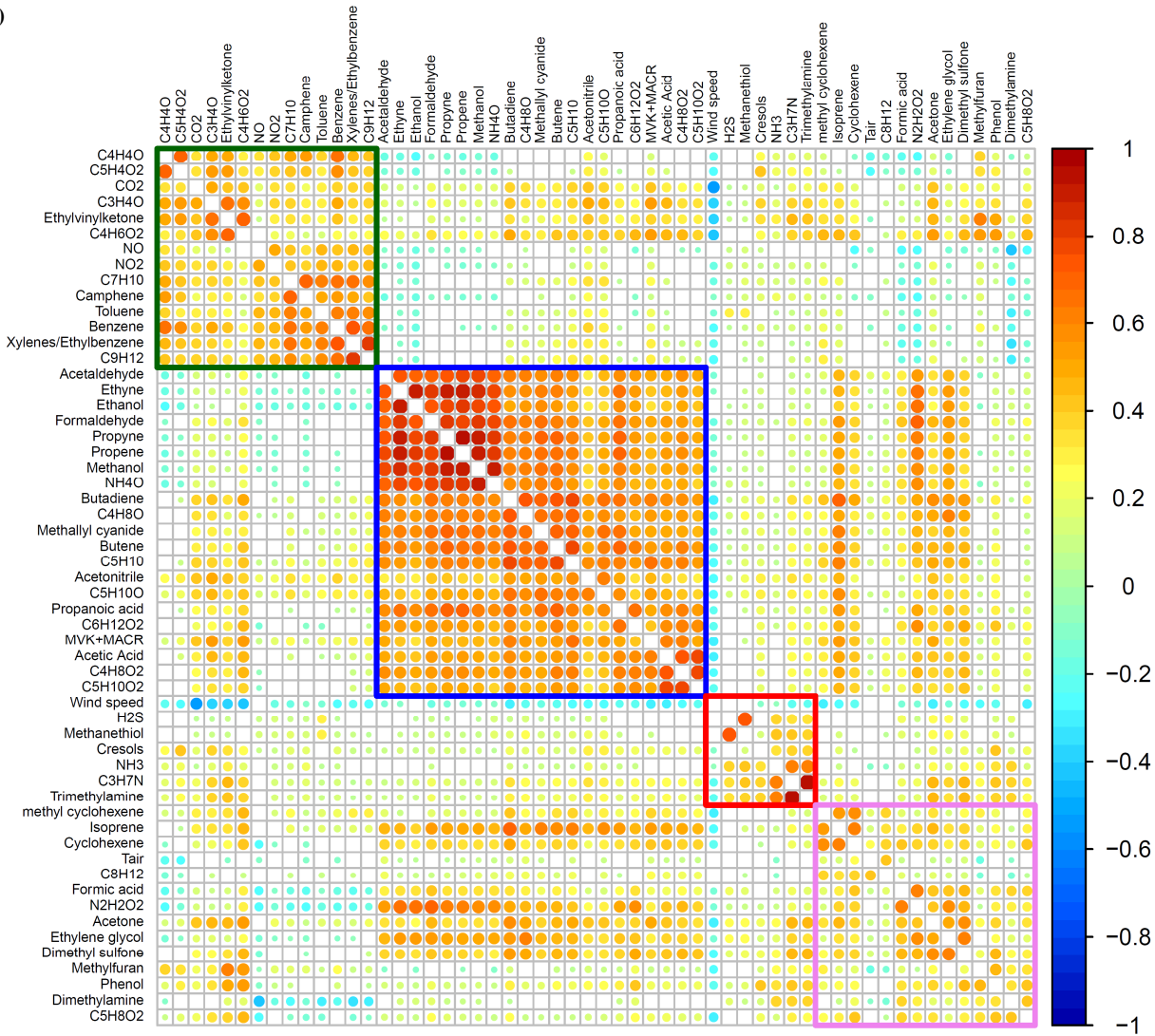
640 we can suppose that the source of VOCs in this group was mainly related to dairy cattle  
641 respiration, which is known to emit several VOCs (Oertel et al., 2018; Spinhirne et al., 2004).  
642 This result is also supported by the positive correlation between acetone (and the other  
643 compounds in this group) and CO<sub>2</sub>. Finally, the air temperature was very weakly correlated with  
644 VOCs, although it was included in this last group.

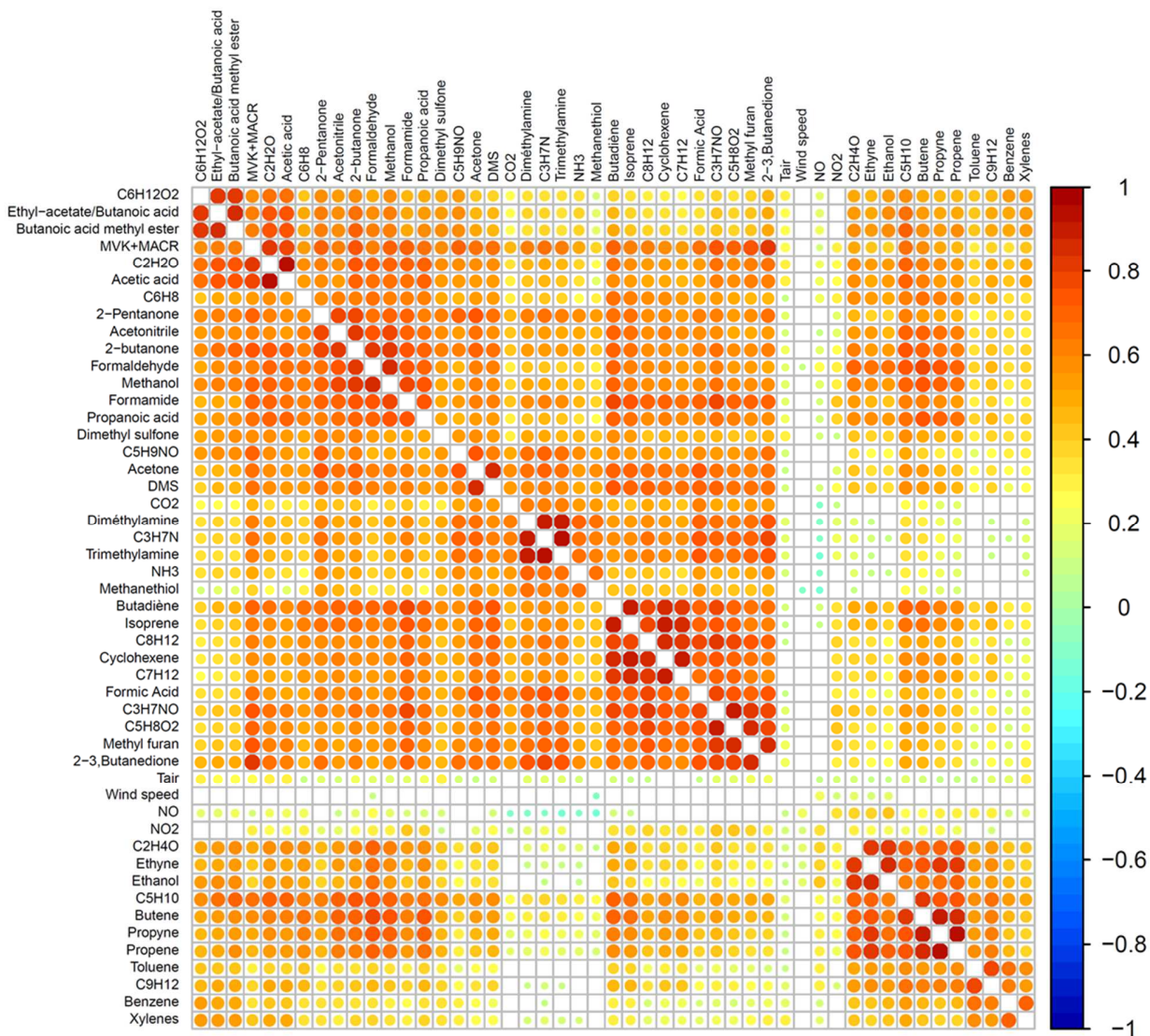
645 In the sheep pen, almost all of the VOCs were positively correlated to each other, regardless of  
646 the chemical family (hydrocarbons, N-containing species or oxygenated compounds, Figure 4b).  
647 On the contrary, none of them were correlated with wind speed ( $p$  values  $< 0.005$ ) and all the  
648 VOCs were only barely correlated to air temperature. One can note that NO was not correlated  
649 with any VOC, and NO<sub>2</sub> only slightly with a few VOCs. BTEX and C<sub>9</sub>H<sub>12</sub> (identified as benzene  
650 derivatives) were frequently attributed to anthropogenic sources, even though they were already  
651 reported inside farm buildings or sheep breath analysis (Ciganek and Neca, 2008; Fischer et al.,  
652 2015). For an anthropogenic combustion source, BTEX would be strongly correlated with NO<sub>x</sub>  
653 (NO+NO<sub>2</sub>), and especially with NO in the case of local engine exhaust (Jiang et al., 2017;  
654 Seinfeld and Pandis, 2006). This was for example the case in the stable, as explained above. But  
655 in the sheep pen, BTEX were not correlated with NO<sub>x</sub> (Figure 4.b), confirming that both NO<sub>x</sub> and  
656 BTEX did not arise from the same anthropogenic combustion source. Since BTEX compounds  
657 were not correlated with wind speed, we can therefore assume that they originate from the sheep  
658 pen (Figure 4.b). CO<sub>2</sub> can be used in the sheep pen as an animal emission tracer, whereas NH<sub>3</sub>  
659 could be mostly related to emissions from manure. Even if the  $k$ -means analysis did not reveal  
660 any optimal number of groups, we can see that NH<sub>3</sub> was highly correlated to trimethylamine and  
661 C<sub>3</sub>H<sub>7</sub>N. Thus, these two amines were likely to be emitted by the animal excreta together with  
662 NH<sub>3</sub>. It is difficult to go further in this analysis as CO<sub>2</sub> and NH<sub>3</sub> were correlated, meaning that  
663 animal, manure and feeding operation emissions cannot be well separated in the sheep pen when  
664 only considering time-based correlations. The absence of groups in the correlation analysis

665 indicates that the main driver of the atmospheric composition inside the sheep pen was probably  
 666 the dynamic flow inside the building rather than the strength of the emission sources.

667

A)





668 **Figure 4:** Correlations between compounds inside the stable (A) and the sheep pen (B). The  
 669 correlation scales (on the left of each graph) range from -1 to 1 (unitless). Blue color means that  
 670 two compounds are negatively correlated, and red colors means that they are positively correlated.  
 671 Empty boxes either correspond to the diagonal (autocorrelation), or to the cases where correlation  
 672 between the compounds were not significant ( $p < 0.005$ ). The order of the compounds is defined  
 673 using a hierarchical clustering approach, based on the distance between the compounds. The  
 674 number of groups was determined as the optimum clustering number from a  $k$ -means analysis.  
 675 For the sheep pen, no optimum has been found, explaining why there is no group on Figure 4.b.

#### 4.6. NH<sub>3</sub> Emission rates

Mean ventilation rates have been estimated to be around 440 000 m<sup>3</sup> h<sup>-1</sup> and 230 000 m<sup>3</sup> h<sup>-1</sup> in the dairy stable and the sheep pen, which is similar to previous studies in naturally ventilated buildings (Ngwabie et al., 2014; Schmithausen et al., 2018; Wang et al., 2016). The ventilation rate inside the sheep pen was lower than in the stable due to smaller windows. The mean residence times inside both buildings, deduced from the mean ventilation rates, was estimated to be around 3 minutes in the stable, and around 6 minutes in the sheep pen. The residence time and the ventilation rate variability are nevertheless highly dependent on external wind speed and specific actions such as the opening lateral doors in the buildings. For example, in the sheep pen, the residence time can fall below one minute when the lateral doors are open.

NH<sub>3</sub> emission rates for the stable and the sheep pen were estimated to be 9.7 (±7.1) kg N day<sup>-1</sup> and 8.8 (±5.8) kg N day<sup>-1</sup> (values between brackets are the standard deviation, representing the temporal variability of the emissions throughout the measurement campaign) (Figure 5.a). NH<sub>3</sub> emissions from each building were roughly similar, although NH<sub>3</sub> mixing ratios were higher inside the sheep pen (Figure 3). This was due to the lower ventilation rate that led to lower dilution in the sheep pen than in the dairy stable. The NH<sub>3</sub> emission rates calculated here were in the same order of magnitude as that previously reported for the same farm by Loubet et al. (2012), using inverse modelling on a crop field downwind the farm. They reported a value of 8.3 kg N day<sup>-1</sup> for the whole farm, slightly lower than the value calculated in the present study. This difference could be due to the seasonality effect, but also to an underestimation due to the absence of deposition parameters in the inversion model (Loubet et al. 2012). It was shown above that animals and their excreta were the main source of VOCs inside both buildings. It thus makes sense to normalize emissions by the number of animals, or the amount of living units (LU, 1 LU = 500 kg) as usually performed in similar studies. The normalization by the number of animals shows that a dairy cow emitted more NH<sub>3</sub> than a sheep (Figure 5.b), which was due to the

701 different weight of animals. We calculated that for the dairy stable and the sheep pen, emission  
702 rates by animals were  $17.3 (\pm 12.7)$  kg N year<sup>-1</sup> animal<sup>-1</sup> and  $3.1 (\pm 1.9)$  kg N year<sup>-1</sup> animal<sup>-1</sup>  
703 respectively (Figure 5.c). These emission factors are in the same order of magnitude as those  
704 frequently used in emission inventories (Aneja et al., 2012; Battye, 2003; Behera et al., 2013;  
705 Bouwman et al., 1997). For example, Bouwman et al. (1997) used an emission rate of 40-50 kg N  
706 year<sup>-1</sup> animal<sup>-1</sup> for dairy cattle and 1.0 kg N year<sup>-1</sup> animal<sup>-1</sup> for sheep, in a global scale estimation.  
707 A study on Indian agricultural emissions conducted by Aneja et al. (2012) referred to NH<sub>3</sub>  
708 emission rates of 4.3 kg N year<sup>-1</sup> animal<sup>-1</sup> and 1.4 kg N year<sup>-1</sup> animal<sup>-1</sup> for dairy cattle and sheep,  
709 respectively. In Europe, Van der Hoek used emission rates of 28.5 kg N year<sup>-1</sup> animal<sup>-1</sup> for dairy  
710 cattle and 0.2 kg N year<sup>-1</sup> animal<sup>-1</sup> for sheep. In conclusion, it appears that dairy cattle NH<sub>3</sub>  
711 emission rates obtained in our study are in the range of previous emission rates reported, whereas  
712 sheep emission rates are slightly higher. As the weight of a dairy cow and a sheep are very  
713 different, normalization by the living units (i.e. 500 kg of animal weight) is frequently performed.  
714 Emission rates were estimated to be  $1.8 (\pm 1.3)$  g N h<sup>-1</sup> LU<sup>-1</sup> and  $2.2 (\pm 1.4)$  g N h<sup>-1</sup> LU<sup>-1</sup> for the  
715 dairy stable and the sheep pen, respectively (Figure 5.b). These values were in agreement with  
716 previous studies conducted in naturally ventilated buildings (Koerkamp et al., 1998; Ngwabie et  
717 al., 2014, 2009; Wang et al., 2016). Our study shows that, for an equivalent amount of living  
718 units, sheep pen emissions of NH<sub>3</sub> are only slightly higher than that of the dairy stable, (Figure  
719 5.b).

#### 720 **4.7. VOC emissions**

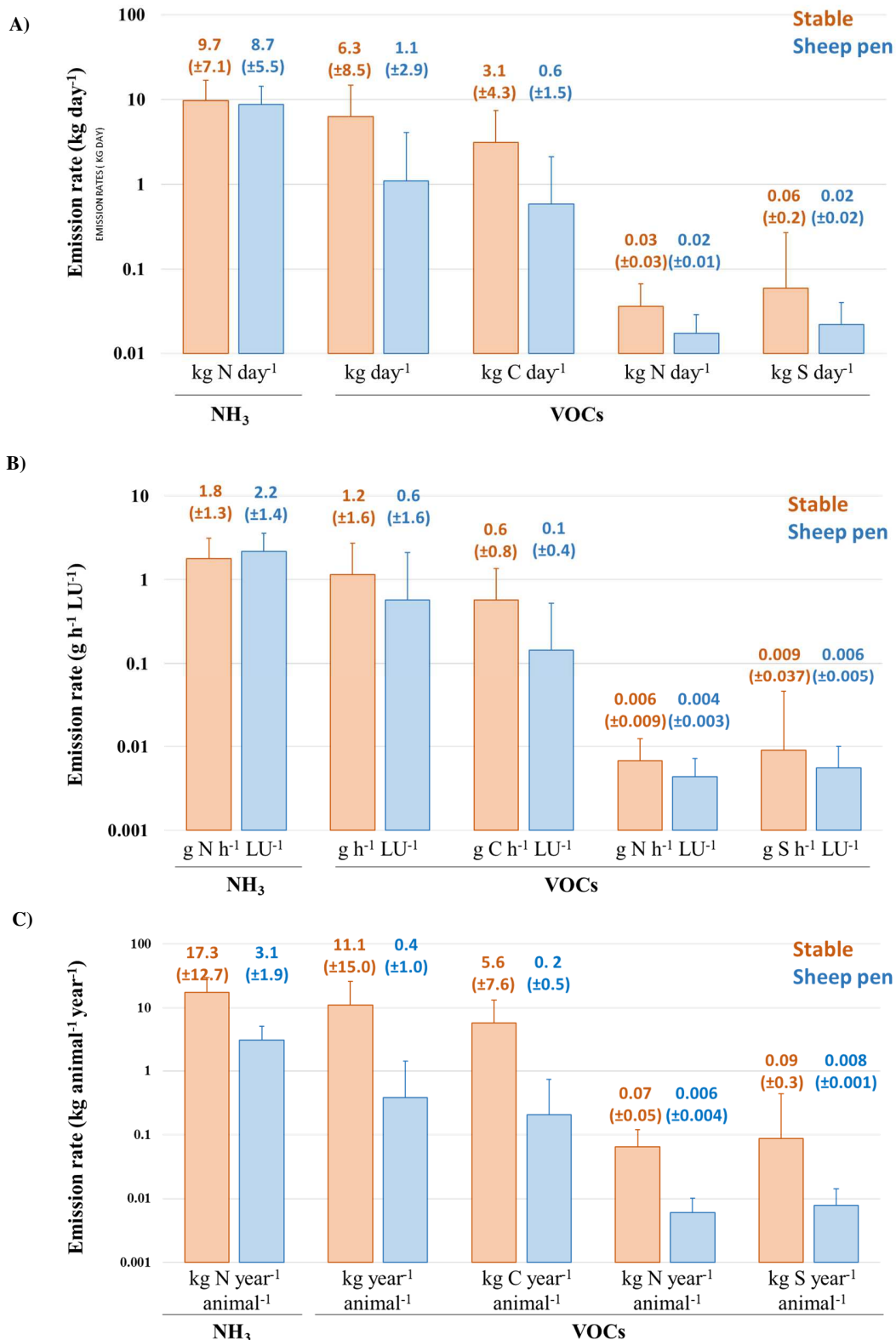
721 For VOCs, we calculated emission rates only for compounds with mean mixing ratios higher  
722 inside the buildings than outside. This resulted in 231 VOCs emitted (80% of the 289 identified)  
723 for the dairy stable, and 177 for the sheep pen (76% of the 233 identified). Table S3 lists the 10  
724 most emitted VOCs with their corresponding mean emission rates, together with NH<sub>3</sub> and NO<sub>x</sub>.  
725 Detailed emission rates for each VOC can be found in the associated data file. The emission rates

726 for the sum of all VOCs have been calculated to be  $6.3 (\pm 8.5) \text{ kg day}^{-1}$  for the dairy stable and  
727  $1.1 (\pm 2.9) \text{ kg day}^{-1}$  for the sheep pen (Figure 5.a). Conversely to  $\text{NH}_3$ , the dairy stable was found  
728 to emit about six times more VOCs than the sheep pen. The sum of all VOCs represented 52.8%  
729 of the  $\text{NH}_3$  emissions in the stable, and 10.3% in the sheep pen (as a mass ratio, considering  $\text{NH}_3$   
730 emissions in kg of  $\text{NH}_3$ ). We also evaluated that a sheep emitted much less VOCs than a dairy  
731 cow: VOC emission rates were  $11.1 (\pm 15.0) \text{ kg year}^{-1} \text{ animal}^{-1}$  for a dairy cow and  $0.4 (\pm 1.0) \text{ kg}$   
732  $\text{year}^{-1} \text{ animal}^{-1}$  for sheep (Figure 5.c). This was expected considering the difference in animal  
733 weight, but emissions from dairy cows are still higher if normalized by living units: VOC  
734 emission rates were estimated to be  $1.2 (\pm 1.6) \text{ g h}^{-1} \text{ LU}^{-1}$  and  $0.6 (\pm 1.3) \text{ g h}^{-1} \text{ LU}^{-1}$  in the dairy  
735 stable and the sheep pen. The difference of emitted VOCs between dairy cows and sheep was  
736 therefore not only due to the animal weight, but also in the metabolism of the animals and the  
737 nature of their excreta. This is an interesting point considering that the feeding regime for both  
738 sheep and cows is quite similar in our study.

739 In both farm buildings, the 10 most emitted VOCs contributed to more than 90% of the total VOC  
740 emissions (Figure S5). In term of quantitative balance, it is thus unnecessary to measure all the  
741 VOCs. But for chemical air quality studies or odor activity studies, low emissions of VOCs could  
742 be very important. For example, Yuan et al. (2017) showed that phenolic species constituted only  
743 a few percentage of emissions from concentrated animal feeding operations in Colorado (USA),  
744 whereas they dominated the reactivity with the  $\text{NO}_3$  radicals.

745 In the stable ethanol was measured as the most concentrated VOC (Figure 3). Logically, it was  
746 the most emitted VOC in both buildings (Table S3). Ethanol emission rates were estimated to be  
747  $6.1 (\pm 8.3) \text{ kg year}^{-1} \text{ animal}^{-1}$ . Methanol is the second most emitted VOC in the stable, with  
748 emission rate of  $0.6 (\pm 0.8) \text{ kg year}^{-1} \text{ animal}^{-1}$  (Table S3). These values are generally in agreement  
749 with previous studies (Ngwabie et al., 2007; Shaw et al., 2007; Sun et al., 2008). However,  
750 discrepancies in dairy methanol emissions can be found in the literature. For example, (Shaw et

751 al., 2007) used a chamber to measure methanol emission rates from lactating cows of 0.4 ( $\pm 0.2$ )  
752 kg year<sup>-1</sup> animals<sup>-1</sup>, very close to our study. But Sun et al. (2008), in a study equivalent to that of  
753 Shaw et al. (2007), reported methanol emission rates of 6.1 kg year<sup>-1</sup> animals<sup>-1</sup>. This point  
754 illustrates the variability of VOC emission rates between different studies and more investigations  
755 are required to better constrain emission rates. Acetaldehyde was the third most emitted VOC,  
756 with an emission rate of 1.1 ( $\pm 1.4$ ) kg year<sup>-1</sup> animals<sup>-1</sup>. This result differs from other studies where  
757 acetaldehyde was not reported as the one of most important VOCs (Filipy et al., 2006; Ngwabie et  
758 al., 2008; Sun et al., 2008). After ethanol, methanol, and acetaldehyde, monoterpenes (C<sub>10</sub>H<sub>16</sub>,  
759 identified as camphene) were the most emitted VOCs, followed by acetone. The most abundant  
760 N-containing compound was trimethylamine (C<sub>3</sub>H<sub>9</sub>N). As suggested above, H<sub>2</sub>S was only emitted  
761 in the stable and could be proposed as a tracer of the dairy stable. This was also the case of NO  
762 and toluene, but they could not be proposed as tracers because several other sources (especially  
763 motor vehicles) may emit these compounds in the vicinity of the farm. Emissions of other  
764 compounds associated with farm buildings, such as cresols, indole and phenol, were not in the  
765 most emitted compounds. However it is essential to characterize their emission rates due to their  
766 high odor activity value (Feilberg et al., 2010; Hansen et al., 2016). The detailed emission rates  
767 for such compounds are provided in the associated data file.



**Figure 3:** Mean emission rates of NH<sub>3</sub>, the sum of VOCs, and VOCs in terms of carbon (C), nitrogen (N) and sulfur (S), for the dairy stable (orange bars) and the sheep pen (blue bars). Emission rates are given A) by building (in kg day<sup>-1</sup>), B) by living unit in each building (in g h<sup>-1</sup> LU<sup>-1</sup>) and C) by animals (in kg year<sup>-1</sup> animals<sup>-1</sup>). Numbers above each bar plot give the corresponding mean emission rate value and its standard deviations in parenthesis.

769 The most emitted VOC in the sheep pen was ethanol, as in stable, with an emission rate of 0.3  
770 ( $\pm 0.8$ ) kg year<sup>-1</sup> animals<sup>-1</sup>. Methanol was the 2<sup>nd</sup> most emitted VOC. Methanol emission rates  
771 were one order of magnitude lower than ethanol with  $2.9 \times 10^{-2}$  ( $\pm 0.2 \times 10^{-2}$ ) kg year<sup>-1</sup> animals<sup>-1</sup> in  
772 the sheep pen. Thus, the two VOCs with higher emission rates were similar between the stable  
773 and the sheep pen. But the magnitude of their emissions were considerably higher in the dairy  
774 stable (Figure 5). These values were lower by at least one order of magnitude compared to the  
775 only previous study on sheep VOC emissions (Ngwabie et al., 2007). This could be due to *i*) the  
776 different methodologies to estimate the emission rates *ii*) their use of a conventional quadrupole  
777 PTR-MS not being able to separate isobaric compounds (such as <sup>17</sup>O<sup>16</sup>O<sup>+</sup> and O<sub>2</sub>.H<sup>+</sup> ions) and *iii*)  
778 the difference between the two farms (agricultural practices, climate, animals, etc.) and especially  
779 the animal feeding regime. Acetone and trimethylamine were the most emitted VOCS after  
780 ethanol and methanol. This result is also in agreement with that of Ngwabie et al. (2007). The  
781 qualitative analysis of the main emitted VOCs seems to confirm the findings of this study.  
782 However, the magnitude of VOC emissions is lower in our study. Differences may arise from  
783 several factors (composition of the animal feed, model used to calculate emission rates,  
784 agricultural practices, etc.) and more studies are required to better understand VOC emissions  
785 from sheep farms. We also highlighted that the sheep pen emitted NO<sub>2</sub> but no NO. The NO<sub>2</sub>  
786 emission rate was lower but close to VOC emission rates, with a mean emission rate of 0.1 ( $\pm 0.1$ )  
787 kg year<sup>-1</sup> animals<sup>-1</sup>). There were also two S-containing compounds in the 10 most emitted VOCs  
788 by the sheep pen, DMS and dimethylsulfone (Table S3). These compounds are of interest as they  
789 were not emitted by the stable. C<sub>9</sub>H<sub>12</sub> and C<sub>3</sub>H<sub>7</sub>N were also only emitted by the sheep pen. These  
790 four VOCs could be assessed as tracers of sheep pen emissions.

#### 791 **4.8. VOC emission rates in terms of C, N and S**

792 Emission rates were also calculated for each VOC in terms of C, N, and S in both buildings  
793 (Figure 5). The stable emitted about five times more C through VOCs than the sheep pen;

794 emission rates for the sum of VOCs in terms of C were  $3.1 (\pm 4.3) \text{ kg}_C \text{ day}^{-1}$  in the stable and  $0.6$   
795  $(\pm 1.5) \text{ kg}_C \text{ day}^{-1}$  in the sheep pen (Figure 5.a). This is even more contrasted when emission rates  
796 were calculated per animals (Figure 5.c), with values of  $5.6 (\pm 7.6) \text{ kg}_C \text{ year}^{-1} \text{ animals}^{-1}$  for the  
797 stable and  $0.2 (\pm 0.5) \text{ kg}_C \text{ year}^{-1} \text{ animals}^{-1}$  for the sheep pen.

798 The emission factors for the N contained in VOCs were  $3 \times 10^{-2} (\pm 3 \times 10^{-2}) \text{ kg}_N \text{ day}^{-1}$  and  $2.0 \times 10^{-2}$   
799  $(\pm 1.0 \times 10^{-2}) \text{ kg}_N \text{ day}^{-1}$  for the stable and the sheep pen, respectively (Figure 5.a). Contrary to what  
800 was found for  $\text{NH}_3$ , the emission factor of N emitted through VOCs was higher in the stable than  
801 in sheep pen, even when the emission rates were expressed as function of living units or animals  
802 (Figure 5.b and 5.c). These emission rates were very low compared to  $\text{NH}_3$  emission rate. In terms  
803 of N balance, the N emitted through VOCs only represents 0.4% and 0.2 % of the  $\text{NH}_3$  emission  
804 factor in the stable and the sheep pen (in amount of emitted N). As a result, there is no need to  
805 measure VOCs in future nitrogen cycle assessment studies.

806 The S emission factor for the sum of VOCs was  $6.0 \times 10^{-2} (\pm 0.2) \text{ kgs day}^{-1}$  and  $2.0 \times 10^{-2} (\pm 2.0 \times 10^{-2})$   
807  $\text{ kgs day}^{-1}$  in the dairy stable and the sheep pen. As for C and N, the amount of S emitted was  
808 higher in the stable than in the sheep pen. DMS was the most emitted S-containing compound in  
809 the sheep pen, accounting for 40 % of the sheep pen S emissions. Surprisingly, the dairy stable  
810 did not emit DMS (*i.e.* mixing ratios outside were higher than inside the building), while some  
811 studies reported strong emissions from dairy buildings (Filipy et al., 2006; Ngwabie et al., 2008;  
812 Shaw et al., 2007). 67 % of S emitted in the dairy stable could be attributed to  $\text{H}_2\text{S}$  (no  $\text{H}_2\text{S}$   
813 emissions were recorded for the sheep pen). Feilberg et al. (2017) found a ratio between  $\text{H}_2\text{S}$  and  
814  $\text{NH}_3$  of 0.06, whereas it was 0.004 in our study. Thus, it seems that the dairy stable was not a  
815 strong S emitter in contrast to the literature.

816 Figure 6 represents the chemical fingerprint of VOC emissions. The fingerprint of VOC  
817 emissions was mostly composed of C, for more than 90 % in each building. This is logical  
818 considering that most of the detected VOCs were oxygenated VOCs and hydrocarbons that

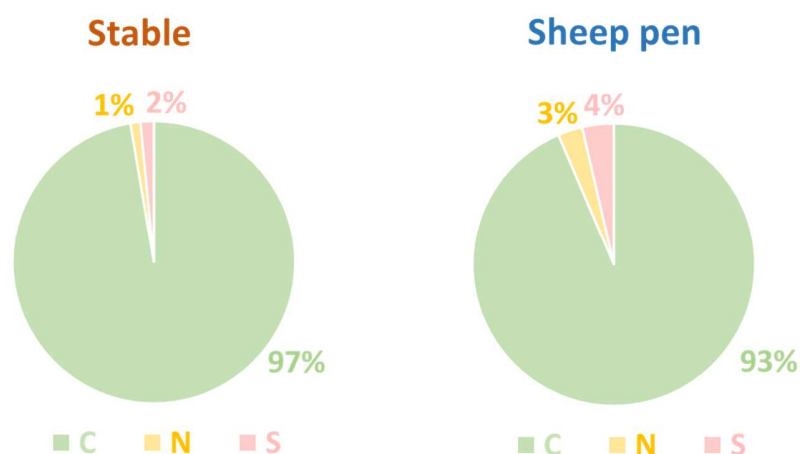
819 contained a large number of C atoms, and that N or S containing VOCs mostly had a few atoms.  
820 N and S were found in a greater proportion in the sheep pen, but the emission factors were greater  
821 in the stable. The chemical compounds and the magnitude of the emissions were thus different in  
822 each building. Finally, C/N/S composition of VOC emissions allowed identification of differences  
823 between the buildings, contrary to what was found above for mixing ratios (Figures 2 and 6).

824 Figure 6 showed that N containing compounds were a small but significant part of emitted VOCs,  
825 especially in the sheep pen. NH<sub>3</sub> and amines (TMA- trimethylamine, DMA-dimethylamine,  
826 indole and others) could be important species for atmospheric chemistry, as they can lead to new  
827 particle formation and secondary organic aerosols (Duporté et al., 2016; Lehtipalo et al., 2018;  
828 Yao et al., 2018; Yu et al., 2012). Especially, Yu et al. (2012) demonstrated that amines and NH<sub>3</sub>  
829 catalyze the formation rate of stable clusters from sulfuric acid and water mixtures. Thus,  
830 considering the high VOC concentrations inside the buildings, SOA formation could be expected.  
831 However, aerosol chemical composition as measured by the ACSM revealed that the PM1  
832 chemical composition inside farm buildings was not very different compared to ambient  
833 measurements performed 20 km from the farm. Thus, VOC emissions did not significantly affect  
834 the aerosol chemical composition close to the source (*i.e.* inside the building or outside close to  
835 them). Hiranuma et al. (2010) observed a similar result close to an open-air cattle feeding facility.  
836 This could be due to the very short residence time inside the buildings (in the order of minutes),  
837 which was not long enough for secondary aerosol formation to affect the fine particle composition  
838 (Hallquist et al., 2009). This could also be the result of low oxidant levels inside the buildings that  
839 do not allow strong semi-volatile production. Finally, it was demonstrated that farm buildings  
840 emitted primary particles mostly in the coarse mode (Cambra-López et al., 2010). But the  
841 formation of fine secondary aerosols in the vicinity of the farm seems to be limited, and may only  
842 probably occur in the plume emitted by the farm (Lammel et al. 2004).

#### 843 **4.9. Estimation of VOC emissions from livestock at national scale**

844 The emission factors for VOCs were estimated for the first time in a sheep pen and a dairy stable  
845 at a farm in France. To scale up VOC emissions, previous studies used NH<sub>3</sub> emission inventories  
846 at a national scale. A ratio between VOCs and NH<sub>3</sub> emission rates can then be applied to estimate  
847 VOC emissions at large scales (Hobbs et al., 2004). Following the French Interprofessional  
848 Technical Centre for Studies on Air Pollution (CITEPA), NH<sub>3</sub> emissions due to livestock were  
849 about 246.6 kt in 2016. We estimated from our results that the amount of VOCs emitted was  
850 31.5 % of the amount of NH<sub>3</sub> due to livestock (mean of the sheep pen and the dairy stable).  
851 Applying this ratio would lead to a VOC emission of 77.7 kt year<sup>-1</sup> for the year 2016 in France.  
852 CITEPA estimated that VOC emissions from livestock in 2016 were around three times larger  
853 than the present one (201.6 kt year<sup>-1</sup>, CITEPA, February 2019). For comparison, traffic road  
854 emissions of VOCs for the same period were estimated to be 66.2 kt year<sup>-1</sup>. Livestock VOC  
855 emissions are therefore significant when compared to other anthropogenic sources, even if they  
856 are lower than expected. The difference between our estimation and the CITEPA may be due to  
857 several factors. Our estimation is based on measurements performed in November. Filipy et al.  
858 (2006) showed that VOC emissions were higher in summer, probably due to higher temperatures.  
859 Our annual estimation thus probably underestimated the mean annual emission, which may partly  
860 explain the difference with the CITEPA estimation. Another factor affecting the difference is the  
861 lack of studies about VOC emissions from farm buildings conducted in France, to better constrain  
862 emission inventories. Thus, the CITEPA estimation was mostly based on studies conducted in  
863 foreign countries, where agricultural standards and practices could be different. Finally, there are  
864 large uncertainties in both estimates and the difference between the two may not be significant.  
865 More studies are thus needed to better constrain national scale estimations and reduce  
866 uncertainties.

867 The estimation of national VOC emissions from livestock in the present study should be  
868 interpreted very carefully, as this study covered only one farm during a relatively short field  
869 campaign. More studies in different farms and during different seasons are needed to reduce the  
870 uncertainties for agricultural emissions. Long term measurements are also required as emission  
871 factors may change during the season. For example, it was shown for some VOCs that emission



**Figure 4 :** Speciation of VOC emissions by amount of C, N, and S in the sheep pen and the dairy stable.

872 factors may differ from one order of magnitude between seasons (Filipy et al., 2006).  
873 Nevertheless, the present study already highlights the meaning of livestock management as a  
874 significant source of VOCs.

## 875 5. Conclusion

876 This study revealed that both sheep and dairy cattle farming emitted a large spectrum of VOCs.  
877 The results highlighted that combining online mass spectrometric and off-line chromatographic  
878 techniques is essential to better characterize VOC emissions, especially in environments enriched  
879 with VOCs, such as farm buildings. In both buildings VOCs were mostly oxygenated compounds  
880 and hydrocarbons. N-containing compounds and S-containing compounds were found in lower  
881 proportions but could be key in assessing odor issues as well as implications for atmospheric

882 chemistry. We showed that the difference in the fingerprint of gas phase compounds emitted by  
883 the stable and the sheep pen was small if we only pay attention to chemical families. Tracers for  
884 each building in the experimental farm can now be proposed. For the stable, Triazine, H<sub>2</sub>S, 1-  
885 butene, isopentane, pentane and acetaldehyde have been identified as potential tracers. For the  
886 sheep pen most of tracers were nitrogen containing compounds. Among them, methylpiperidine,  
887 pyridine, dimethylpyridine and benzenepropanenitrile were highlighted. DMS was also observed  
888 to be mostly emitted by the sheep pen.

889 Our results suggest that animals and litter inside the sheep pen were the main source of VOCs  
890 based on the correlation analysis. In the dairy stable the correlation analysis highlighted 3  
891 different sources. We evidenced that the litter on the soil was a strong emitter of N and S  
892 containing compounds, through the biodegradation of animal excreta. The farming activities using  
893 a tractor inside the stable has shown to emit hydrocarbons (mainly BTEX) and NO<sub>x</sub>. The third  
894 source identified is represented by the animal respiration. A future study focused on VOCs  
895 contained in dairy cattle and sheep breath at the Grignon farm would support our findings and  
896 help to separate animal and excreta emissions.

897 Emission rates have shown that, at the animal level, a dairy cow emitted more NH<sub>3</sub>, NO<sub>x</sub>, and  
898 VOCs than a sheep. But at the farm level, the sheep pen was found to emit roughly as much NH<sub>3</sub>  
899 as the stable. The emission of N through VOCs was negligible compared to the NH<sub>3</sub> emissions.  
900 Thus, regarding the N balance, the N released in the gas phase was mainly released through NH<sub>3</sub>.  
901 As a conclusion, it is thus maybe not necessary to consider the loss of N through VOCs for  
902 agronomical nitrogen budget studies at farm levels.

903 Despite emissions of NH<sub>3</sub> and many VOCs, the aerosol chemical composition was not affected by  
904 farm emissions. It may be explained by a low reaction time and low oxidant levels inside the  
905 buildings. As a result, we propose that secondary aerosol formation can be most significant in the

906 plume of pollutants emitted by the farm, rather than inside the buildings. This assumption needs  
907 to be further investigated in future studies.

908 Based on the new emission rates provided in this study, we estimated that livestock VOC  
909 emissions could be overestimated by one order of magnitude. However, more studies in different  
910 periods and farms are required to reduce uncertainties about emissions and to understand their  
911 driving factors.

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917 **Competing interests:** The authors declare no competing of interest.

918 **Data and materials availability:** More details about the VOCs identified with PTR-Qi-TOF-MS,  
919 GC-FID and TD-GC-MS can be found on the online associated data file. The emission factors for  
920 individual VOCs from each building are also given in the associated data file

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