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

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#### 24 Abstract

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

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

#### 40 Highlights

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

#### 45 **1. Introduction**

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

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

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

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

Animal husbandries are also reported to be a source of atmospheric particles (Cambra Lopez, 2010). It is well established that coarse particles are mainly primary biologic particles related to 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  $\mu$ 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.

In this context, a field campaign was carried out at an experimental farm in the western region of 99 Paris (France). The aim of the study was first to characterize the VOC fingerprint inside a dairy 100 101 stable and a sheep pen, which were both naturally ventilated buildings. On-line (Proton Transfer Reaction - Quadrupole ion guide - Time Of Flight - Mass Spectrometry, PTR-Qi-TOF-MS) and 102 off-line (Thermal Desorption-Gas Chromatography - Mass Spectrometry, GC-MS and Gas 103 Chromatography – Flame Ionization Detector, GC-FID) measurements were conducted outside 104 and inside both buildings. Then, fine aerosol chemical composition (using an ACSM) was 105 measured to characterize the contribution of livestock to the PM1 loading. Finally, a CO<sub>2</sub> mass 106 balance model was used to estimate NH3 and VOC emission rates and emission factors from both 107 buildings. 108

#### 109 **2. Materials and methods**

#### 110 **2.1. Experimental set up**

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

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

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#### 2.2. Sampling and instrumentation

#### 2.2.1. Ancillary measurements 143

Wind speed and direction were measured inside the buildings and outside using a 3-dimension 144 sonic anemometer (R3, Gill instruments). CO<sub>2</sub> was measured with an open path infrared gas 145 analyser (LI-7500, LI-COR biosciences). The mobile laboratory van used in this study was 146 147 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 148 level. Nitrogen oxides (NOx, being the sum of NO and NO2) were monitored with a 149 150 chemiluminescent gas analyser (model 42C, Thermo Fischer scientific). The  $NO_x$  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 151 campaign. A Teflon filter ( $\emptyset = 0.45 \,\mu$ M, Pall Life Sciences 4785 Ion Chromatography (IC) 152 Acrodisc Syringe Filters) placed at the inlet prevented particles from entering the instrument. 153

NH<sub>3</sub> measurements were performed every 2 minutes using a commercial laser photoacoustic-154 based analyser (LSE Monitors B.V., the Netherlands). The inlet was 1.2 m Teflon tubing (1/8 inch 155 diameter) heated at 40-45 °C; the inlet flow inside the analyzer was 0.040 L min<sup>-1</sup>. A Teflon filter 156 was added at the inlet of the tubing to prevent particles from entering the instrument. The NH<sub>3</sub> 157 analyzer was calibrated before the campaign by the manufacturer and had a detection limit of 1-2 158 ppb. 159

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### 2.2.2. Online VOC analysis

VOCs were measured online using a proton transfer reaction - quadrupole ion guide - time of 161 flight - mass spectrometer (PTR-Qi-TOF-MS, Ionicon analytik GmbH), that has been fully 162 described by Abis et al. (2018). Air was sampled using 1.5 m long Teflon tubing with 1/8 inch 163 164 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 ( $\emptyset = 0.45 \,\mu$ M, Pall 165 Life Sciences 4785 Ion Chromatography (IC) Acrodisc Syringe Filters) was placed at the entry of 166

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

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#### 2.2.3. Offline VOC analysis

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

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

Canister sampling was also performed by sampling the air for 15 minutes every 4 hours (Table 207 S1). Air sampled by canisters was analysed by GC-FID (HP 6890) equipped with a CP-Al<sub>2</sub>O<sub>3</sub> 208 Na<sub>2</sub>SO<sub>4</sub> column, providing a complementary analysis of small hydrocarbons. A pre-concentrator 209 (Entech 7200) was placed at the inlet of the instrument to allow automatic injections. A standard 210 cylinder with 5 non methane hydrocarbons (NMHC, Messer) was used to check that the 211 instrument was functioning correctly and an international reference standard containing 32 212 NMHC from C2 to C10 (NPL, National Physics Laboratory, Teddington, UK) was used for 213 214 calibrations.

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#### 2.2.4. Chemical composition of particles

In order to characterise the aerosol composition inside the farm buildings, an Aerosol Chemical 216 Speciation Monitor (ACSM) was used during the field campaign, providing near real time 217 concentrations of submicron organic matter (OM), nitrate (NO<sub>3</sub><sup>-</sup>); sulphate (SO<sub>4</sub><sup>2-</sup>), ammonium 218 (NH<sub>4</sub><sup>+</sup>) and chloride (Cl<sup>-</sup>). The measurement principle of the ACSM has been extensively 219 described elsewhere (Ng et al., 2011). Briefly, submicron particles are successively sampled at 3 220 L min<sup>-1</sup>, sub-sampled at 85 mL min<sup>-1</sup>, focused through an aerodynamic lens, and eventually flash-221 vaporized over a 600°C-heated tungsten vaporizer, followed by ionization by EI at 70 keV. 222 Fragments are separated by quadrupole, and a fragmentation table is applied to retrieve the 223 concentrations of the above-listed components. The ACSM has been calibrated from the injection 224 of 300 nm ammonium nitrate particles, as described in Ng et al. (2011). Comparison with filter 225 samples (filter sampling and analysis are described below) allowed for validation of the obtained 226 calibration values (Figure S3). A slope of 1.16 has been obtained when comparing ACSM 227 concentrations with filter sampling. This value was slightly higher than what was observed for 228 long-term published ACSM datasets (e.g.Budisulistiorini et al., 2014; Petit et al., 2015). Still, this 229 value was considered as satisfactory given i) the few number of data point (n=10); ii) the 230 relatively low observed concentrations, always below 3 µg/m3; iii) the associated uncertainties 231 for NO3 with ACSM (15%, Crenn et al., 2015) and filter sampling (5-10%, Bressi et al., 2013). 232 Aerosols composition was also recorded at the same time at the SIRTA measurement station 233 located 20 km south-east from the farm (48°42'32.0"N, 2°08'55.5"E) (https://sirta.ipsl.fr/). 234

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 m<sup>3</sup>/h. The sampling time

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

#### 249 **3. Methodology**

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

PTR-Qi-TOF mass spectra were all analysed using PTR-Viewer 3.2.8.0 (Ionicon analytik GmbH). 251 To identify the emitted VOCs, we determined a separate peak table for each location (dairy stable, 252 sheep pen, outdoor). For that purpose, we used 30 minutes averaged mass spectra to be 253 statistically relevant. To exclude impurities from our analysis, the mass spectra obtained with pure 254 zero air was subtracted from ambient mass spectra. In the case of the sheep pen dataset, we 255 determined the peak table by scanning several 30 minutes mean mass spectra selected during 256 different hours of the day and night. For the stable, we determined the peak table by analysing 257 mass spectra corresponding to contrasting situations. We considered that CO<sub>2</sub> may be a good 258 tracer for animal activity and NH<sub>3</sub> a good tracer for litter emissions. We hence kept the four 259 following situations: high CO<sub>2</sub>/high NH<sub>3</sub>, high CO<sub>2</sub>/low NH<sub>3</sub>, low CO<sub>2</sub>/high NH<sub>3</sub> and low 260 CO<sub>2</sub>/low NH<sub>3</sub>. Mass spectra from these 4 regimes were successively inspected, to cover all 261 possible cases. For the outdoor measurements, we chose mass spectra at different times of the day 262 and determined peak tables from these spectra. For each of the 3 locations, we excluded periods 263

when NO and/or NO<sub>2</sub> mixing ratios were too high, to avoid situations where anthropogenic combustion sources (*e.g.* tractor passing by) could have biased our analysis. Once the peak tables were determined, the counts per second for each peak were integrated over each one-second mass spectra using PTR-Viewer 3.2.8.0. We then averaged over 5 min the obtained data. For PTR-Qi-TOF-MS, molecular formulae were proposed based on *i*) the exact m/z value, *ii*) the theoretical isotopic distribution of the associated molecular formula, and *iii*) the coherence of the atoms 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 Inc.). Automatic peak detection and mass spectrum deconvolution were performed using 272 Unknowns Analysis (B.06.00) software. Each compound was accompanied by a deconvoluted 273 spectrum, which was compared to the NIST (National Institute of Standards and Technology, 274 2011) Mass Spectrum database to allow its identification. A minimum match factor of 70 % 275 between the observed and reference mass spectra was required. Each compound was then 276 277 manually scrutinized to confirm the proposed formula. For each proposed compound, the retention time was analysed regarding the its physico-chemical properties, (e.g. boiling point). For 278 example, we compared the retention time of compounds from the same chemical group, to ensure 279 that compounds with low boiling points were not eluted later than compounds with high boiling 280 points. An example of a total ion chromatogram is shown in Figure S4, highlighting compounds 281 identified by both TD-GC-MS and PTR-Qi-TOF-MS, or only by TD-GS-MS. 282

283 **3.2. Calculation of emission rates** 

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

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

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

The ventilation flow rate, which was considered the same for all gases, was estimated from CO<sub>2</sub> as (Hassouna et al., 2015; Pedersen et al., 2008):

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

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

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

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

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

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

$$Hp = \alpha \times BW^{0.75} + \beta \times Y \tag{4}$$

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

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

325 **3.3. Statistical analysis** 

All statistics were performed with R software (Rstudio version 1.0.153). First, the normality of each VOC measured with the PTR-Qi-TOF-MS was tested using a Shapiro-Wilk test. Then, we computed the correlation between each VOC for the sheep pen, the stable, and outside. As the distribution for each compound was not normal according to the Shapiro-Wilk tests (they are mostly right skewed), correlations were calculated using Kendall correlation test. The *p* values lower than 0.005 were rejected and not considered as significant for correlation analysis in Figure 4. The optimal number of groups as represented on Figure 4 was determined by a *k*-means analysis, which allows determination of the optimum number of clusters for a given dataset (number of clusters that best explain variance). Then, the classification of VOCs inside the 4 respective groups has been performed using a classical hierarchical clustering.

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

#### 343 **4. Results**

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

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

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

In the sheep pen (delimited by the blue fonts in Figure 1), clear and reproducible diurnal cycles of gas concentrations can be observed and easily explained by the ventilation variability. Indeed, in the evening, the large lateral doors of the sheep pen were closed, leading to accumulation of pollutants in the building during the night. As soon as the doors were opened in the early morning, the concentration of pollutants dropped due to increased dilution with external air. In the stable, no specific diurnal variations were observed. Variations in NH<sub>3</sub> and CO<sub>2</sub> concentrations were thus probably due to other parameters, notably the magnitude of the sources.

365 Regarding VOCs, trimethylamine (C<sub>3</sub>H<sub>9</sub>N) was also higher in the farm buildings than outside. Its temporal evolution seems to be highly correlated to NH<sub>3</sub>, rather than CO<sub>2</sub>. This may indicate a 366 common source of NH<sub>3</sub> and trimethylamine. It has been shown that NH<sub>3</sub> and trimethylamine are 367 co-emitted in animal husbandries. It was first suggested that the rumen could be the main source 368 of trimethylamine and NH<sub>3</sub> in dairy barns (Kuhn et al., 2011). But Sintermann et al. (2014) 369 showed that there is no correlation between methane (tracer of rumen emissions) and 370 trimethylamine (also no correlation with NH<sub>3</sub>). Very recently, using real time VOC 371 measurements, Gierschner et al. (2019) did not observe direct trimethylamine emissions from 372 dairies. Thus, it is clear that dairy excreta (urine + feces) are the main source of both NH<sub>3</sub> and 373 trimethylamine in dairy farming (Sinterman et al. 2014). The correlations between compounds 374 will be further investigated below in an effort to identify common sources of VOCs (section 4.5). 375 Two VOCs that were identified as potential tracers for the dairy stable and the sheep pen are also 376 377 represented on Figure 1. Acetaldehyde was found at higher mixing ratios inside the stable than in the sheep pen or outdoor. As a result, acetaldehyde may be used as a tracer of the dairy stable 378 emissions. Dimethylsulfide (DMS, C<sub>2</sub>H<sub>6</sub>S) mixing ratios in the dairy stable were similar to the 379

outside. Thus, it seems that the sheep pen was the main source of DMS in the farm, and that the 380 dairy stable did not emit DMS. The absence of DMS emissions from the dairy stable differs from 381 previous studies on dairy farm emissions, where DMS was often reported (Filipy et al., 2006; 382 Ngwabie et al., 2007). NH<sub>4</sub><sup>+</sup> concentration in PM<sub>1</sub> are available during the second part of the 383 campaign. While NH<sub>3</sub> was more concentrated inside the building, it was somewhat surprising to 384 find that NH<sub>4</sub><sup>+</sup> was present at similar levels in both farm buildings as outside. We also compared 385 NH4<sup>+</sup> concentrations measured at the farm with those observed at the SIRTA station. 386 Concentrations were in the same range and followed the same temporal trend, suggesting that 387  $NH_3$  is mostly present in the gas phase. This result is in agreement with a previous study 388 conducted at a dairy feedlot (Hiranuma et al., 2010) which showed that NH<sub>3</sub> is mostly gaseous 389 and does not affect aerosol loading 3.5 km downwind of the feedlot. These observations may be 390 explained by a timescale for transport that is shorter than the gas/particle partitioning process, or 391 limited by the amount of species that chemically react with ammonia via a condensation reaction 392 (e.g., nitric acid to form ammonium nitrate, sulfuric acid leading to ammonium sulfate, etc. ) 393 (Seinfeld and Pandis, 2006). The same reasoning can be applied for the other components of the 394 aerosol composition (see Figure S4). Only 3 peaks of organic matter were higher at the farm than 395 at the SIRTA station and these could be attributed to a tractor passing close to the mobile 396 laboratory. Thus, we can conclude that farm building emissions did not lead to significant 397 modification to the chemical composition of sub-micron aerosols. This will be further discussed 398 in relation to gaseous emissions and residence time inside both buildings. 399

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  $\mu$ g 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**

Combining the three techniques (GC-FID, TD-GC-MS and PTR-Qi-TOF-MS), more than 400 404 compounds were detected during the whole measurement period. All the identified compounds 405 are listed in the associated data file, and the number of identified compounds by each technique 406 can be found in Table S2. Information about the parameters used for identification, such as PTR-407 Qi-TOF-MS mass resolution, or GC retention time can be found in the supplementary data file. 408 Using the PTR-Qi-TOF-MS, 387 molecular formulas were successfully attributed. 62 molecular 409 formulas among the 387 detected by the PTR-Qi-TOF-MS were also identified using off-line TD-410 GC-MS, and 8 using GC-FID (Table S2). Considering that these measurement techniques are 411 independent, the number of common compounds underlines the consistency of the identification 412 process. Only three compounds were identified in all measurement techniques: benzene, toluene 413 and C<sub>7</sub>H<sub>14</sub> isomers. This is not surprising given that the range of VOCs detected by each 414 technique was very different. The GC-FID detected C2-C8 hydrocarbons (alkane, alkene or 415 alkyne), whereas the TD-GC-MS was not set up to measure small hydrocarbons (the first 416 hydrocarbon detected by TD-GC-MS was benzene), and the PTR-Qi-TOF-MS cannot measure 417 linear alkanes. The only alkanes detected using the PTR-Qi-TOF-MS were cyclic alkanes. For 418 example,  $C_7H_{14}$  and  $C_5H_{10}$  could be identified as cyclic alkanes rather than alkenes, based on the 419 chromatographic analysis (see the associated data file). Nevertheless, the possibility that a 420 corresponding alkene, isomeric to the cyclic alkane, was detected by the PTR-Qi-TOF-MS and 421 not detected by GC-FID cannot be fully excluded. A similar conclusion was drawn for TD-GC-422 MS and PTR-Qi-TOF-MS: only cyclic alkanes were measured by the PTR-Qi-TOF-MS (e.g. 423 cyclopentane or cyclobutane). Thus, the PTR-Qi-TOF-MS did not detect any linear alkane, except 424 methane. Methane indeed provided a significant signal at m/z 17.038 (corresponding to 425 protonated methane, CH<sub>4</sub>H<sup>+</sup>) despite its low proton affinity (118 kcal mol<sup>-1</sup>) probably due to very 426

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

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

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

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

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

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

dimethylamine (C<sub>2</sub>H<sub>7</sub>N), formamide (CH<sub>3</sub>NO), triazine (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>) or C<sub>4</sub>H<sub>5</sub>N. The observation of 476 triazine is interesting as it was only measured inside the stable. We observed short-chain sulfur 477 compounds, also known to be strongly odorant such as methanethiol (CH<sub>4</sub>S), dimethyl sulfide 478 (C<sub>2</sub>H<sub>6</sub>S) and dimethylsulfoxide (C<sub>2</sub>H<sub>6</sub>OS) (Feilberg et al., 2010; Schiffman et al., 2001). TD-GC-479 MS analysis confirmed the presence of benzothiazole (C7H5NS) in emissions from the stable and 480 allowed identification of C5H7NS as 2,4-dimethyl-thiazole. Two chlorinated compounds were 481 also measured: chloramide and dichloromethane. Dichloromethane was previously reported in 482 emissions from pig and cattle buildings (Ciganek and Neca, 2008; Schiffman et al., 2001). But, to 483 the best of our knowledge, chloramide is reported here for the first time in dairy stable emissions. 484

485







34%

Halogenated compounds

■ O4 and more compounds

O2 compounds

39%

14%

8%

In the sheep pen, hydrocarbons constituted 31% of the 233 identified molecular formulas, while 490 they represented around 33% in the dairy stable. Most of the hydrocarbons identified were cyclic 491 alkanes (Supplementary data file). The presence of several aromatic compounds was also 492 observed and could have important implications for atmospheric chemistry, due to their reactivity 493 and their ability to form secondary organic aerosols (Atkinson and Arey, 2007; Tomaz et al., 494 2017). We also noticed that isoprene was emitted inside the sheep pen, and no specific 495 monoterpene was identified using TD-GC-MS, as in the stable. Octane, a C<sub>8</sub>H<sub>18</sub> compound, was 496 only identified in the sheep pen, whereas the same molecular formula corresponded to 2,2,4-497 trimethyl-pentane in the stable. Oxygenated compounds represented 50% of the identified 498 molecular formulas, practically the same proportion as in the stable (Figure 2). Oxygenated 499 compounds contained less O atoms than in the stable, as less molecular formulas contained more 500 than three oxygen atoms (1% in the sheep pen compared to 6% in the stable). Our identification 501 highlights that oxygenated VOCs were mostly carboxylic acids, ketones, or alcohols, and a few 502 aldehydes. As in the stable, few long-chain aldehydes were identified in the sheep pen, but some 503 of these oxygenated compounds, such as 6-methyl-1-octanol (C<sub>9</sub>H<sub>20</sub>O) were not reported in the 504 sheep pen. That means that the fingerprints of oxygenated compounds in the sheep pen and dairy 505 stable were different. Exactly as in the stable, we observed that for oxygenated compounds and 506 hydrocarbons, many molecular formulas identified had the same number of carbon atoms. Again, 507 it suggests that oxygenated compounds may partly originate from reaction of hydrocarbons with 508 the oxidants. In the sheep pen, the proportion of nitrogen compounds was slightly higher than in 509 the stable (15% against 13%). Odorant compounds such as trimethylamine or pyridine derivatives 510 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), 511 512 and benzenepropanenitrile ( $C_9H_9N$ ) were specific to the sheep pen (*i.e.* not detected elsewhere) and could hence be used as tracers of sheep pen emissions. Seven S-containing compounds were 513 measured inside the sheep pen. Among them, methanethiol (CH<sub>4</sub>S), dimethylsulfide (C<sub>2</sub>H<sub>6</sub>S), 514

dimethylsulfoxide ( $C_2H_6O_8$ ) and dimethylsulfone ( $C_2H_6O_2S$ ) were reported to be strongly odorant compounds (Hansen et al., 2016; Schiffman et al., 2001). The two other sulfur compounds were thiazole compounds. We observed one halogenated compound, dichlorobenzene ( $C_6H_4Cl_2$ ), which was not reported in the stable nor outdoor.

237 molecular formulas were identified during the outdoor experiment. This number is very close 519 to that in the sheep pen, and lower than in the stable. This is logical considering that the location 520 of the mobile van outside was closer to the sheep pen (Figure S1). Hydrocarbons represented 34% 521 of the identified molecular formulas, which is a little higher than in both buildings (Figure 2). 522 Alkenes, alkynes, cyclic alkanes were identified, and some aromatic compounds. As in the 523 buildings, we noticed that many hydrocarbons had the same number of carbon atoms, ranging 524 from 1 to 22. The proportion of oxygenated compounds was slightly higher outdoor than in both 525 buildings (53% outdoor, and 49% inside both buildings). Another difference compared to the 526 chemical fingerprint inside the buildings was the lower proportion of oxygenated compounds that 527 528 contained 1 or 2 oxygen atoms (Figure 2). This means that oxygenated compounds were more oxidized outside than inside the two buildings. This was expected considering that measurement 529 inside the buildings were closer to the VOC sources, and supports the hypothesis that some of the 530 oxygenated compounds resulted from the oxidation of hydrocarbons. N-containing compounds 531 represented only 10% of the identified molecular formulas (Figure 2), which was a lower fraction 532 than inside the buildings. The same observation applied for S-containing compounds, which only 533 represented 2%. Acetamide (C<sub>2</sub>H<sub>5</sub>NO) was identified outside but was not observed in the 534 buildings, suggesting that it may come from other sources such as the nearby animal feed store or 535 manure digester (Figure S1). Three halogenated compounds were identified outdoor. Among 536 them chloramide and dichloromethane were also found in the stable, but not in the sheep pen. 537

#### 538

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

Figure 3 presents the median mixing ratios and percentiles (25th and 75th percentiles) of the 20 539 most abundant compounds in the stable, in the sheep pen and outdoor. In the three locations, the 540 most abundant compounds were CO<sub>2</sub> and NH<sub>3</sub>. CO<sub>2</sub> median concentrations exceeded 1000 ppm 541 in the sheep pen. The mixing ratios of NH<sub>3</sub> measured inside the buildings were in the same range 542 as previous studies, exceeding the ppm level (Hensen et al., 2009; Huang and Guo, 2018; 543 Ngwabie et al., 2008, 2007; Ni et al., 2012). For NH<sub>3</sub>, median mixing ratios in the sheep pen and 544 the stable were about 40 and 18 times higher than outside, respectively. In the sheep pen and the 545 stable,  $CO_2$  median levels were about 2.5 times and 1.5 times higher than the outdoor mixing 546 ratios, respectively. Thus, NH<sub>3</sub> enrichment inside both buildings was higher than CO<sub>2</sub> enrichment, 547 as already observed in naturally ventilated buildings (Ngwabie et al., 2014, 2007). Both CO<sub>2</sub> and 548 NH<sub>3</sub> levels were higher in the sheep pen than in the stable, in agreement with the study of 549 Ngwabie et al. (2007). 550

The most concentrated VOCs were mainly small-oxygenated compounds. In both 551 buildings, ethanol (C<sub>2</sub>H<sub>6</sub>O) was the most abundant VOC whereas methanol was the most emitted 552 VOC outdoor. Our results are quite similar to other studies, where ethanol was more concentrated 553 than methanol (Ngwabie et al., 2008, 2007). Ethanol median mixing ratios were around 130 ppb, 554 48 ppb and 42 ppb in the stable, the sheep pen and outdoor, respectively. These mixing ratios 555 were in the range of previous studies in various farm buildings (Blunden et al., 2005; Ni et al., 556 2012; Yuan et al., 2017). In our study, ethanol and methanol mixing ratios were very close 557 (Figure 3). However, ethanol was usually one order of magnitude higher than methanol. This 558 difference may arise from different feedings, as it is supposed to be the main source of ethanol in 559 farm buildings (Yuan et al., 2017). For example, in the study of Ngwabie et al. (2008), cows were 560 fed with a mix of corn silage, grass silage, rape expeller, pressed beet pulp, and barley straw. In 561

our study, dairy cows and sheep were mainy fed with corn and alfalfa silage, completed withpress beet pulp ground ear corn and potato.



**Figure 2 :** Median mixing ratios and percentiles ( $25^{th}$  and  $75^{th}$  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)

564

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

In the stable, acetaldehyde (C<sub>2</sub>H<sub>4</sub>O) is the 4<sup>th</sup> most abundant VOC, with mixing ratios close to that 569 of acetic acid (Figure 3). Acetaldehyde was ranked only in sixth position in the sheep pen and 570 outside, and median mixing ratios were one order of magnitude lower than in the stable. This was 571 the case for most of the VOCs that were more concentrated in the stable than in the sheep pen and 572 outside (Figure 3). Only a few hydrocarbons  $(C_xH_y)$  were among the most concentrated 573 compounds. Toluene was one of the most concentrated compounds only in the stable. For butene, 574 the mixing ratios were comparable inside and outside the farm buildings. This means that both 575 576 buildings were not strong sources of butene.

Figure 3 shows that nitrogen oxides  $(NO_x)$  mixing ratios were higher in the buildings than 577 outside, meaning that both buildings can be considered as a source of  $NO_x$ . Both NO and  $NO_2$ 578 were more concentrated inside the stable than outdoor. However, in the sheep pen, only NO<sub>2</sub> was 579 higher than outside (NO mixing ratios were very close in the sheep pen and outside, see Figure 3). 580 Trimethylamine ( $C_3H_9N$ ) was the most abundant N-containing compound after NH<sub>3</sub>, in both 581 buildings (Figure 3). Trimethylamine was one of the few compounds listed in Figure 3 that was 582 more concentrated in the sheep pen than in the stable. For both buildings, mixing ratios were in 583 agreement with previous studies in dairy or sheep farms (Ngwabie et al., 2008, 2007). We 584 observed that there was more N- and S-containing compounds among the 20 most concentrated 585 compounds in the sheep pen than in the stable and outdoor (Figure 3). H<sub>2</sub>S was one of the most 586 587 concentrated S containing compounds inside the stable but was not detected in the sheep pen or outdoor. H<sub>2</sub>S may hence be used as a tracer for stable emissions within the whole farm (Figure 3). 588 H<sub>2</sub>S was already reported inside farm buildings, and is known to be co-emitted with NH<sub>3</sub> and 589

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>).

597 Finally,  $NH_3$ ,  $NO_x$  and VOCs levels inside the building greatly exceeded the levels outside. 598 Higher concentrations lead to a higher exposure levels for animals and farmers inside the 599 buildings. The effect of such exposure on animal and human health should be further investigated.

#### 600 **4.5. Correlation between different compounds**

We performed a correlation analysis between VOCs with a mean mixing ratio above 0.1 ppb (to 601 keep only the most significant VOCs). This criterion lead to a subset of 50 VOCs for the stable 602 and 42 for the sheep pen. The correlation was based on the temporal evolution of each compound. 603 The aim of such correlation analysis is to see which VOCs correlated to each other, and with 604 other physico-chemical parameters such as NO<sub>x</sub>, CO<sub>2</sub>, NH<sub>3</sub>, temperature and wind speed. Hence, 605 a high temporal correlation between compounds may underline similar emission processes or 606 species involved in a same chemical process, as evidenced by Sinterman et al. (2004) to 607 differentiate between animal and excreta emissions. The aim of the correlation analysis was to 608 determine whether all the VOCs originated from one or several sources. The correlations obtained 609 in the sheep pen and the stable are represented in Figures 4a, and 4b. 610

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  $NO_x$  and  $CO_2$ 

(group 2 in the Figure 4.a). Markers of anthropogenic combustion sources, such as BTEX, 615 trimethyl benzene, propyl benzene, and  $NO_x$  were found in this group.  $CO_2$  could be emitted by 616 combustion sources, in addition to animal respiration, explaining why it was in this group but 617 with low correlation. As all the compounds were anti-correlated with wind speed, the 618 619 anthropogenic source should be inside the stable. This suggests that farming activities implying a tractor (performing mulching for example) may be the source of the compounds in this group. 620 This was also confirmed by the onsite personnel, as they frequently used tractors for some 621 activities in the stable. However, they do not have a detailed report of activities that allowed to 622 exactly assign the concentration peaks to these activities. 623

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

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

In the sheep pen, almost all of the VOCs were positively correlated to each other, regardless of 645 the chemical family (hydrocarbons, N-containing species or oxygenated compounds, Figure 4b). 646 On the contrary, none of them were correlated with wind speed (p values < 0.005) and all the 647 VOCs were only barely correlated to air temperature. One can note that NO was not correlated 648 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 649 derivatives) were frequently attributed to anthropogenic sources, even though they were already 650 651 reported inside farm buildings or sheep breath analysis (Ciganek and Neca, 2008; Fischer et al., 2015). For an anthropogenic combustion source, BTEX would be strongly correlated with NO<sub>x</sub> 652  $(NO+NO_2)$ , and especially with NO in the case of local engine exhaust (Jiang et al., 2017; 653 Seinfeld and Pandis, 2006). This was for example the case in the stable, as explained above. But 654 655 in the sheep pen, BTEX were not correlated with  $NO_x$  (Figure 4.b), confirming that both  $NO_x$  and BTEX did not arise from the same anthropogenic combustion source. Since BTEX compounds 656 were not correlated with wind speed, we can therefore assume that they originate from the sheep 657 pen (Figure 4.b).  $CO_2$  can be used in the sheep pen as an animal emission tracer, whereas  $NH_3$ 658 could be mostly related to emissions from manure. Even if the k-means analysis did not reveal 659 any optimal number of groups, we can see that NH<sub>3</sub> was highly correlated to trimethylamine and 660 C<sub>3</sub>H<sub>7</sub>N. Thus, these two amines were likely to be emitted by the animal excreta together with 661 662 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 animal, manure and feeding operation emissions cannot be well separated in the sheep pen when 663 only considering time-based correlations. The absence of groups in the correlation analysis 664

665 indicates that the main driver of the atmospheric composition inside the sheep pen was probably

the dynamic flow inside the building rather than the strength of the emission sources.

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

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#### 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 677 dairy stable and the sheep pen, which is similar to previous studies in naturally ventilated 678 buildings (Ngwabie et al., 2014; Schmithausen et al., 2018; Wang et al., 2016). The ventilation 679 rate inside the sheep pen was lower than in the stable due to smaller windows. The mean 680 residence times inside both buildings, deduced from the mean ventilation rates, was estimated to 681 be around 3 minutes in the stable, and around 6 minutes in the sheep pen. The residence time and 682 the ventilation rate variability are nevertheless highly dependent on external wind speed and 683 specific actions such as the opening lateral doors in the buildings. For example, in the sheep pen, 684 the residence time can fall below one minute when the lateral doors are open. 685

NH<sub>3</sub> emission rates for the stable and the sheep pen were estimated to be 9.7 ( $\pm$ 7.1) kg N day<sup>-1</sup> 686 and 8.8 (±5.8) kg N day<sup>-1</sup> (values between brackets are the standard deviation, representing the 687 temporal variability of the emissions throughout the measurement campaign) (Figure 5.a). NH<sub>3</sub> 688 emissions from each building were roughly similar, although NH<sub>3</sub> mixing ratios were higher 689 inside the sheep pen (Figure 3). This was due to the lower ventilation rate that led to lower 690 dilution in the sheep pen than in the dairy stable. The NH<sub>3</sub> emission rates calculated here were in 691 the same order of magnitude as that previously reported for the same farm by Loubet et al. (2012), 692 using inverse modelling on a crop field downwind the farm. They reported a value of 8.3 kg N 693 day<sup>-1</sup> for the whole farm, slightly lower than the value calculated in the present study. This 694 difference could be due to the seasonality effect, but also to an underestimation due to the absence 695 of deposition parameters in the inversion model (Loubet et al. 2012). It was shown above that 696 animals and their excreta were the main source of VOCs inside both buildings. It thus makes 697 698 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 699 shows that a dairy cow emitted more  $NH_3$  than a sheep (Figure 5.b), which was due to the 700

different weight of animals. We calculated that for the dairy stable and the sheep pen, emission 701 rates by animals were 17.3 (±12. 7) kg N year-1 animal-1 and 3.1 (±1.9) kg N year-1 animal-1 702 respectively (Figure 5.c). These emission factors are in the same order of magnitude as those 703 frequently used in emission inventories (Aneja et al., 2012; Battye, 2003; Behera et al., 2013; 704 Bouwman et al., 1997). For example, Bouwman et al. (1997) used an emission rate of 40-50 kg N 705 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. 706 A study on Indian agricultural emissions conducted by Aneja et al. (2012) referred to NH<sub>3</sub> 707 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, 708 respectively. In Europe, Van der Hoek used emission rates of 28.5 kg N year<sup>-1</sup> animal<sup>-1</sup> for dairy 709 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> 710 emission rates obtained in our study are in the range of previous emission rates reported, whereas 711 sheep emission rates are slightly higher. As the weight of a dairy cow and a sheep are very 712 different, normalization by the living units (i.e. 500 kg of animal weight) is frequently performed. 713 Emission rates were estimated to be 1.8 (±1.3) g N h<sup>-1</sup> LU<sup>-1</sup> and 2.2 (±1.4) g N h<sup>-1</sup> LU<sup>-1</sup> for the 714 dairy stable and the sheep pen, respectively (Figure 5.b). These values were in agreement with 715 previous studies conducted in naturally ventilated buildings (Koerkamp et al., 1998; Ngwabie et 716 al., 2014, 2009; Wang et al., 2016). Our study shows that, for an equivalent amount of living 717 units, sheep pen emissions of NH<sub>3</sub> are only slightly higher than that of the dairy stable, (Figure 718 5.b). 719

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

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

for the sum of all VOCs have been calculated to be 6.3 ( $\pm$ 8.5) kg day<sup>-1</sup> for the dairy stable and 726 1.1 ( $\pm 2.9$ ) kg day<sup>-1</sup> for the sheep pen (Figure 5.a). Conversely to NH<sub>3</sub>, the dairy stable was found 727 to emit about six times more VOCs than the sheep pen. The sum of all VOCs represented 52.8% 728 of the NH<sub>3</sub> emissions in the stable, and 10.3% in the sheep pen (as a mass ratio, considering NH<sub>3</sub> 729 emissions in kg of NH<sub>3</sub>). We also evaluated that a sheep emitted much less VOCs than a dairy 730 cow: VOC emission rates were 11.1 ( $\pm$ 15.0) kg year<sup>-1</sup> animals<sup>-1</sup> for a dairy cow and 0.4 ( $\pm$ 1.0) kg 731 year<sup>-1</sup> animal<sup>-1</sup> for sheep (Figure 5.c). This was expected considering the difference in animal 732 weight, but emissions from dairy cows are still higher if normalized by living units: VOC 733 emission rates were estimated to be 1.2 ( $\pm$ 1.6) g h<sup>-1</sup> LU<sup>-1</sup> and 0.6 ( $\pm$ 1.3) g h<sup>-1</sup> LU<sup>-1</sup> in the dairy 734 stable and the sheep pen. The difference of emitted VOCs between dairy cows and sheep was 735 therefore not only due to the animal weight, but also in the metabolism of the animals and the 736 nature of their excreta. This is an interesting point considering that the feeding regime for both 737 sheep and cows is quite similar in our study. 738

In both farm buildings, the 10 most emitted VOCs contributed to more than 90% of the total VOC emissions (Figure S5). In term of quantitative balance, it is thus unnecessary to measure all the VOCs. But for chemical air quality studies or odor activity studies, low emissions of VOCs could be very important. For example, Yuan et al. (2017) showed that phenolic species constituted only a few percentage of emissions from concentrated animal feeding operations in Colorado (USA), whereas they dominated the reactivity with the NO<sub>3</sub> radicals.

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

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



**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.

The most emitted VOC in the sheep pen was ethanol, as in stable, with an emission rate of 0.3 769 (±0.8) kg year<sup>-1</sup> animals<sup>-1</sup>. Methanol was the 2<sup>nd</sup> most emitted VOC. Methanol emission rates 770 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 771 the sheep pen. Thus, the two VOCs with higher emission rates were similar between the stable 772 and the sheep pen. But the magnitude of their emissions were considerably higher in the dairy 773 774 stable (Figure 5). These values were lower by at least one order of magnitude compared to the only previous study on sheep VOC emissions (Ngwabie et al., 2007). This could be due to *i*) the 775 different methodologies to estimate the emission rates *ii*) their use of a conventional quadrupole 776 PTR-MS not being able to separate isobaric compounds (such as  ${}^{17}O^{16}O^+$  and  $O_2.H^+$  ions) and *iii*) 777 the difference between the two farms (agricultural practices, climate, animals, etc.) and especially 778 the animal feeding regime. Acetone and trimethylamine were the most emitted VOCS after 779 ethanol and methanol. This result is also in agreement with that of Ngwabie et al. (2007). The 780 qualitative analysis of the main emitted VOCs seems to confirm the findings of this study. 781 However, the magnitude of VOC emissions is lower in our study. Differences may arise from 782 several factors (composition of the animal feed, model used to calculate emission rates, 783 agricultural practices, etc.) and more studies are required to better understand VOC emissions 784 from sheep farms. We also highlighted that the sheep pen emitted NO<sub>2</sub> but no NO. The NO<sub>2</sub> 785 emission rate was lower but close to VOC emission rates, with a mean emission rate of 0.1 ( $\pm 0.1$ 786 kg year<sup>-1</sup> animals<sup>-1</sup>). There were also two S-containing compounds in the 10 most emitted VOCs 787 by the sheep pen, DMS and dimethylsulfone (Table S3). These compounds are of interest as they 788 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 789 four VOCs could be assessed as tracers of sheep pen emissions. 790

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#### 1 4.8. VOC emission rates in terms of C, N and S

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

emission rates for the sum of VOCs in terms of C were 3.1 ( $\pm$ 4.3) kg<sub>c</sub> day<sup>-1</sup> in the stable and 0.6 ( $\pm$ 1.5) kg<sub>c</sub> day<sup>-1</sup> in the sheep pen (Figure 5.a). This is even more contrasted when emission rates were calculated per animals (Figure 5.c), with values of 5.6 ( $\pm$ 7.6) kg<sub>c</sub> year<sup>-1</sup> animals<sup>-1</sup> for the stable and 0.2 ( $\pm$ 0.5) kg<sub>c</sub> year<sup>-1</sup> animals<sup>-1</sup> for the sheep pen.

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

The S emission factor for the sum of VOCs was  $6.0 \times 10^{-2}$  (±0.2) kgs day<sup>-1</sup> and  $2.0 \times 10^{-2}$  (±  $2.0 \times 10^{-2}$ 806 <sup>2</sup>) kg<sub>S</sub> day<sup>-1</sup> in the dairy stable and the sheep pen. As for C and N, the amount of S emitted was 807 higher in the stable than in the sheep pen. DMS was the most emitted S-containing compound in 808 the sheep pen, accounting for 40 % of the sheep pen S emissions. Surprisingly, the dairy stable 809 did not emit DMS (i.e. mixing ratios outside were higher than inside the building), while some 810 studies reported strong emissions from dairy buildings (Filipy et al., 2006; Ngwabie et al., 2008; 811 Shaw et al., 2007). 67 % of S emitted in the dairy stable could be attributed to H<sub>2</sub>S (no H<sub>2</sub>S 812 emissions were recorded for the sheep pen). Feilberg et al. (2017) found a ratio between H<sub>2</sub>S and 813 NH<sub>3</sub> of 0.06, whereas it was 0.004 in our study. Thus, it seems that the dairy stable was not a 814 strong S emitter in contrast to the literature. 815

Figure 6 represents the chemical fingerprint of VOC emissions. The fingerprint of VOC emissions was mostly composed of C, for more than 90 % in each building. This is logical considering that most of the detected VOCs were oxygenated VOCs and hydrocarbons that contained a large number of C atoms, and that N or S containing VOCs mostly had a few atoms.
N and S were found in a greater proportion in the sheep pen, but the emission factors were greater
in the stable. The chemical compounds and the magnitude of the emissions were thus different in
each building. Finally, C/N/S composition of VOC emissions allowed identification of differences
between the buildings, contrary to what was found above for mixing ratios (Figures 2 and 6).

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

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

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

The estimation of national VOC emissions from livestock in the present study should be interpreted very carefully, as this study covered only one farm during a relatively short field campaign. More studies in different farms and during different seasons are needed to reduce the uncertainties for agricultural emissions. Long term measurements are also required as emission 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.

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

### 875 **5. Conclusion**

This study revealed that both sheep and dairy cattle farming emitted a large spectrum of VOCs. The results highlighted that combining online mass spectrometric and off-line chromatographic techniques is essential to better characterize VOC emissions, especially in environments enriched with VOCs, such as farm buildings. In both buildings VOCs were mostly oxygenated compounds and hydrocarbons. N-containing compounds and S-containing compounds were found in lower proportions but could be key in assessing odor issues as well as implications for atmospheric chemistry. We showed that the difference in the fingerprint of gas phase compounds emitted by the stable and the sheep pen was small if we only pay attention to chemical families. Tracers for each building in the experimental farm can now be proposed. For the stable, Triazine, H<sub>2</sub>S, 1butene, isopentane, pentane and acetaldehyde have been identified as potential tracers. For the sheep pen most of tracers were nitrogen containing compounds. Among them, methylpiperidine, pyridine, dimethylpyridine and benzenepropanenitrile were highlighted. DMS was also observed to be mostly emitted by the sheep pen.

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

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

Despite emissions of  $NH_3$  and many VOCs, the aerosol chemical composition was not affected by farm emissions. It may be explained by a low reaction time and low oxidant levels inside the buildings. As a result, we propose that secondary aerosol formation can be most significant in the

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

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