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

Authors

Julien Kammer[1,2,*], Céline Décuq[1], Dominique Baisnée[2], Raluca Ciuraru[1], Florence Lafouge[1], Pauline Buysse[1], Sandy Bsaibes[2], Ben Henderson[3], Simona M. Cristescu[3], Rachid Benabdallah[1], Varunesh Chandra[1], Brigitte Durand[1], Oliver Fanucci[1], Jean-Eudes Petit[2], Francois Truong[2], Nicolas Bonnaire[2], Roland Sarda-Estève[2], Valerie Gros[2] and Benjamin Loubet[1*]

Affiliations

[1]INRA, UMR ECOSYS, INRA, AgroParisTech, Université Paris-Saclay, 78850 Thiverval-Grignon, France

[2]Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, IPSL, Université Paris-Saclay, 91191 Gif-sur-Yvette, France

[3]Department of Molecular and Laser Physics, IMM, Radboud University, Nijmegen, the Netherlands

[*]**Corresponding authors:**

Julien Kammer

Laboratoire des Sciences du Climat et de l'Environnement (LSCE)

CEA-CNRS- University of Versailles Saint-Quentin-en-Yvelines (OSVQ)

Orme des merisiers, Building 714

91191 Gif/Yvette, France

Tel.: +33 1 30 81 55 41

Mail: julien.kammer@lsce.ispl.fr; julien.kammer@gmail.com

Abstract

Agricultural activities highly contribute to atmospheric pollution, but the diversity and the magnitude of their emissions are still subject to large uncertainties. A field measurement campaign was conducted to characterize gaseous and particulate emissions from an experimental farm in France containing a sheep pen and a dairy stable. During the campaign, more than four hundred volatile organic compounds (VOCs) were characterized using an original combination of online and off-line measurements. Carbon dioxide (CO_2) and ammonia (NH_3) were the most concentrated compounds inside the buildings, followed by methanol, acetic acid and acetaldehyde. A CO_2 mass balance model was used to estimate NH_3 and VOC emission rates. To our knowledge, this study constitutes the first evaluation of emission rates for most of the identified VOCs. The measurements show that the dairy stable emitted more VOCs than the sheep pen. Despite strong VOC and NH_3 emissions, the chemical composition of particles indicates that gaseous farm emissions do not affect the loading of fine particles inside the farm and is mainly explained by the low residence time inside the buildings. The experimental dataset obtained in this work will help to improve emissions inventories for agricultural activities.

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

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

1. Introduction

Agricultural activities are one of the major sources of pollutants in the atmosphere. Agricultural emissions comprise both particulate and gaseous pollutants which can affect air quality as well as climate. For example, at the global scale, agriculture is the main source of ammonia (NH_3) in the 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 agricultural activities, livestock management is recognized as a significant source of NH_3, and estimated to contribute 34-40% of global NH_3 emissions (Behera et al., 2013; Schmithausen et al., 2018). Livestock is also a strong emitter of greenhouse gases such as methane (CH_4) and carbon dioxide (CO_2) (Hempel et al., 2016; Huang et al., 2015; Maldaner et al., 2018; Ngwabie et al., 2014). Other studies have shown that farm buildings emitting numerous volatile organic compounds (VOCs) may be as important as traffic road contributions (Ciganek and Neca, 2008; Yuan et al., 2017). VOCs are also key species for atmospheric chemistry and climate that are able to produce secondary pollutants, such as ozone and aerosols (Atkinson and Arey, 2003; Curci et al., 2009; Hallquist et al., 2009). The chemical reactivity of VOCs strongly affects their ability to generate ozone and aerosols (Seinfeld and Pandis, 2006) and it is therefore essential to identify the chemical nature of the VOCs emitted by farm buildings and evaluate the magnitude of their emissions. Several studies have shown that oxygenated VOCs, such as methanol, ethanol, acetone and acetic acid, dominate dairy cattle VOC emissions (Ngwabie et al., 2008; Sun et al., 2008). Emissions of odorant compounds are also frequently reported, for example dimethylsulfide (C_2H_6S), cresols (methyl phenol, C_7H_8) and trimethylamine (C_3H_9N) (Feilberg et al., 2010).

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

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

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 (particles with an aerodynamic diameter below 1 µm). Whether PM1 are of secondary or primary origin is still unclear (Lammel et al 2004). The strong emissions of ammonia and VOCs could potentially lead to strong secondary particle formation. Thus, online chemical characterization of the sub-micron aerosol using an aerosol chemical speciation monitor (ACSM) could greatly help 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 Paris (France). The aim of the study was first to characterize the VOC fingerprint inside a dairy 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 off-line (Thermal Desorption-Gas Chromatography – Mass Spectrometry, GC-MS and Gas Chromatography – Flame Ionization Detector, GC-FID) measurements were conducted outside and inside both buildings. Then, fine aerosol chemical composition (using an ACSM) was measured to characterize the contribution of livestock to the PM1 loading. Finally, a CO_2 mass balance model was used to estimate NH_3 and VOC emission rates and emission factors from both buildings.

2. Materials and methods

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 measurement period). As a result, the field campaign was divided in two main parts: the first one, when only the PTR-Qi-TOFMS was available, and the second part when the ACSM was available. The number of animals and the feeding were kept constant through the whole experiment, thus we can suppose that results from both periods could be extended to the whole experiment. A detailed time window describing the availability of the instruments during the campaign is provided in Figure S2. All the other instruments described below were available throughout the field campaign. The dairy stable was investigated during 16th -20th November 2017 (with the PTR-Qi-TOF-MS) and also 28th November to 1st December 2017 (with the ACSM). The van was located in a corner of the stable, which was naturally ventilated (Figure S1). A total of 205 animals were kept inside the stable during the campaign: 173 dairy cows and 32 calves, with a mean weight of about 550 kg per animal. For dairy cows, the milk yield per animal was 30 kg. The sheep pen was investigate between 20th and 22nd November 2017 (with the PTR-Qi-TOF-MS) and also 24th - 28th November 2017 (with the ACSM). As for the stable, the sheep pen was a naturally ventilated building. However, the openings in the sheep pen were smaller and a lower air exchange rate is thus expected in the sheep pen than the dairy stable. A total of 1041 sheep were in the building during the measurement period, 488 ewes, 534 lambs (males and females) and 19 rams. The mean body weight was estimated to be about 80 kg per animal. Finally, we moved the mobile laboratory outside to a location close to both the sheep pen and the dairy stable for the period 22nd - 24th November 2017 (with the PTR-Qi-TOF-MS, then the ACSM). At this outdoor location, there was a manure digester and some storage areas for animal feed and manure (Figure S1). All of these can be important sources of VOCs and ammonia (Blunden and Aneja, 2008; Yuan et al., 2017). Tractors were moving outdoors and inside the farm buildings which 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_2 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_x, being the sum of NO and NO_2) were monitored with a 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^{-1} 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_3 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 (⅛ inch diameter) heated at 40-45 °C; the inlet flow inside the analyzer was 0.040 L min^{-1}. A Teflon filter was added at the inlet of the tubing to prevent particles from entering the instrument. The NH_3 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^{-1}, 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 the sampling line to remove particles from the air. The PTR-Qi-TOF-MS operated in standard conditions, with a drift pressure set between 3 mbar (in the sheep pen and outside) and 3.5 mbar (in the stable), a drift temperature of 80 °C and a drift voltage close to 751 V (in the sheep pen and outside) and 878 V (in the stable). These conditions were set to ensure a constant E/N ratio (where E is the electric field strength and N the gas number density) about 133 Td (1 Td = 10^{-17} V cm^{-2}). This value for the E/N ratio limits fragmentation and lowers the sensitivity of the protonation rate to variations in relative humidity (Pang, 2015; Tani et al., 2003). Blanks were performed daily with high purity zero air (Alphagaz 1, zero air: 80% nitrogen, 20% oxygen, purity: 99.9999%, Air Liquide) to check instrument background signal, and calibrations were frequently performed with a toluene gas standard (102±10 ppb, Messer) diluted in zero air. 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 tested the instrument sensitivity to methanol and ethanol after the field campaign. The tests showed that, under the conditions of the experiment (i.e. E/N = 133 Td), the sensitivity for methanol and ethanol is 3.25 and 35 times less elevated than the sensitivity for toluene. It was thus decided to correct the mixing ratios of both alcohols with their respective correction factors. For all the other compounds, the sensitivity calculated using the toluene standard was used. Fragmentation of several compounds (especially acetic acid at m/z 43, monoterpenes at m/z 81 was taken into account by considering the sum of the molecular mass ion and the fragmented ions to contribute to the total concentration). During the measurements, mass spectra up to m/z 510 were recorded every second.

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^{-1} for 6 hours. Then, ambient air was sampled during 3 to 5 hours at 0.5 L min^{-1} and regulated with a mass flow controller (Bronkhorst) (Table S1). After exposure, cartridges were stored in the dark at a temperature of 4°C until analysis. Tubes were desorbed using a thermo-desorption unit (TDU) from Gerstel, which was programmed to desorb the tubes from 50 to 260 °C for 10 min at a rate of 60 °C/min. VOCs were cryo-focused in the 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) at 12 °C/s^{-1} to inject the trapped compounds into the chromatographic column. Separation of the VOCs was achieved using an Agilent 7890B gas chromatograph fitted with a capillary column (30 m length, 0.25 mm inner diameter, 0.25 μm df, DB624 column, Restek). The oven temperature was initially set at 40 ºC for 5 min, heated at a rate of 11 ºC/min to 60 ºC, then heated at a rate of 20°C/min to 220°C and maintained for 2 minutes. Helium was used as carrier gas. Detection of the VOCs was performed with an Agilent 5977A mass spectrometric detector. The Electronic Impact (EI) mode was at +70 eV; the monitoring was from m/z 36 to 300. The ion source and Quadruple analyser temperature were respectively set at 230 and 150 °C.

Canister sampling was also performed by sampling the air for 15 minutes every 4 hours (Table S1). Air sampled by canisters was analysed by GC-FID (HP 6890) equipped with a CP-Al_2O_3 Na_2SO_4 column, providing a complementary analysis of small hydrocarbons. A pre-concentrator (Entech 7200) was placed at the inlet of the instrument to allow automatic injections. A standard cylinder with 5 non methane hydrocarbons (NMHC, Messer) was used to check that the instrument was functioning correctly and an international reference standard containing 32 NMHC from C2 to C10 (NPL, National Physics Laboratory, Teddington, UK) was used for 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 (NO_3^-); sulphate (SO_4^{2-}), ammonium (NH_4^+) and chloride (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 min^{-1}, sub-sampled at 85 mL 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 µg/m3; iii) the associated uncertainties for NO3 with ACSM (15%, Crenn 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 m^3/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 MOhm) for 45 min in an ultrasonic bath. The extracts were then filtered using Acrodisc filters (Pall Life Sciences, Bulk IC Acrodisc 25 mm) with a porosity of 0.2 µm to remove particles. To prevent bacteria activity, 6 µL of chloroform was added to each vial. Cations were analysed on a CS16 pre-column (2 mm diameter) and column with an IC (Dionex, Model DX-600). Anions were analysed on a AS11HC pre-column (2 mm diameter) and column with an IC (Dionex, Model ICS2000). Annual laboratory EMEP IC inter-comparison studies were performed and showed errors lower than 10% for every cited ion (accessible at https://projects.nilu.no//ccc/intercomparison/DQO-G-36.pdf, Lab 50).

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). To identify the emitted VOCs, we determined a separate peak table for each location (dairy stable, sheep pen, outdoor). For that purpose, we used 30 minutes averaged mass spectra to be statistically relevant. To exclude impurities from our analysis, the mass spectra obtained with pure zero air was subtracted from ambient mass spectra. In the case of the sheep pen dataset, we determined the peak table by scanning several 30 minutes mean mass spectra selected during different hours of the day and night. For the stable, we determined the peak table by analysing mass spectra corresponding to contrasting situations. We considered that CO_2 may be a good tracer for animal activity and NH_3 a good tracer for litter emissions. We hence kept the four following situations: high CO_2/high NH_3, high CO_2/low NH_3, low CO_2/high NH_3 and low CO_2/low NH_3. Mass spectra from these 4 regimes were successively inspected, to cover all possible cases. For the outdoor measurements, we chose mass spectra at different times of the day and determined peak tables from these spectra. For each of the 3 locations, we excluded periods when NO and/or NO_2 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.

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 Unknowns Analysis (B.06.00) software. Each compound was accompanied by a deconvoluted spectrum, which was compared to the NIST (National Institute of Standards and Technology, 2011) Mass Spectrum database to allow its identification. A minimum match factor of 70 % between the observed and reference mass spectra was required. Each compound was then 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 example, we compared the retention time of compounds from the same chemical group, to ensure that compounds with low boiling points were not eluted later than compounds with high boiling points. An example of a total ion chromatogram is shown in Figure S4, highlighting compounds identified by both TD-GC-MS and PTR-Qi-TOF-MS, or only by TD-GS-MS.

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:

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

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

The ventilation flow rate, which was considered the same for all gases, was estimated from CO_2 as (Hassouna et al., 2015; Pedersen et al., 2008):

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

Where $CO_{2_{HPU}}$ (in g h^{-1} hpu^{-1}) is the CO_2 production rate by heat production unit, $A_{animals}$ (unitless) is the relative animal activity, HPU is the number of heat production units (1 heat production unit = 1000 W), $CO_{2_{indoor}}$ and $CO_{2_{\mathrm{outdoor}}}$ (in g m^3) are the CO_2 concentrations inside and outside the building, respectively. As recommended in the literature, $CO_{2_{HPU}}$ for the dairy stable and sheep pen were set to 393 g h^{-1} hpu^{-1} and 344 g h^{-1} hpu^{-1}, respectively (Hassouna et al., 2015; Pedersen et al., 2008; Schmithausen et al., 2018). These values are specifically recommended for farm buildings and take into account both animal respiration and CO_2 contributions from manure. $A_{animals}$ was estimated using equation 3 (Pederson et al., 2002):

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

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_2 production was not corrected for animal activity, and the ventilation flow rate equation for sheep pen was estimated with $\mathrm{A}_{\mathrm{animals}} = 1$.

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, α and β are coefficient from the literature (Pedersen et al., 2008, 1998; Pederson et al., 2002; Schmithausen et al., 2018). For a cow, α is 5.6 and β is 2. For sheep (ewe or lamb) α is 6.4 and β is 145.

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

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.

4. Results

4.1. Time series

Figure 1 presents the time series of CO_2 and NH_3 mixing ratios for the entire measurement campaign (dairy stable, sheep pen and outdoor), as well as two VOCs (trimethylamine and dimethylsulfide) previously reported in the literature as emitted by farm buildings (Feilberg et al., 2010; Ngwabie et al., 2008, 2007; Shaw et al., 2007; Sun et al., 2008). NH_4^+ concentrations (in the particle phase) inside the farm and at SIRTA are also presented in Figure 1. Firstly, CO_2 and NH_3 mixing ratios were much higher in both buildings than outdoor. Both compounds also roughly followed similar trends which showed concentrations were higher in the sheep pen than in the dairy stable. In addition, CO_2 and NH_3 mixing ratios were quite similar during the two periods (The PTR-Qi-TOF-MS and the ACSM periods). Concentrations are similar for the two stable periods (orange area at the beginning and the end of the campaign in Figure 1) as well as for the two sheep pen periods. This result confirmed that the PTR-Qi-TOF-MS and ACSM 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_3 and CO_2 concentrations were thus probably due to other parameters, notably the magnitude of the sources.

Regarding VOCs, trimethylamine (C_3H_9N) was also higher in the farm buildings than outside. Its temporal evolution seems to be highly correlated to NH_3, rather than CO_2. This may indicate a common source of NH_3 and trimethylamine. It has been shown that NH_3 and trimethylamine are co-emitted in animal husbandries. It was first suggested that the rumen could be the main source of trimethylamine and NH_3 in dairy barns (Kuhn et al., 2011). But Sintermann et al. (2014) showed that there is no correlation between methane (tracer of rumen emissions) and trimethylamine (also no correlation with NH_3). Very recently, using real time VOC measurements, Gierschner et al. (2019) did not observe direct trimethylamine emissions from dairies. Thus, it is clear that dairy excreta (urine + feces) are the main source of both NH_3 and trimethylamine in dairy farming (Sinterman et al. 2014). The correlations between compounds will be further investigated below in an effort to identify common sources of VOCs (section 4.5). Two VOCs that were identified as potential tracers for the dairy stable and the sheep pen are also 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 emissions. Dimethylsulfide (DMS, C_2H_6S) mixing ratios in the dairy stable were similar to the outside. Thus, it seems that the sheep pen was the main source of DMS in the farm, and that the dairy stable did not emit DMS. The absence of DMS emissions from the dairy stable differs from previous studies on dairy farm emissions, where DMS was often reported (Filipy et al., 2006; Ngwabie et al., 2007). NH_4^+ concentration in PM_1 are available during the second part of the campaign. While NH_3 was more concentrated inside the building, it was somewhat surprising to find that NH_4^+ was present at similar levels in both farm buildings as outside. We also compared NH_4^+ concentrations measured at the farm with those observed at the SIRTA station. Concentrations were in the same range and followed the same temporal trend, suggesting that NH_3 is mostly present in the gas phase. This result is in agreement with a previous study conducted at a dairy feedlot (Hiranuma et al., 2010) which showed that NH_3 is mostly gaseous and does not affect aerosol loading 3.5 km downwind of the feedlot. These observations may be explained by a timescale for transport that is shorter than the gas/particle partitioning process, or limited by the amount of species that chemically react with ammonia via a condensation reaction (e.g., nitric acid to form ammonium nitrate, sulfuric acid leading to ammonium sulfate, etc.) (Seinfeld and Pandis, 2006). The same reasoning can be applied for the other components of the aerosol composition (see Figure S4). Only 3 peaks of organic matter were higher at the farm than at the SIRTA station and these could be attributed to a tractor passing close to the mobile laboratory. Thus, we can conclude that farm building emissions did not lead to significant modification to the chemical composition of sub-micron aerosols. This will be further discussed in relation to gaseous emissions and residence time inside both buildings.

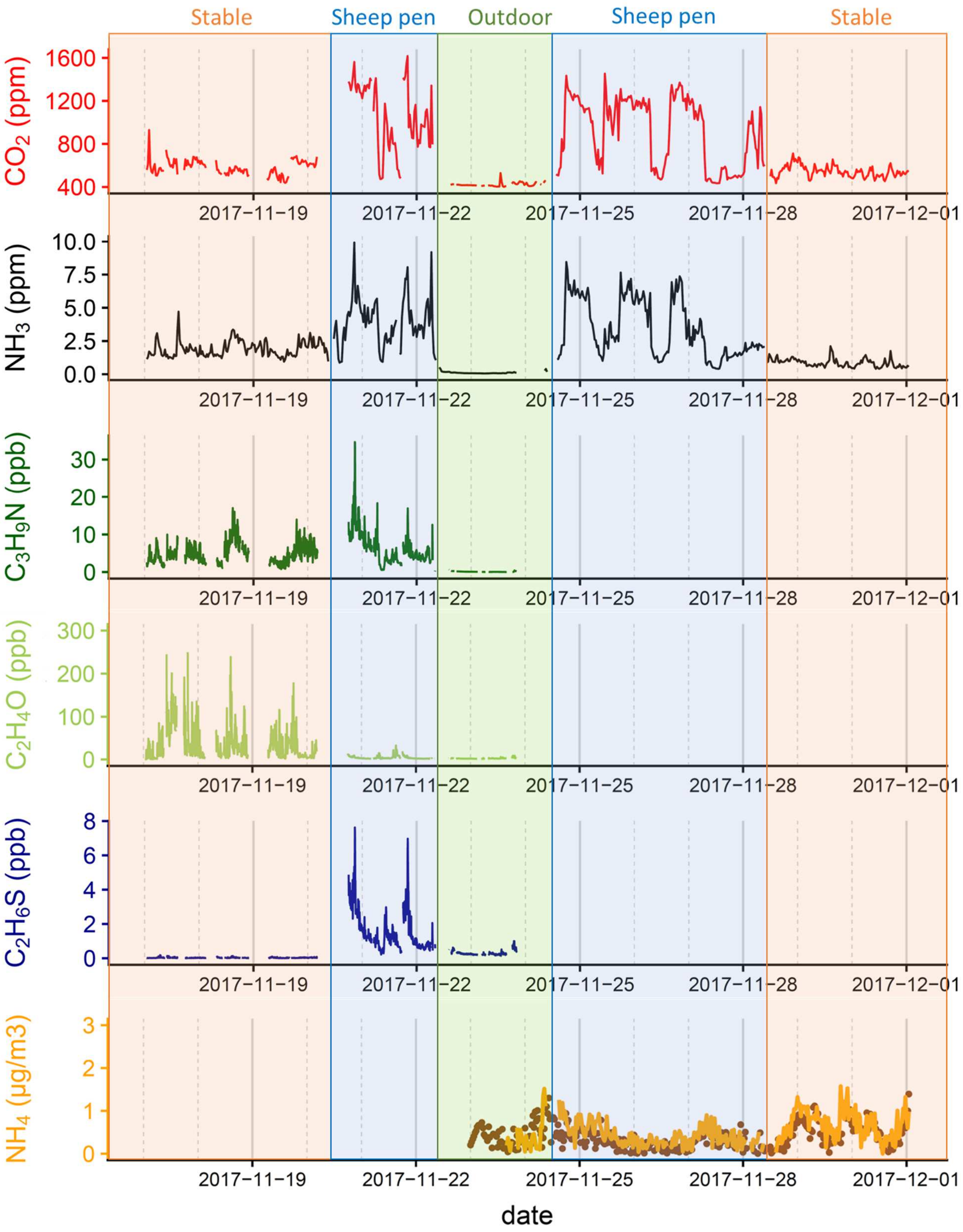

Figure 1: Time series of carbon dioxide (CO_2 in ppm), ammonia (NH_3 in ppm), trimethylamine (C_3H_9N in ppb), acetaldehyde (C_2H_4O in ppb), dimethylsulfide (DMS, C_2H_6S in ppb), and ammonium (NH_4^+, in µg m^{-3}) for the experimental farm (light brown line) and the SIRTA station (brown points) during 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.

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4.2. Identification of VOCs

Combining the three techniques (GC-FID, TD-GC-MS and PTR-Qi-TOF-MS), more than 400 compounds were detected during the whole measurement period. All the identified compounds are listed in the associated data file, and the number of identified compounds by each technique can be found in Table S2. Information about the parameters used for identification, such as PTR-Qi-TOF-MS mass resolution, or GC retention time can be found in the supplementary data file. Using the PTR-Qi-TOF-MS, 387 molecular formulas were successfully attributed. 62 molecular formulas among the 387 detected by the PTR-Qi-TOF-MS were also identified using off-line TD-GC-MS, and 8 using GC-FID (Table S2). Considering that these measurement techniques are independent, the number of common compounds underlines the consistency of the identification process. Only three compounds were identified in all measurement techniques: benzene, toluene and C_7H_{14} isomers. This is not surprising given that the range of VOCs detected by each technique was very different. The GC-FID detected C_2-C_8 hydrocarbons (alkane, alkene or alkyne), whereas the TD-GC-MS was not set up to measure small hydrocarbons (the first hydrocarbon detected by TD-GC-MS was benzene), and the PTR-Qi-TOF-MS cannot measure linear alkanes. The only alkanes detected using the PTR-Qi-TOF-MS were cyclic alkanes. For example, C_7H_{14} and C_5H_{10} could be identified as cyclic alkanes rather than alkenes, based on the chromatographic analysis (see the associated data file). Nevertheless, the possibility that a corresponding alkene, isomeric to the cyclic alkane, was detected by the PTR-Qi-TOF-MS and not detected by GC-FID cannot be fully excluded. A similar conclusion was drawn for TD-GC-MS and PTR-Qi-TOF-MS: only cyclic alkanes were measured by the PTR-Qi-TOF-MS (*e.g.* cyclopentane or cyclobutane). Thus, the PTR-Qi-TOF-MS did not detect any linear alkane, except methane. Methane indeed provided a significant signal at m/z 17.038 (corresponding to protonated methane, CH_4H^+) despite its low proton affinity (118 kcal mol^{-1}) probably due to very 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_2 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_8H_{16} using PTR-Qi-TOF-MS. TD-GC-MS analysis identified 3 cyclic alkanes with this formula (ethyl-cyclohexane; 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.

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 them were alkenes; many aromatic hydrocarbons were detected, such as BTEX (benzene, toluene, ethylbenzene and xylenes) and some polycyclic aromatic hydrocarbons (PAHs), as naphthalene or acenaphthene derivatives for example. Typical hydrocarbons frequently attributed to biogenic origin (isoprene, monoterpenes and sesquiterpenes) were also reported in the dairy stable (Schiffman et al., 2001). It is interesting to note that many molecular formulas identified had the same number of carbon atoms (from 1 to 20 carbon atoms), with the number of hydrogen atoms 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 that isopentane, 1-butene and 2,2,4-trimethyl-pentane were detected only in the stable. These compounds may hence be specific tracers for dairy stable emissions. About half of the compounds (49%) were oxygenated with molecular formulas $C_xH_yO_z$. Most of them contained between one and three oxygen atoms, as shown in Figure 2. Only 6% of oxygenated compounds contained 4 or more oxygen atoms. Thus, most of the oxygenated compounds in the stable were not highly oxidized VOCs. As for hydrocarbons, oxygenated compounds with the same number of carbon atoms and the same number of oxygen atoms were detected. The number of carbon atoms ranged from 1 to 16. Most of the hydrocarbons had the same number of carbon atoms as the oxygenated compounds (except for those with 17 carbon atoms). We can hypothesize that, in addition to the classical microbial degradation pathways, some oxygenated compounds may have been produced by gas phase or heterogeneous (reaction occurring at surfaces) oxidation of hydrocarbons (with OH radical or ozone). Based on the results from the 3 instruments, we observed many characteristic groups of oxygenated compounds in significant proportions inside the stable: alcohols, carboxylic acids, ketones, ethers, aldehydes and even esters. We noticed that oxygenated 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 molecular formulas. Most of them were small amines or amide compounds, such as dimethylamine (C_2H_7N), formamide (CH_3NO), triazine ($C_3H_3N_3$) or C_4H_5N. The observation of triazine is interesting as it was only measured inside the stable. We observed short-chain sulfur compounds, also known to be strongly odorant such as methanethiol (CH_4S), dimethyl sulfide (C_2H_6S) and dimethylsulfoxide (C_2H_6OS) (Feilberg et al., 2010; Schiffman et al., 2001). TD-GC-MS analysis confirmed the presence of benzothiazole (C_7H_5NS) in emissions from the stable and allowed identification of C_5H_7NS as 2,4-dimethyl-thiazole. Two chlorinated compounds were also measured: chloramide and dichloromethane. Dichloromethane was previously reported in emissions from pig and cattle buildings (Ciganek and Neca, 2008; Schiffman et al., 2001). But, to the best of our knowledge, chloramide is reported here for the first time in dairy stable emissions.

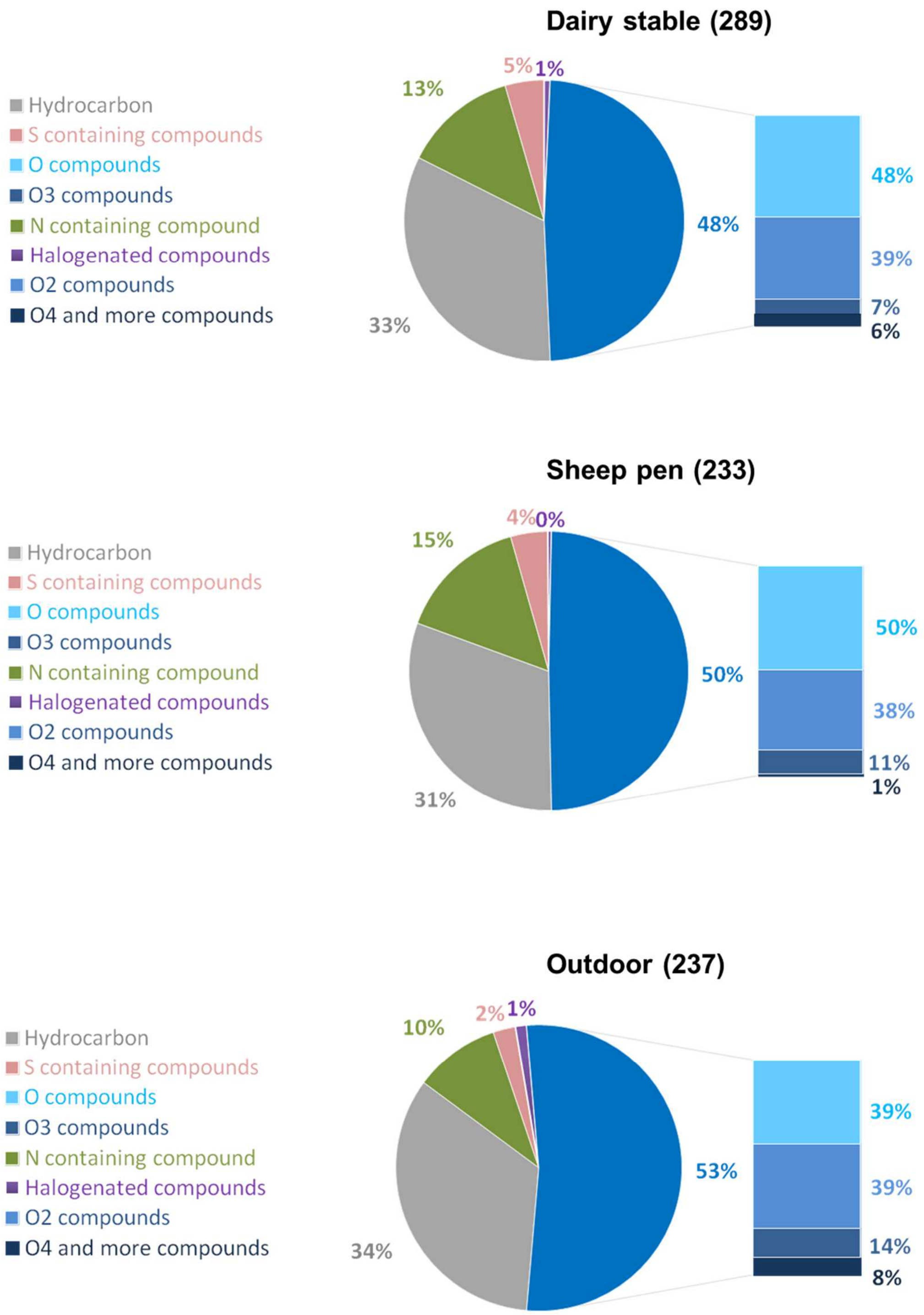


Figure 2: Classification of compounds detected inside the stable, the sheep pen and outdoor. The oxygenated compounds are further classified by the number of oxygen atoms (in the right part of each graph). The total number of identified molecular formulas identified in the different measurement locations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

In the sheep pen, hydrocarbons constituted 31% of the 233 identified molecular formulas, while they represented around 33% in the dairy stable. Most of the hydrocarbons identified were cyclic alkanes (Supplementary data file). The presence of several aromatic compounds was also observed and could have important implications for atmospheric chemistry, due to their reactivity and their ability to form secondary organic aerosols (Atkinson and Arey, 2007; Tomaz et al., 2017). We also noticed that isoprene was emitted inside the sheep pen, and no specific monoterpene was identified using TD-GC-MS, as in the stable. Octane, a C_8H_{18} compound, was only identified in the sheep pen, whereas the same molecular formula corresponded to 2,2,4-trimethyl-pentane in the stable. Oxygenated compounds represented 50% of the identified molecular formulas, practically the same proportion as in the stable (Figure 2). Oxygenated compounds contained less O atoms than in the stable, as less molecular formulas contained more than three oxygen atoms (1% in the sheep pen compared to 6% in the stable). Our identification highlights that oxygenated VOCs were mostly carboxylic acids, ketones, or alcohols, and a few aldehydes. As in the stable, few long-chain aldehydes were identified in the sheep pen, but some of these oxygenated compounds, such as 6-methyl-1-octanol ($C_9H_{20}O$) were not reported in the sheep pen. That means that the fingerprints of oxygenated compounds in the sheep pen and dairy stable were different. Exactly as in the stable, we observed that for oxygenated compounds and hydrocarbons, many molecular formulas identified had the same number of carbon atoms. Again, it suggests that oxygenated compounds may partly originate from reaction of hydrocarbons with the oxidants. In the sheep pen, the proportion of nitrogen compounds was slightly higher than in the stable (15% against 13%). Odorant compounds such as trimethylamine or pyridine derivatives were notably observed. Pyridine (C_5H_5N), methylpiperidine ($C_6H_{13}N$), dimethylpyridine (C_7H_9N), 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 measured inside the sheep pen. Among them, methanethiol (CH_4S), dimethylsulfide (C_2H_6S), dimethylsulfoxide (C_2H_6Os) 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 to that in the sheep pen, and lower than in the stable. This is logical considering that the location of the mobile van outside was closer to the sheep pen (Figure S1). Hydrocarbons represented 34% of the identified molecular formulas, which is a little higher than in both buildings (Figure 2). Alkenes, alkynes, cyclic alkanes were identified, and some aromatic compounds. As in the buildings, we noticed that many hydrocarbons had the same number of carbon atoms, ranging from 1 to 22. The proportion of oxygenated compounds was slightly higher outdoor than in both buildings (53% outdoor, and 49% inside both buildings). Another difference compared to the chemical fingerprint inside the buildings was the lower proportion of oxygenated compounds that 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 inside the buildings were closer to the VOC sources, and supports the hypothesis that some of the oxygenated compounds resulted from the oxidation of hydrocarbons. N-containing compounds represented only 10% of the identified molecular formulas (Figure 2), which was a lower fraction than inside the buildings. The same observation applied for S-containing compounds, which only represented 2%. Acetamide (C_2H_5NO) was identified outside but was not observed in the buildings, suggesting that it may come from other sources such as the nearby animal feed store or manure digester (Figure S1). Three halogenated compounds were identified outdoor. Among 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 (25th and 75th 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_2 and NH_3. CO_2 median concentrations exceeded 1000 ppm in the sheep pen. The mixing ratios of NH_3 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_3, 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_2 median levels were about 2.5 times and 1.5 times higher than the outdoor mixing ratios, respectively. Thus, NH_3 enrichment inside both buildings was higher than CO_2 enrichment, as already observed in naturally ventilated buildings (Ngwabie et al., 2014, 2007). Both CO_2 and NH_3 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_2H_6O) 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 our study, dairy cows and sheep were mainy fed with corn and alfalfa silage, completed with press beet pulp ground ear corn and potato.

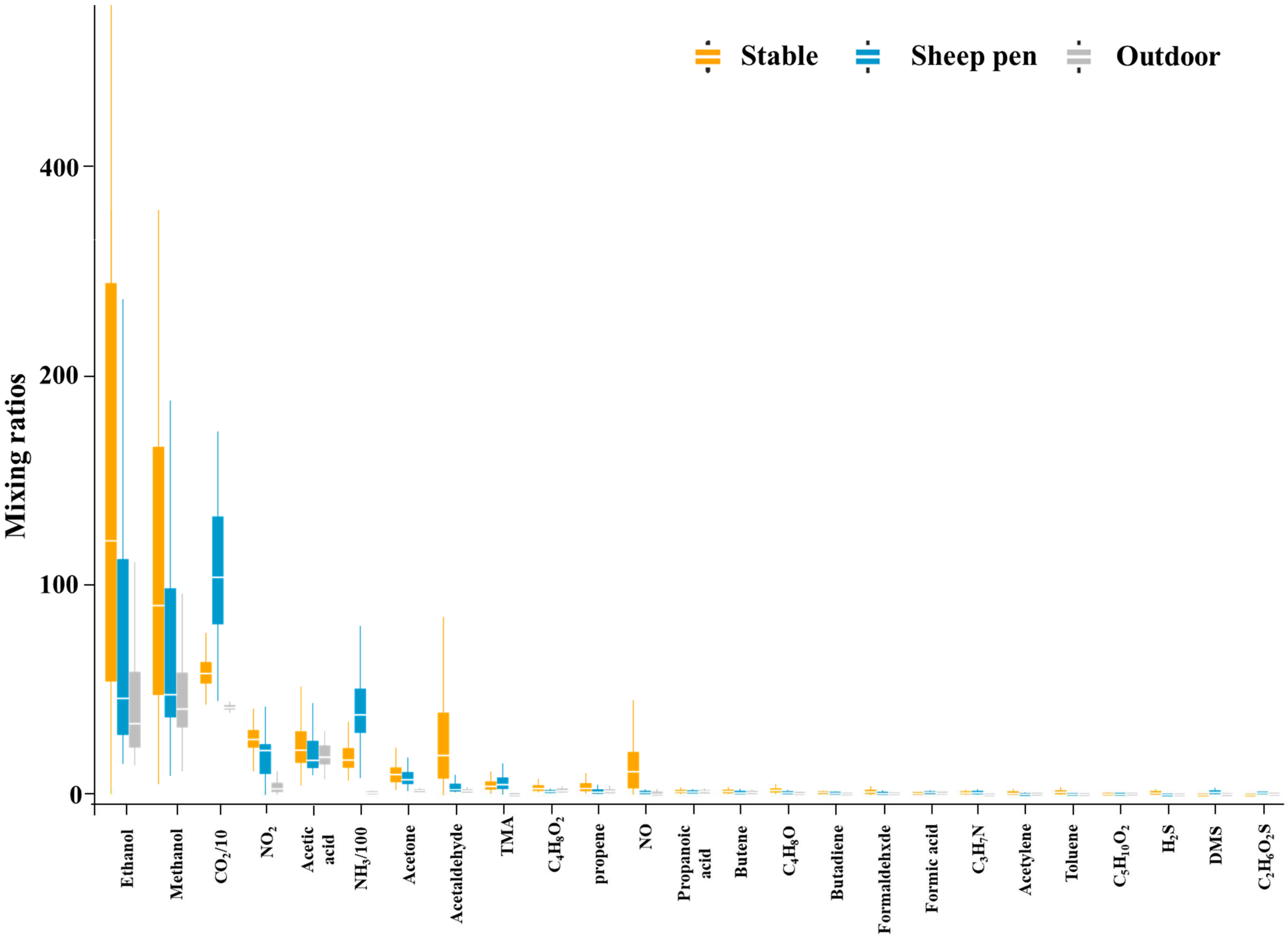


Figure 2 : Median mixing ratios and percentiles (25th and 75th as end of boxes) of the 20 most concentrated compounds inside the dairy stable, the sheep pen, and outside. All the means and the percentiles are given in ppb, except for CO_2 in ppm. Not that NH_3 was divided by 100 for scaling reasons. TMA: trimethylamine (C_3H_9N); DMS : dimethylsulfide (C_2H_6S)

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 3rd most concentrated VOC in the dairy stable, sheep pen and outdoor.

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

Figure 3 shows that nitrogen oxides (NO_x) mixing ratios were higher in the buildings than outside, meaning that both buildings can be considered as a source of NO_x. Both NO and NO_2 were more concentrated inside the stable than outdoor. However, in the sheep pen, only NO_2 was higher than outside (NO mixing ratios were very close in the sheep pen and outside, see Figure 3). Trimethylamine (C_3H_9N) was the most abundant N-containing compound after NH_3, in both buildings (Figure 3). Trimethylamine was one of the few compounds listed in Figure 3 that was more concentrated in the sheep pen than in the stable. For both buildings, mixing ratios were in agreement with previous studies in dairy or sheep farms (Ngwabie et al., 2008, 2007). We observed that there was more N- and S-containing compounds among the 20 most concentrated compounds in the sheep pen than in the stable and outdoor (Figure 3). H_2S was one of the most concentrated S containing compounds inside the stable but was not detected in the sheep pen or outdoor. H_2S may hence be used as a tracer for stable emissions within the whole farm (Figure 3). 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_2S 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_2H_6S) and dimethylsulfone ($C_2H_6O_2S$), 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_3).

Finally, NH_3, NO_x 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_x, CO_2, NH_3, 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.

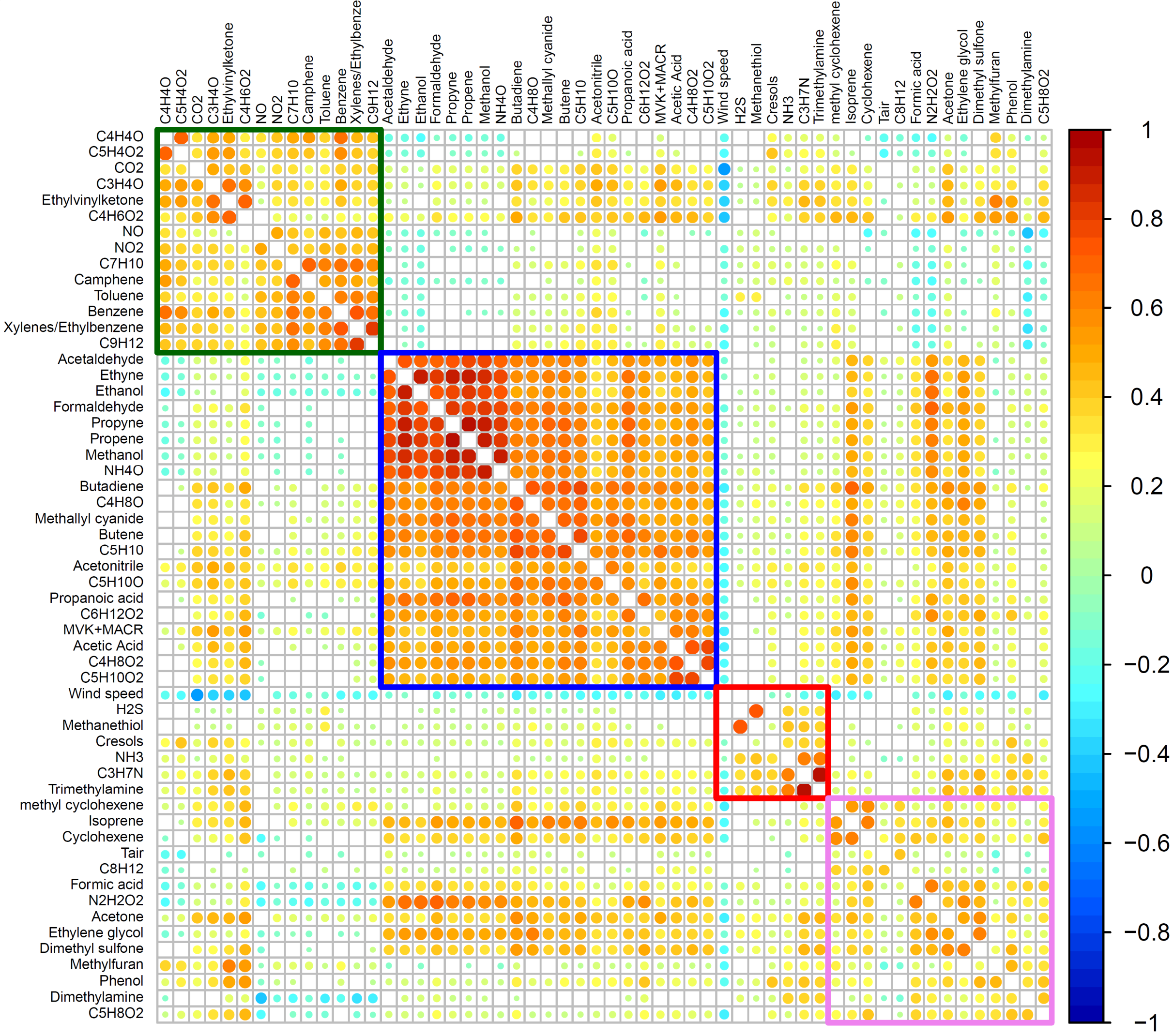
As indicated in Figure 4a, VOCs in the stable were anti-correlated with wind speed, indicating that VOCs were emitted inside the stable and did not come from external sources. *k*-means analysis revealed that four groups can be identified on the correlation heat-map. A first group of 14 compounds included hydrocarbons and oxygenated compounds, in addition to NO_x and CO_2

(group 2 in the Figure 4.a). Markers of anthropogenic combustion sources, such as BTEX, trimethyl benzene, propyl benzene, and NO_x were found in this group. CO_2 could be emitted by combustion sources, in addition to animal respiration, explaining why it was in this group but with low correlation. As all the compounds were anti-correlated with wind speed, the 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. This was also confirmed by the onsite personnel, as they frequently used tractors for some activities in the stable. However, they do not have a detailed report of activities that allowed to exactly assign the concentration peaks to these activities.

The second group of 21 compounds (group 1 in Figure 4.a) was mainly composed of hydrocarbons and oxygenated compounds. There were also 3 N-containing compounds, 1 S-containing compound and air temperature. Ethanol and methanol, the two most concentrated VOCs were in this group and were strongly correlated with the other VOCs in this group. As explained above, feeding operations are supposed to be the main source of these alcohols (Yuan et al., 2017). We thus supposed that the feeding operations are the source the VOCs included in the group 2. Six compounds and wind speed comprised the third group: 2 N-containing compounds, 2 S-containing compounds, cresols and NH_3. Most of these compounds have a strong unpleasant odor. The presence of NH_3 and small S-containing compounds suggests that the main source for this group was dairy cattle excreta. This is strengthened by the presence of cresols in this group, well known to be associated with urea and feces (Mackie et al., 1998; Shaw et al., 2007; Sun et al., 2008). Mackie et al. (1998) explained that cresols are produced during the microbial degradation of tyrosine and associated with the production of phenol. Logically, phenol 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 compounds, 1 S-containing compounds. Considering that acetone was mainly emitted by animals, 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_2. 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 the chemical family (hydrocarbons, N-containing species or oxygenated compounds, Figure 4b). On the contrary, none of them were correlated with wind speed (p values < 0.005) and all the VOCs were only barely correlated to air temperature. One can note that NO was not correlated with any VOC, and NO_2 only slightly with a few VOCs. BTEX and C_9H_{12} (identified as benzene derivatives) were frequently attributed to anthropogenic sources, even though they were already 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_x ($NO+NO_2$), and especially with NO in the case of local engine exhaust (Jiang et al., 2017; Seinfeld and Pandis, 2006). This was for example the case in the stable, as explained above. But 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 were not correlated with wind speed, we can therefore assume that they originate from the sheep pen (Figure 4.b). CO_2 can be used in the sheep pen as an animal emission tracer, whereas NH_3 could be mostly related to emissions from manure. Even if the *k*-means analysis did not reveal any optimal number of groups, we can see that NH_3 was highly correlated to trimethylamine and C_3H_7N. Thus, these two amines were likely to be emitted by the animal excreta together with NH_3. It is difficult to go further in this analysis as CO_2 and NH_3 were correlated, meaning that animal, manure and feeding operation emissions cannot be well separated in the sheep pen when only considering time-based correlations. The absence of groups in the correlation analysis 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.

A)



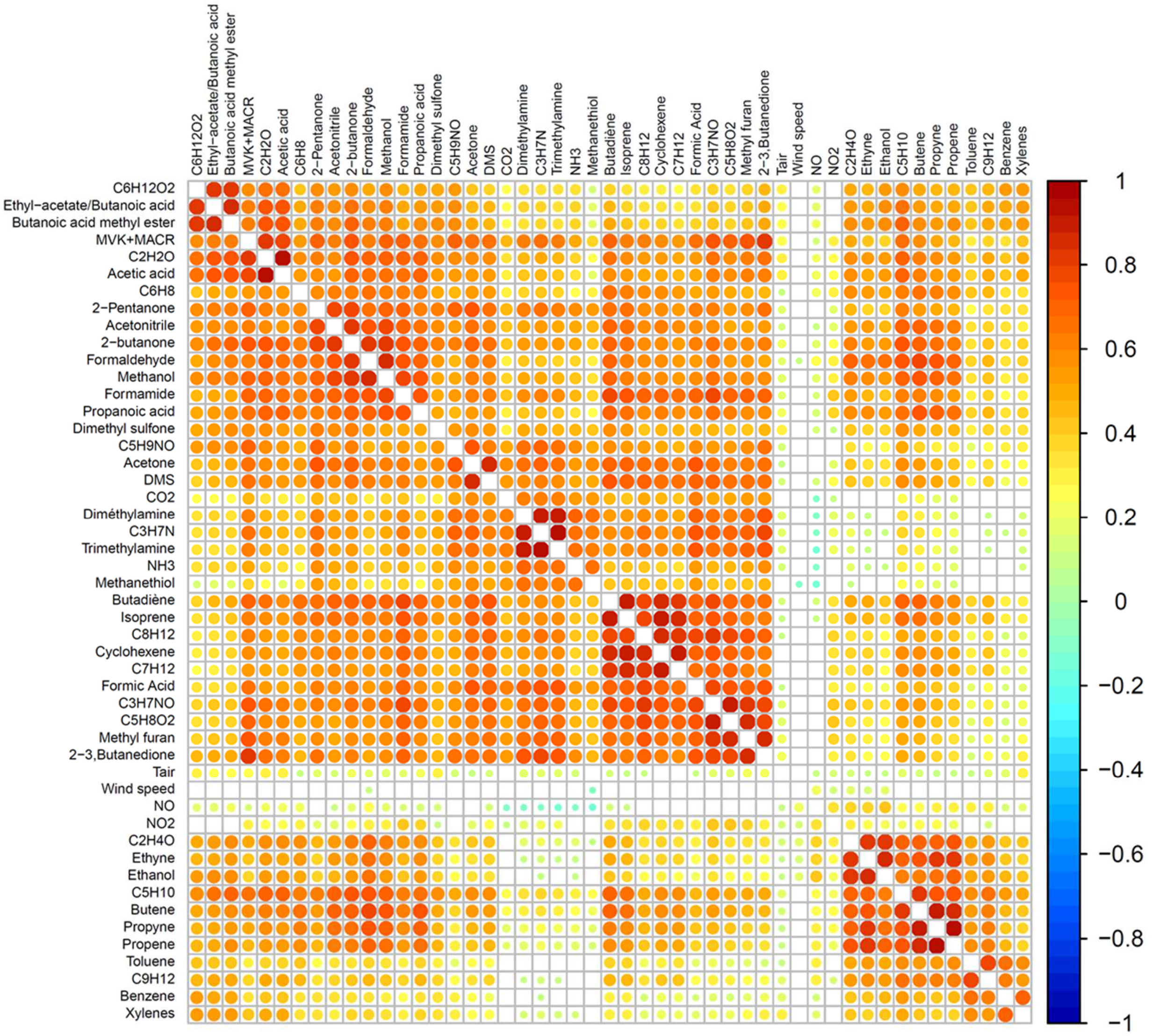


Figure 4: Correlations between compounds inside the stable (A) and the sheep pen (B). The correlation scales (on the left of each graph) range from -1 to 1 (unitless). Blue color means that two compounds are negatively correlated, and red colors means that they are positively correlated. Empty boxes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

4.6. NH_3 Emission rates

Mean ventilation rates have been estimated to be around 440 000 m^3 h^{-1} and 230 000 m^3 h^{-1} 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_3 emission rates for the stable and the sheep pen were estimated to be 9.7 (±7.1) kg N day^{-1} and 8.8 (±5.8) kg N day^{-1} (values between brackets are the standard deviation, representing the temporal variability of the emissions throughout the measurement campaign) (Figure 5.a). NH_3 emissions from each building were roughly similar, although NH_3 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_3 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^{-1} 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_3 than a sheep (Figure 5.b), which was due to the different weight of animals. We calculated that for the dairy stable and the sheep pen, emission 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} respectively (Figure 5.c). These emission factors are in the same order of magnitude as those frequently used in emission inventories (Aneja et al., 2012; Battye, 2003; Behera et al., 2013; Bouwman et al., 1997). For example, Bouwman et al. (1997) used an emission rate of 40-50 kg N year^{-1} animal^{-1} for dairy cattle and 1.0 kg N year^{-1} animal^{-1} for sheep, in a global scale estimation. A study on Indian agricultural emissions conducted by Aneja et al. (2012) referred to NH_3 emission rates of 4.3 kg N year^{-1} animal^{-1} and 1.4 kg N year^{-1} animal^{-1} for dairy cattle and sheep, respectively. In Europe, Van der Hoek used emission rates of 28.5 kg N year^{-1} animal^{-1} for dairy cattle and 0.2 kg N year^{-1} animal^{-1} for sheep. In conclusion, it appears that dairy cattle NH_3 emission rates obtained in our study are in the range of previous emission rates reported, whereas sheep emission rates are slightly higher. As the weight of a dairy cow and a sheep are very different, normalization by the living units (i.e. 500 kg of animal weight) is frequently performed. Emission rates were estimated to be 1.8 (±1.3) g N h^{-1} LU^{-1} and 2.2 (±1.4) g N h^{-1} LU^{-1} for the dairy stable and the sheep pen, respectively (Figure 5.b). These values were in agreement with previous studies conducted in naturally ventilated buildings (Koerkamp et al., 1998; Ngwabie et al., 2014, 2009; Wang et al., 2016). Our study shows that, for an equivalent amount of living units, sheep pen emissions of NH_3 are only slightly higher than that of the dairy stable, (Figure 5.b).

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_3 and NO_x. 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 (±8.5) kg day^{-1} for the dairy stable and 1.1 (±2.9) kg day^{-1} for the sheep pen (Figure 5.a). Conversely to NH_3, the dairy stable was found to emit about six times more VOCs than the sheep pen. The sum of all VOCs represented 52.8% of the NH_3 emissions in the stable, and 10.3% in the sheep pen (as a mass ratio, considering NH_3 emissions in kg of NH_3). We also evaluated that a sheep emitted much less VOCs than a dairy cow: VOC emission rates were 11.1 (±15.0) kg year^{-1} animals^{-1} for a dairy cow and 0.4 (±1.0) kg year^{-1} animal^{-1} for sheep (Figure 5.c). This was expected considering the difference in animal weight, but emissions from dairy cows are still higher if normalized by living units: VOC emission rates were estimated to be 1.2 (±1.6) g h^{-1} LU^{-1} and 0.6 (±1.3) g h^{-1} LU^{-1} in the dairy stable and the sheep pen. The difference of emitted VOCs between dairy cows and sheep was therefore not only due to the animal weight, but also in the metabolism of the animals and the nature of their excreta. This is an interesting point considering that the feeding regime for both sheep and cows is quite similar in our study.

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_3 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 (±8.3) kg year^{-1} animal^{-1}. Methanol is the second most emitted VOC in the stable, with emission rate of 0.6 (±0.8) kg year^{-1} animal^{-1} (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 (±0.2) kg $year^{-1}$ $animals^{-1}$, very close to our study. But Sun et al. (2008), in a study equivalent to that of Shaw et al. (2007), reported methanol emission rates of 6.1 kg $year^{-1}$ $animals^{-1}$. This point illustrates the variability of VOC emission rates between different studies and more investigations are required to better constrain emission rates. Acetaldehyde was the third most emitted VOC, with an emission rate of 1.1 (±1.4) kg $year^{-1}$ $animals^{-1}$. This result differs from other studies where acetaldehyde was not reported as the one of most important VOCs (Filipy et al., 2006; Ngwabie et al., 2008; Sun et al., 2008). After ethanol, methanol, and acetaldehyde, monoterpenes ($C_{10}H_{16}$, identified as camphene) were the most emitted VOCs, followed by acetone. The most abundant N-containing compound was trimethylamine (C_3H_9N). As suggested above, H_2S was only emitted in the stable and could be proposed as a tracer of the dairy stable. This was also the case of NO and toluene, but they could not be proposed as tracers because several other sources (especially motor vehicles) may emit these compounds in the vicinity of the farm. Emissions of other compounds associated with farm buildings, such as cresols, indole and phenol, were not in the most emitted compounds. However it is essential to characterize their emission rates due to their high odor activity value (Feilberg et al., 2010; Hansen et al., 2016). The detailed emission rates for such compounds are provided in the associated data file.

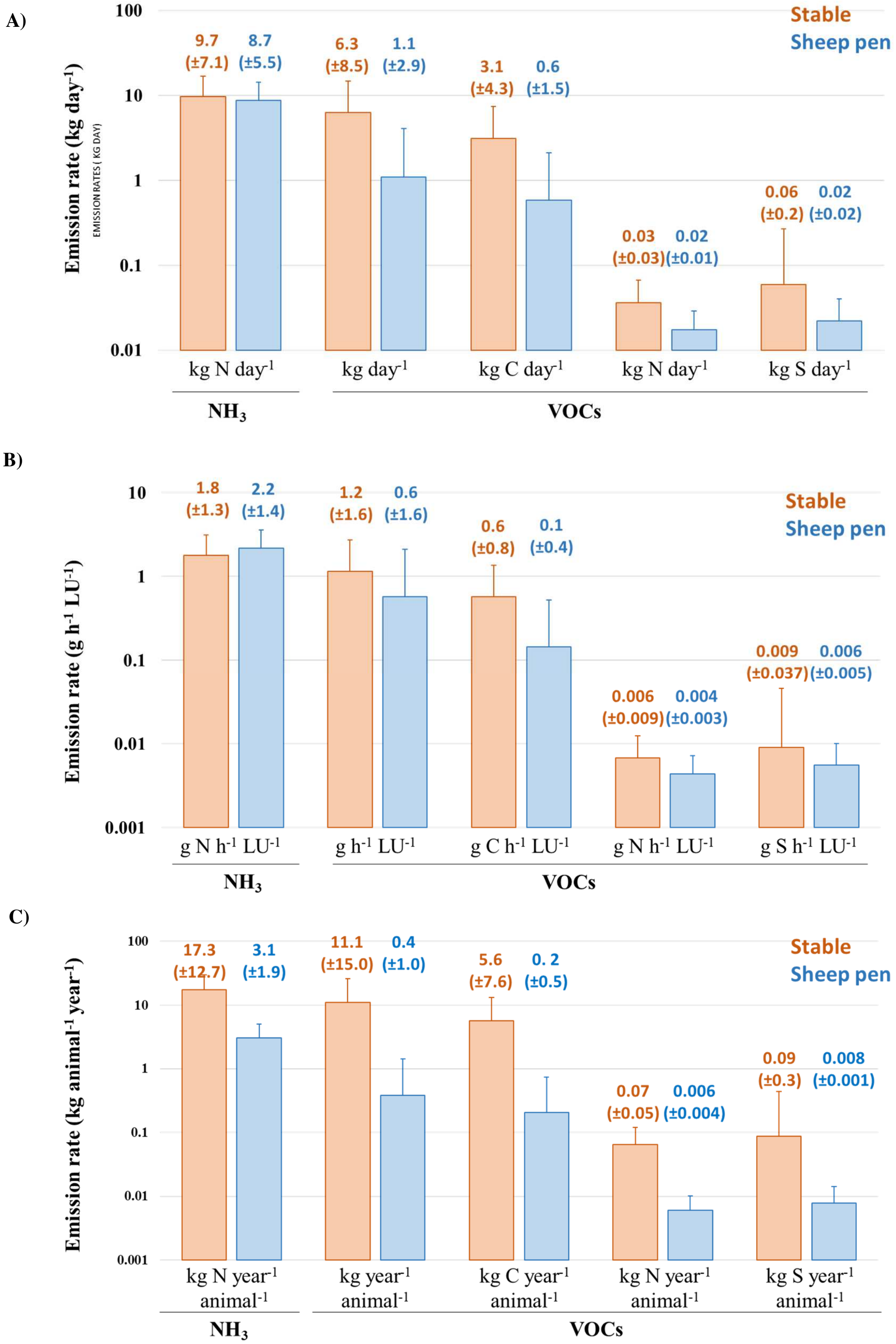


Figure 3: Mean emission rates of NH_3, the sum of VOCs, and VOCs in terms of carbon (C), nitrogen (N) and sulfur (S), for the dairy stable (orange bars) and the sheep pen (blue bars). Emission rates are given A) by building (in kg day^{-1}), B) by living unit in each building (in g h^{-1} LU^{-1}) and C) by animals (in kg year^{-1} animals^{-1}). 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 (±0.8) kg $year^{-1}$ $animals^{-1}$. Methanol was the 2nd most emitted VOC. Methanol emission rates were one order of magnitude lower than ethanol with 2.9×10^{-2} ($\pm0.2\times10^{-2}$) kg $year^{-1}$ $animals^{-1}$ in the sheep pen. Thus, the two VOCs with higher emission rates were similar between the stable and the sheep pen. But the magnitude of their emissions were considerably higher in the dairy 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 different methodologies to estimate the emission rates *ii*) their use of a conventional quadrupole PTR-MS not being able to separate isobaric compounds (such as $^{17}O^{16}O^+$ and $O_2.H^+$ ions) and *iii*) the difference between the two farms (agricultural practices, climate, animals, etc.) and especially the animal feeding regime. Acetone and trimethylamine were the most emitted VOCS after ethanol and methanol. This result is also in agreement with that of Ngwabie et al. (2007). The qualitative analysis of the main emitted VOCs seems to confirm the findings of this study. However, the magnitude of VOC emissions is lower in our study. Differences may arise from several factors (composition of the animal feed, model used to calculate emission rates, agricultural practices, etc.) and more studies are required to better understand VOC emissions from sheep farms. We also highlighted that the sheep pen emitted NO_2 but no NO. The NO_2 emission rate was lower but close to VOC emission rates, with a mean emission rate of 0.1 (±0.1 kg $year^{-1}$ $animals^{-1}$). There were also two S-containing compounds in the 10 most emitted VOCs by the sheep pen, DMS and dimethylsulfone (Table S3). These compounds are of interest as they were not emitted by the stable. C_9H_{12} and C_3H_7N were also only emitted by the sheep pen. These four VOCs could be assessed as tracers of sheep pen emissions.

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 (±4.3) kg_C day^{-1} in the stable and 0.6 (±1.5) kg_C day^{-1} 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 (±7.6) kg_C $year^{-1}$ $animals^{-1}$ for the stable and 0.2 (±0.5) kg_C $year^{-1}$ $animals^{-1}$ for the sheep pen.

The emission factors for the N contained in VOCs were 3×10^{-2} ($\pm3\times10^{-2}$) kg_N day^{-1} and 2.0×10^{-2} ($\pm1.0\times10^{-2}$) kg_N day^{-1} for the stable and the sheep pen, respectively (Figure 5.a). Contrary to what was found for NH_3, the emission factor of N emitted through VOCs was higher in the stable than in sheep pen, even when the emission rates were expressed as function of living units or animals (Figure 5.b and 5.c). These emission rates were very low compared to NH_3 emission rate. In terms of N balance, the N emitted through VOCs only represents 0.4% and 0.2 % of the NH_3 emission factor in the stable and the sheep pen (in amount of emitted N). As a result, there is no need to measure VOCs in future nitrogen cycle assessment studies.

The S emission factor for the sum of VOCs was 6.0×10^{-2} (±0.2) kg_S day^{-1} and 2.0×10^{-2} ($\pm$ 2.0×10^{-2}) kg_S day^{-1} in the dairy stable and the sheep pen. As for C and N, the amount of S emitted was higher in the stable than in the sheep pen. DMS was the most emitted S-containing compound in the sheep pen, accounting for 40 % of the sheep pen S emissions. Surprisingly, the dairy stable did not emit DMS (*i.e.* mixing ratios outside were higher than inside the building), while some studies reported strong emissions from dairy buildings (Filipy et al., 2006; Ngwabie et al., 2008; Shaw et al., 2007). 67 % of S emitted in the dairy stable could be attributed to H_2S (no H_2S emissions were recorded for the sheep pen). Feilberg et al. (2017) found a ratio between H_2S and NH_3 of 0.06, whereas it was 0.004 in our study. Thus, it seems that the dairy stable was not a strong S emitter in contrast to the literature.

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, especially in the sheep pen. NH_3 and amines (TMA- trimethylamine, DMA-dimethylamine, indole and others) could be important species for atmospheric chemistry, as they can lead to new particle formation and secondary organic aerosols (Duporté et al., 2016; Lehtipalo et al., 2018; Yao et al., 2018; Yu et al., 2012). Especially, Yu et al. (2012) demonstrated that amines and NH_3 catalyze the formation rate of stable clusters from sulfuric acid and water mixtures. Thus, considering the high VOC concentrations inside the buildings, SOA formation could be expected. However, aerosol chemical composition as measured by the ACSM revealed that the PM1 chemical composition inside farm buildings was not very different compared to ambient measurements performed 20 km from the farm. Thus, VOC emissions did not significantly affect the aerosol chemical composition close to the source (*i.e.* inside the building or outside close to them). Hiranuma et al. (2010) observed a similar result close to an open-air cattle feeding facility. This could be due to the very short residence time inside the buildings (in the order of minutes), which was not long enough for secondary aerosol formation to affect the fine particle composition (Hallquist et al., 2009). This could also be the result of low oxidant levels inside the buildings that do not allow strong semi-volatile production. Finally, it was demonstrated that farm buildings emitted primary particles mostly in the coarse mode (Cambra-López et al., 2010). But the formation of fine secondary aerosols in the vicinity of the farm seems to be limited, and may only probably occur in the plume emitted by the farm (Lammel et al. 2004).

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 at a farm in France. To scale up VOC emissions, previous studies used NH_3 emission inventories at a national scale. A ratio between VOCs and NH_3 emission rates can then be applied to estimate VOC emissions at large scales (Hobbs et al., 2004). Following the French Interprofessional Technical Centre for Studies on Air Pollution (CITEPA), NH_3 emissions due to livestock were about 246.6 kt in 2016. We estimated from our results that the amount of VOCs emitted was 31.5 % of the amount of NH_3 due to livestock (mean of the sheep pen and the dairy stable). Applying this ratio would lead to a VOC emission of 77.7 kt year^{-1} for the year 2016 in France. CITEPA estimated that VOC emissions from livestock in 2016 were around three times larger than the present one (201.6 kt year^{-1}, CITEPA, February 2019). For comparison, traffic road emissions of VOCs for the same period were estimated to be 66.2 kt year^{-1}. Livestock VOC emissions are therefore significant when compared to other anthropogenic sources, even if they are lower than expected. The difference between our estimation and the CITEPA may be due to several factors. Our estimation is based on measurements performed in November. Filipy et al. (2006) showed that VOC emissions were higher in summer, probably due to higher temperatures. Our annual estimation thus probably underestimated the mean annual emission, which may partly explain the difference with the CITEPA estimation. Another factor affecting the difference is the lack of studies about VOC emissions from farm buildings conducted in France, to better constrain emission inventories. Thus, the CITEPA estimation was mostly based on studies conducted in foreign countries, where agricultural standards and practices could be different. Finally, there are large uncertainties in both estimates and the difference between the two may not be significant. More studies are thus needed to better constrain national scale estimations and reduce uncertainties.

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 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.

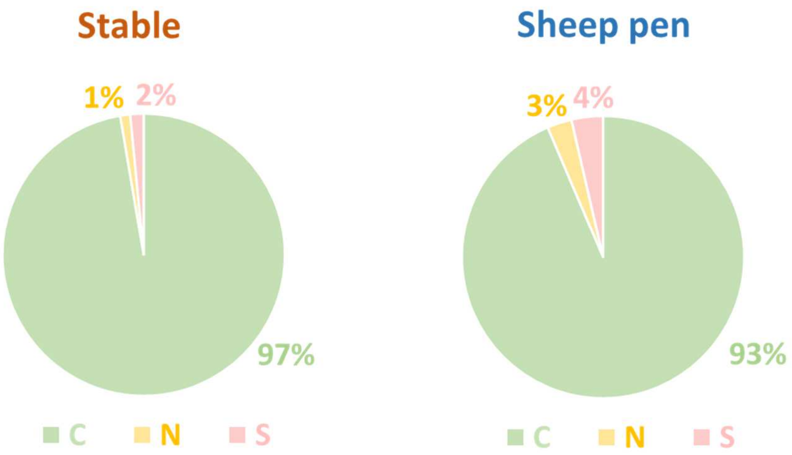


Figure 4 : Speciation of VOC emissions by amount of C, N, and S in the sheep pen and the dairy stable.

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_2S, 1-butene, 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 based on the correlation analysis. In the dairy stable the correlation analysis highlighted 3 different sources. We evidenced that the litter on the soil was a strong emitter of N and S containing compounds, through the biodegradation of animal excreta. The farming activities using a tractor inside the stable has shown to emit hydrocarbons (mainly BTEX) and NO_x. The third source identified is represented by the animal respiration. A future study focused on VOCs contained in dairy cattle and sheep breath at the Grignon farm would support our findings and help to separate animal and excreta emissions.

Emission rates have shown that, at the animal level, a dairy cow emitted more NH_3, NO_x, and VOCs than a sheep. But at the farm level, the sheep pen was found to emit roughly as much NH_3 as the stable. The emission of N through VOCs was negligible compared to the NH_3 emissions. Thus, regarding the N balance, the N released in the gas phase was mainly released through NH_3. 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 plume of pollutants emitted by the farm, rather than inside the buildings. This assumption needs to 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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Competing interests: The authors declare no competing of interest.

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

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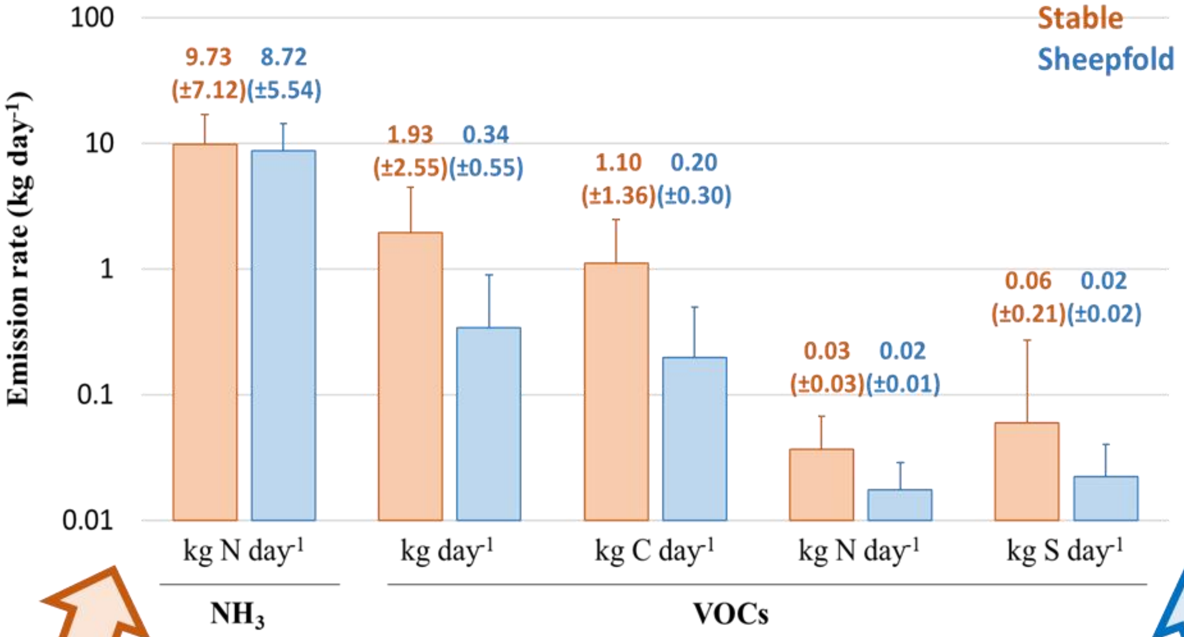
Stable
Sheepfold
Emission rate (kg day^{-1})
100
10
1
0.1
0.01
9.73 (±7.12)
8.72 (±5.54)
1.93 (±2.55)
0.34 (±0.55)
1.10 (±1.36)
0.20 (±0.30)
0.03 (±0.03)
0.02 (±0.01)
0.06 (±0.21)
0.02 (±0.02)
kg N day^{-1}
kg day^{-1}
kg C day^{-1}
kg N day^{-1}
kg S day^{-1}
NH$_3$
VOCs