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Emissions of volatile organic compounds (VOCs) from concentrated animal feeding operations (CAFOs): chemical compositions and separation of sources

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Abstract. Concentrated animal feeding operations (CAFOs) emit a large number of volatile organic compounds (VOCs) to the atmosphere. In this study, we conducted mobile laboratory measurements of VOCs, methane (CH_4) and ammonia (NH_3) downwind of dairy cattle, beef cattle, sheep and chicken CAFO facilities in northeastern Colorado using a hydronium ion time-of-flight chemical-ionization mass spectrometer (H_3O^+ ToF-CIMS), which can detect numerous VOCs. Regional measurements of CAFO emissions in northeastern Colorado were also performed using the NOAA WP-3D aircraft during the Shale Oil and Natural Gas Nexus (SONGNEX) campaign. Alcohols and carboxylic acids dominate VOC concentrations and the reactivity of the VOCs with hydroxyl (OH) radicals. Sulfur-containing and phenolic species provide the largest contributions to the odor activity values and the nitrate radical (NO_3) reactivity of VOC emissions, respectively. VOC compositions determined from mobile laboratory and aircraft measurements generally agree well with each other. The high time-resolution mobile measurements allow for the separation of the sources of VOCs from different parts of the operations occurring within the facilities. We show that the emissions of ethanol are primarily associated with feed storage and handling. Based on mobile laboratory measurements, we apply a multivariate regression analysis using NH_3 and ethanol as tracers to determine the relative importance of animal-related emissions (animal exhalation and waste) and feed-related emissions (feed storage and handling) for different VOC species. Feed storage and handling contribute significantly to emissions of alcohols, carbonyls, carboxylic acids and sulfur-containing species. Emissions of phenolic species and nitrogen-containing species are predominantly associated with animals and their waste.

1 Introduction

Concentrated animal feeding operations (CAFOs) emit many volatile organic compounds (VOCs) into the atmosphere, including carboxylic acids, alcohols, carbonyls, phenolic compounds, sulfur- and nitrogen-containing compounds (Hobbs et al., 2004; Filipy et al., 2006; Sun et al., 2008; Ni et al., 2012). These VOCs can contribute to the formation of ozone (Howard et al., 2010a, b; Gentner et al., 2014) and fine particles (Sintermann et al., 2014; Perraud et al., 2015), both affecting regional air quality. Many VOCs from CAFOs are also responsible for the unpleasant odor problems nearby or downwind of these facilities (McGinn et al., 2003; Rabaud et al., 2003; Parker et al., 2010; Woodbury et al., 2015). Some VOCs (e.g., phenolic species) (US EPA, 2017) from CAFOs are harmful to human health.

There are a large number of potential VOC sources inside a CAFO, potentially including animal exhalation, animal waste in animal pens, flushing lanes, lagoons, silage storage piles and silos, and feed mixtures in feed lanes and bunks (Alanis et al., 2008; Chung et al., 2010). Early studies mainly focused on VOC emissions from animal waste (e.g., slurry and manure) under laboratory conditions (Hobbs et al., 1997, 1998, 2004). Ngwabie et al. (2007, 2008) reported that VOC concentrations in dairy, sheep and pig CAFOs were the highest during animal waste removal and feeding, indicating that large emissions were related to these activities. Recent studies found that VOC concentrations in dairy farms were significantly higher near silage and piles of animal feed (i.e., total mixed rations) than near other places (animal pens, lagoons and flush lanes), suggesting that feed-related sources dominate VOC emissions (Alanis et al., 2008; Chung et al., 2010). Enhancements of some VOCs (e.g., acetone) in animal sheds are also related to animal exhalation (Shaw et al., 2007; Ngwabie et al., 2008; Sintermann et al., 2014). However, the contributions of different sources to individual VOC emissions from a facility are not accurately known (Ngwabie et al., 2008). This poor understanding of VOC sources hinders the development of management practices that reduce VOC emissions in animal feeding facilities (Ngwabie et al., 2007). Thus, a comprehensive characterization of VOC sources and their relative importance within a CAFO is needed.

Many studies of VOCs from animal feeding operations have been conducted with offline analytical methods (Filipy et al., 2006; Alanis et al., 2008; Sun et al., 2008; Chung et al., 2010; Ni et al., 2012). VOCs were collected on filters, or in canisters and cartridges and were quantified in the laboratory using various methods (see reviews in Ni et al., 2012). These offline methods are labor-intensive, which limits the number of VOC samples. Online fast measurement techniques (mainly proton-transfer reaction mass spectrometers, PTR-MS) allow for more detailed investigation of CAFO facilities (Shaw et al., 2007; Ngwabie et al., 2008; Sintermann et al., 2014). The previous online measurements usually used a single stationary sampling inlet either inside a stall or at a fence line, which does not provide spatial distribution information for VOCs in the facilities.

In this study, we deployed a high time-resolution instrument on board a mobile laboratory driven on public roads and a NOAA WP-3D research aircraft to measure VOCs downwind of CAFO facilities. We will use this data set to characterize chemical compositions of VOC emissions and explore different sources within the facilities that contribute to VOC emissions.

2 Experiments

Mobile laboratory measurements were conducted near Greeley in northeastern Colorado, USA. Six different CAFOs were studied, including two dairy farms, two beef feed yards, one sheep feed yard and one egg-laying chicken farm (Table S1 in the Supplement). Among the six CAFOs, emissions of NH_3, N_2O and CH_4 in four facilities (the two dairy farms, one beef cattle feed yard and the sheep feed yard) have been measured previously using an instrumented van (Eilerman et al., 2016). We added a new VOC instrument to the payload, and performed mobile measurements in wintertime (February, 2016) for the six CAFOs by sampling at their downwind flanks 1–2 times for each facility. Duplicated measurements at the same facilities agreed well.

VOCs were measured using a hydronium ion time-of-flight chemical-ionization mass spectrometer (H_3O^+ ToF-CIMS) instrument on the mobile laboratory. Here, we provide a brief description of the instrument (see details in Yuan et al., 2016). VOCs are ionized by H_3O^+ ions in a drift tube, similar to a PTR-MS (de Gouw and Warneke, 2007). The protonated product ions are detected using a high-resolution time-of-flight (ToF) analyzer (Tofwerk AG) ($m/\Delta m = 4000$–6000). A number of VOC species were calibrated using either gravimetrically prepared gas cylinders or permeation tubes (see details in Yuan et al., 2016). VOC background signals in the instrument were determined by passing ambient air through a catalytic converter. The detection limits are compound-dependent and range between 10 and 100 ppt for most VOC species at a time resolution of 1 s. Besides VOCs, two inorganic species, NH_3 and H_2S, were measured at m/z 18.034 (NH_4^+) and m/z 34.995 (H_3S^+) using the H_3O^+ ToF-CIMS, respectively (Li et al., 2014; Müller et al., 2014).

In addition to the H_3O^+ ToF-CIMS, a cavity ring-down spectrometer instrument (Picarro G1301m) measuring methane (CH_4) and carbon dioxide (CO_2) and an off-axis integrated cavity output spectrometer (Los Gatos Research) measuring nitrous oxide (N_2O) along with carbon monoxide (CO) were deployed during the mobile laboratory measurements. Measurements of ambient temperature, relative humidity, wind direction, wind speed and vehicle location were performed using meteorological sensors (R.M. Young 85004 and AirMax 300WX) and a GPS compass system (ComNav G2B). A summary of meteorological conditions during the mobile laboratory measurements is shown in Table S2.

Measurements of agricultural plumes were also performed using the NOAA WP-3D research aircraft in March–April 2015 during the Shale Oil and Natural Gas Nexus (SONGNEX) campaign. Data from three flights (28 March, 29 March, 13 April) over northeastern Colorado are used in this study. VOCs were measured using the same H_3O^+ ToF-CIMS instrument as mobile measurements (Yuan et al., 2016). Another chemical ionization mass spectrometer (CIMS) was used to detect NH_3 during SONGNEX (Nowak et al., 2007). Due to background issues and lower concentrations, NH_3 signals were not retrievable from H_3O^+ ToF-CIMS during the SONGNEX campaign.

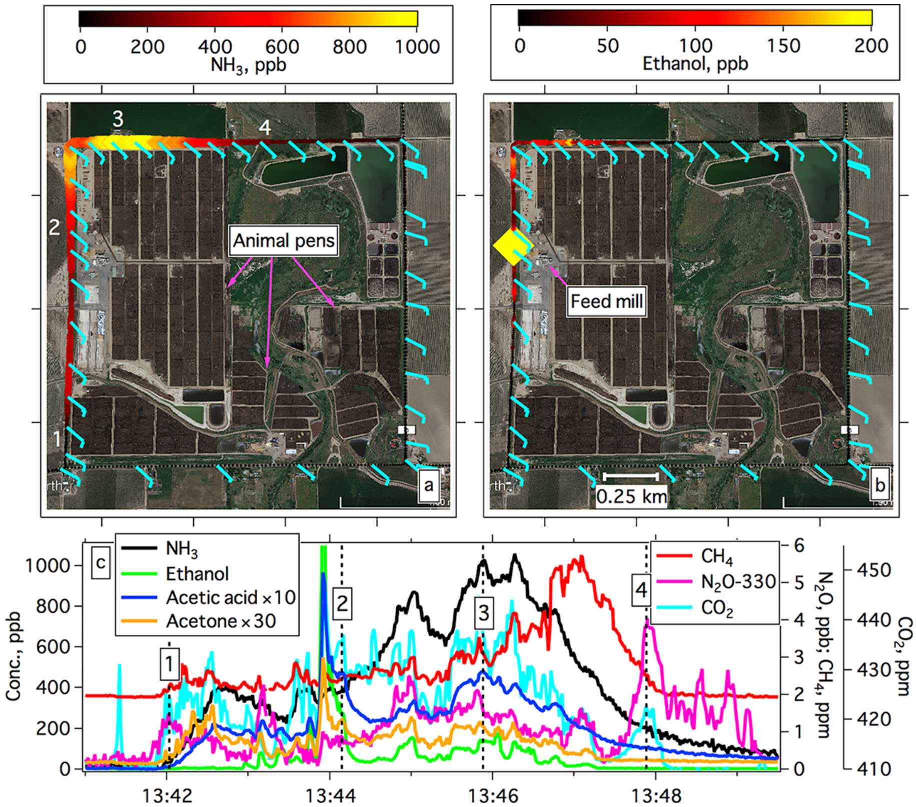

Figure 1. (a, b) Drive track of mobile laboratory color- and size-coded by NH_3 **(a)** and ethanol **(b)** concentrations around a beef feed yard (beef no. 1). The prevailing wind is shown by wind barbs (light blue flags) in the map. **(c)** Time series of NH_3, CH_4, CO_2, N_2O, ethanol, acetic acid and acetone measured downwind of the beef feed yard. Numbers (1–4) in panels **(a)** and **(c)** are used to allow for alignment of the mobile laboratory locations on the map with the corresponding time series in panel **(c)**.

3 Results and discussions

3.1 Spatial distributions from mobile laboratory measurements

Figure 1 shows measured concentrations of NH_3, CH_4, CO_2, N_2O, ethanol (C_2H_5OH), acetic acid (CH_3COOH) and acetone (CH_3COCH_3) around a beef feed yard (beef no. 1). The concentrations of the seven species were enhanced and highly variable downwind of the facility. Different time variations for the seven species were clearly observed. NH_3 concentrations peaked at around 13:46 local time (LT) and the peak location was northwest of this facility, directly downwind of the animal pens. This is consistent with fresh waste of animals (urine and feces) as the main source of NH_3 within a CAFO facility (Hristov et al., 2011). CO_2 and CH_4 are emitted from animal respiration and eructation of the cattle (Shaw et al., 2007; Sintermann et al., 2014; Owen and Silver, 2015). CO_2 ($R = 0.77$) and CH_4 ($R = 0.77$) correlated well with NH_3 between 13:42 and 13:46 LT when NH_3 was high. These observations reflect the fact that animals and their fresh waste may be largely co-located in the animal pens. But, waste cleaning time/practices in the facility were unknown, owing to no access to the facility. Previous mobile and aircraft measurements have also observed enhancements of NH_3 and CH_4 concentrations downwind of animal pens in cattle feedlots (Miller et al., 2015; Hacker et al., 2016). The time variations of two VOCs, acetic acid and acetone, followed reasonably well with both NH_3 and CO_2, suggesting that animals and their waste contributed to the enhancements of the two VOCs. Based on previous studies, the emissions from animal respiration should dominate over waste for acetone, and vice versa for acetic acid (Ngwabie et al., 2008; Sintermann et al., 2014). The similar time variations of NH_3, CO_2, acetone and acetic acids (and less clearly for CH_4) imply that the co-located emissions from animals and their waste may not be separated based on the variations observed (over a short time span of several minutes) while measuring along the downwind flanks.

A single, narrow high-concentration spike (up to 1 ppm) of ethanol was observed around 13:44 LT (Fig. 1). The hotspot of ethanol was located downwind of a feed mill at the west side of the feed yard, indicating that the feed mill and its related activities can emit large amounts of ethanol. Distillers grains, a fermented by-product from ethanol production, are commonly used as an ingredient of feed in beef cattle feed

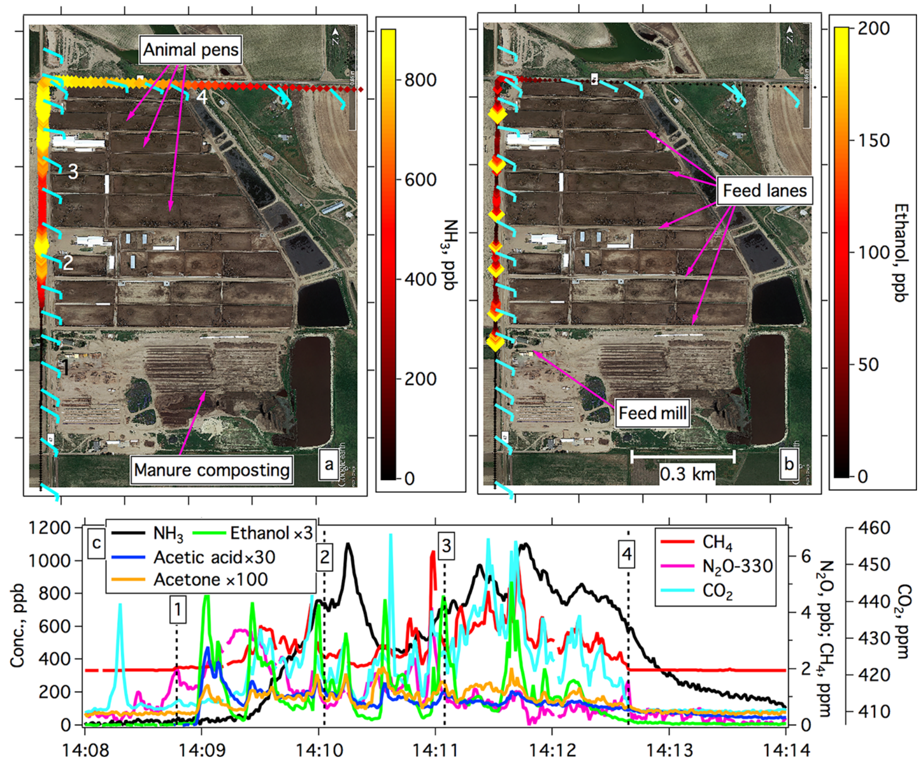

Figure 2. (a, b) Drive track of mobile laboratory color- and size-coded by NH_3 **(a)** and ethanol **(b)** concentrations downwind of a dairy farm (dairy no. 1). The prevailing wind is shown by wind barbs (light blue flags) in the map. **(c)** Time series of NH_3, CH_4, CO_2, N_2O, ethanol, acetic acid and acetone measured downwind of the dairy farm. Numbers (1–4) in panels **(a)** and **(c)** are used to allow for alignment of the mobile laboratory locations on the map with the corresponding time series in panel **(c)**.

yards (Raabe, 2012) (although not known specifically here). Therefore, it is not surprising to observe large emissions of ethanol in the feed mill area. High concentrations of many other VOC species (e.g., acetic acid and acetone) were observed in the feed mill plume, whereas NH_3, CH_4 and N_2O were not enhanced. Combustion sources, possibly due to equipment operation in the feed mill area, are likely responsible for the enhancement of CO_2 and CO at $\sim$ 13:44 LT. VOC emissions from these combustion plumes are negligible (see details in the Supplement, Fig. S1).

Measurements downwind of a dairy farm (dairy no. 1) are shown in Fig. 2. The highest concentrations of NH_3 and CO_2 were observed downwind of the animal pens, similar to the beef feed yard shown in Fig. 1. Interestingly, several high concentration peaks of ethanol were observed along the drive track of the mobile laboratory. These peaks were in close proximity or downwind of the feed lanes (white lines on the satellite image, Fig. 2b). As shown for beef no. 1, feed mills can be an important source of ethanol and other VOCs. Different from the usage of distillers grains in beef cattle feed yards, silage is more commonly used as fodder for dairy cattle (Raabe, 2012). Previous studies showed that ethanol is the most abundant VOC species emitted from feed silage (Hafner et al., 2013). It is expected that VOCs will continue evaporating from the feed mixtures after the feed is delivered to the feed lanes. Time variations of acetic acid (and acetone) correlated more closely with ethanol ($R = 0.72$) than with NH_3 ($R = -0.30$) and CO_2 ($R = -0.14$), which differs from the beef feed yard. This suggests that the three VOCs were mainly from emissions of feed lanes, rather than animals and their waste in this dairy farm.

In addition to animals and their waste (referred to as animal+waste hereafter) and feed storage and handling (referred to as feed storage+handling hereafter), we identified another important VOC source from the other dairy farm studied (dairy no. 2, Fig. S2). High concentrations of ethanol, acetone, dimethyl sulfide (DMS, C_2H_6S) and CH_4 were observed downwind of three milking parlors. Acetic acid was only moderately elevated, whereas NH_3 was not enhanced. Compared to feed storage+handling, emission compositions from the milking parlors are different. The emissions from milking parlors might result from several sources, including animal exhalation and milking-related activities. It is worth noting that we did not distinctly observe emissions from the milking parlor in the dairy farm no. 1, which were potentially mixed with emissions from feed prior to sampling.

The measurements downwind of three other CAFO sites (beef no. 2, the sheep feed yard and the chicken house) are

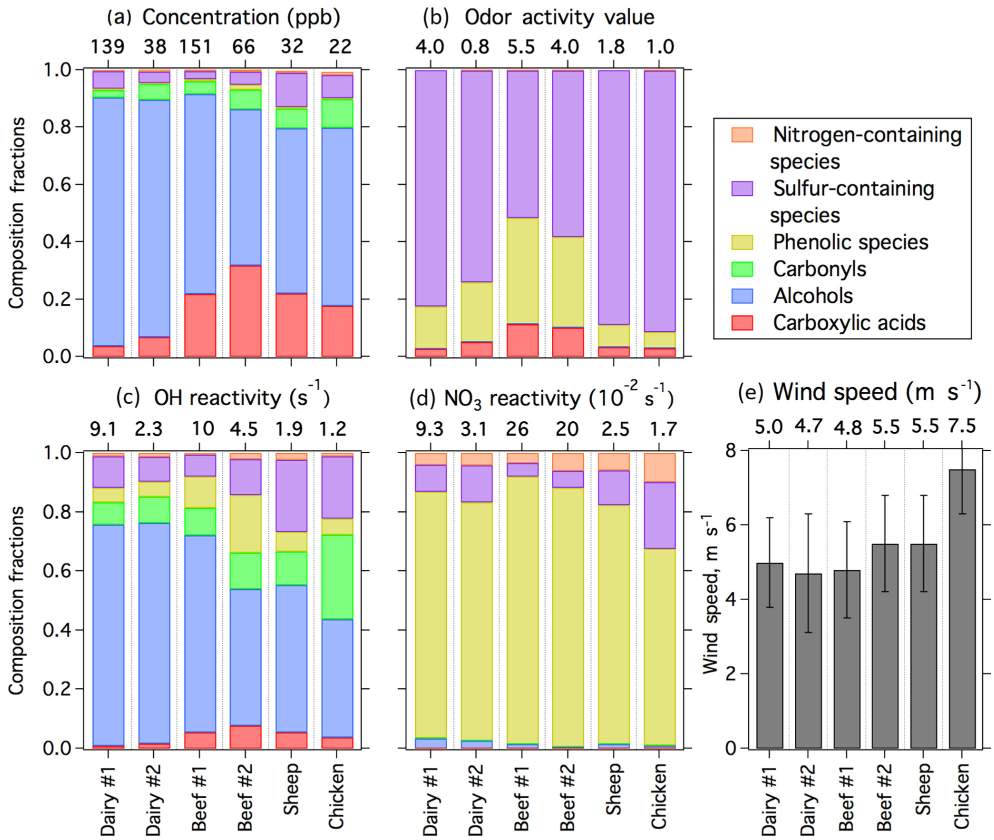

Figure 3. The fractional contributions of different VOC classes to the total VOC concentrations **(a)**, odor activity values **(b)**, OH reactivity **(c)** and NO_3 reactivity **(d)** for the six investigated CAFO sites. The mean wind speeds during the measurements of the CAFO sites are shown in panel **(e)**. The mean values for the five parameters from each CAFO are shown at the top of each panel.

investigated in a similar way, as shown in Figs. 1–2 (and Figs. S2–S3). From this analysis, we identify three main VOC emission sources in animal feeding facilities, namely animal+waste, feed storage+handling and milking parlors. These measurements suggest that combustion sources are not important for VOC emissions in these facilities.

3.2 VOC chemical compositions of different CAFOs

The enhancements of VOCs downwind of each CAFO were integrated to determine the averaged VOC compositions for each facility (Fig. 3). The measured VOC species are divided into six different groups, namely carboxylic acids, alcohols, carbonyls, phenolic species, nitrogen- and sulfur-containing species. The averages of the sum of measured VOC concentrations downwind of the sites are in the range of 22–139 ppb, with higher concentrations at dairy farm no. 1 and the two beef feed yards (wind speeds during the measurements were similar except at the chicken house, Fig. 3e and Table S1). As demonstrated in Fig. 3a, alcohols (55–87 %, mole fractions) and carboxylic acids (4–32 %) represent major classes of VOC from these CAFOs. Other VOC classes account for 8–21 % of VOC concentrations in total.

As discussed in Sect. 1, VOC emissions from CAFOs can contribute to unpleasant odor problems and ozone formation. We utilize odor activity value (OAV) and the OH and NO_3 reactivity to evaluate the relative contribution of each VOC class to the two environmental effects, respectively. The dimensionless OAV is estimated from VOC concentrations divided by the species' single compound odor thresholds (SCOT) ($OAV_i = C_i / SCOT_i$) (Feilberg et al., 2010; Parker et al., 2010; Woodbury et al., 2015). The reported SCOT values in the literature are highly variable and we use the geometric means of literature values for each compound, as compiled in Parker et al. (2010). The averaged total OAVs from all measured VOCs are in the range of 0.8–5.5 at different sites (Fig. 3b). Sulfur-containing species contribute the largest fractions (51–91 %) to total OAVs at different sites, followed by phenolic species (6–37 %) and carboxylic acids (3–11 %). The relative contributions of different species to OAV agree well with previous estimates based on measurements from a beef feed yard (Woodbury et al., 2015).

OH reactivity (OHR) and NO_3 reactivity (NO3R) are determined as the products of VOC concentrations and the respective reaction rate constants of VOCs with the two oxidants (Atkinson et al., 2006) ($OHR_i = C_i \times k_{OH,i}$; $NO3R_i =$

$C_i \times k_{NO_3,i}$). The averaged OH reactivities range between 1 and 10 s^{-1}, which is comparable or lower than the typical OHR observed in urban areas (a few s^{-1} to 50 s^{-1}) (Yang et al., 2016). Alcohols are the largest contributors (40–75 %) to OHR at the sites, although the fractions from carbonyls, phenolic and sulfur-containing species are also significant (Fig. 3c). These results are generally consistent with the finding that ethanol accounts for the majority of ozone formation potential of VOC emissions from a dairy farm (Howard et al., 2008). The averaged NO_3 reactivities range from 0.02 to 0.26 s^{-1}, which are remarkably higher than in urban areas (usually < 0.01 s^{-1}) (Tsai et al., 2014; Brown et al., 2016). In contrast to the OH reactivity, phenolic species account for the largest fractions (66–90 %) of the NO_3 reactivity for all of the sites, with remaining contributions primarily from sulfur- and nitrogen-containing species (Fig. 3d). We note that OAV, OH and NO_3 reactivity are measured along the fence line and they decrease rapidly with downwind distance and dilution (see example in Sect. 3.4 for aircraft measurement results associated with a factor of ∼ 10 lower concentrations than those from mobile laboratory).

3.3 Relative importance of different sources for VOC emissions

As shown in Sect. 3.1, ethanol was primarily emitted from feed storage+handling (and milking parlors), whereas NH_3 and CO_2 were attributed to emissions from animals and their waste. This suggests that these species can be used as tracers to separate the emissions from sources. However, there are two issues that need to be considered: (1) emissions of animal exhalation and waste are largely co-located in the animal pens. As CO_2 is also emitted from combustion sources (see details in the Supplement) and animal exhalation is only important for a few species (e.g., acetone), NH_3 will be used as a tracer for the emissions from animals and their waste. It is worth mentioning that long-term measurements in CAFO facilities could permit separation of the two co-located sources (see example in Sintermann et al., 2014). (2) There is some ethanol attributable to animal+waste emissions that needs to be accounted for. Ethanol concentrations solely from feed emissions ($[C_2H_5OH]_{Feed}$) can be calculated by subtracting the contribution of ethanol by animal+waste from measured ethanol concentrations (see details in the Supplement, Fig. S4).

After correcting ethanol for animal+waste emissions, the contributions of emissions from feed storage+handling and animal+waste to measured VOC enhancements at each individual site can be determined using multivariate linear fits to $[C_2H_5OH]_{Feed}$ and NH_3 concentration ($[NH_3]$).

$$[VOC] = ER_{C_2H_5OH} \times [C_2H_5OH]_{Feed} + ER_{NH_3} \times [NH_3] + [bg] \quad (1)$$

Here, [VOC] and [bg] are measured concentrations of the VOC species and the background concentration outside the CAFO plumes, respectively. $ER_{C_2H_5OH}$ and ER_{NH_3} are the emission ratios of the VOC species relative to ethanol and NH_3 from the emissions of feed storage+handling and animal+waste, respectively. Along with [bg], the emission ratios are determined from the multivariate linear fits.

Based on the fitted parameters from Eq. (1) (and Eq. S3 for dairy farm no. 2), the relative contributions of different sources to the enhancements of various VOC species can be calculated for the investigated sites (Fig. 4). In general, large differences in fractional contributions to VOC enhancements exist among both different VOC species and different animal types. The main findings from Fig. 4 are as follows:

1. Phenol, cresols, butanediones and many nitrogen-containing species are primarily associated with animal+waste emissions for the investigated sites.

2. Both feed storage+handling and animal+waste account for significant fractions of emissions of many oxygenated VOCs and sulfur-containing species.

3. Based on the results from the dairy farm no. 2, emissions from milking parlors contribute significantly to the enhancements of a limited number of VOC species, including ethanol (23 ± 1 %), acetone (35 ± 3 %), acetaldehyde (31 ± 3 %), methanol (18 ± 3 %), MEK (14 ± 2 %) and DMS (14 ± 2 %).

4. Feed storage+handling plays important roles in the emissions of many VOC species from the chicken farm. Based on a news report on the facility, a manure belt system is used to manage manure in this facility. The manure belt system catches the excreta from chicken to transport manure to a separate location for storage. The chicken houses with manure belts usually lead to substantially lower emissions (e.g., NH_3) from animal waste (Wood et al., 2015). It is consistent with significantly lower NH_3 concentrations (0–175 ppb, Fig. S3) at this site compared to ruminant feed yards measured in this study (0–1000 ppb), although wind speed was 36–60 % higher during measurements of the chicken house (7.5 $m\,s^{-1}$) than others (4.7–5.5 $m\,s^{-1}$). It is also possible that emissions of NH_3 and VOCs were treated when in-house air was ventilated out (Wang et al., 2010).

We further determine the contributions of emissions from feed storage+handling, animal+waste and milking parlors to the total VOC concentrations (first columns in Fig. 4, also Fig. S5). Feed storage+handling emissions account for 35–41, 23–30, 13 and 41 % of the summed total VOC concentrations for the investigated dairy farms, beef feed yards, the sheep feed yard and the chicken farm in this study, respectively. The fractional contributions from the sources to odor activity value, OH reactivity and NO_3 reactivity are also calculated (Fig. S5). The contributions from feed storage+handling emissions to the three parameters are gen-

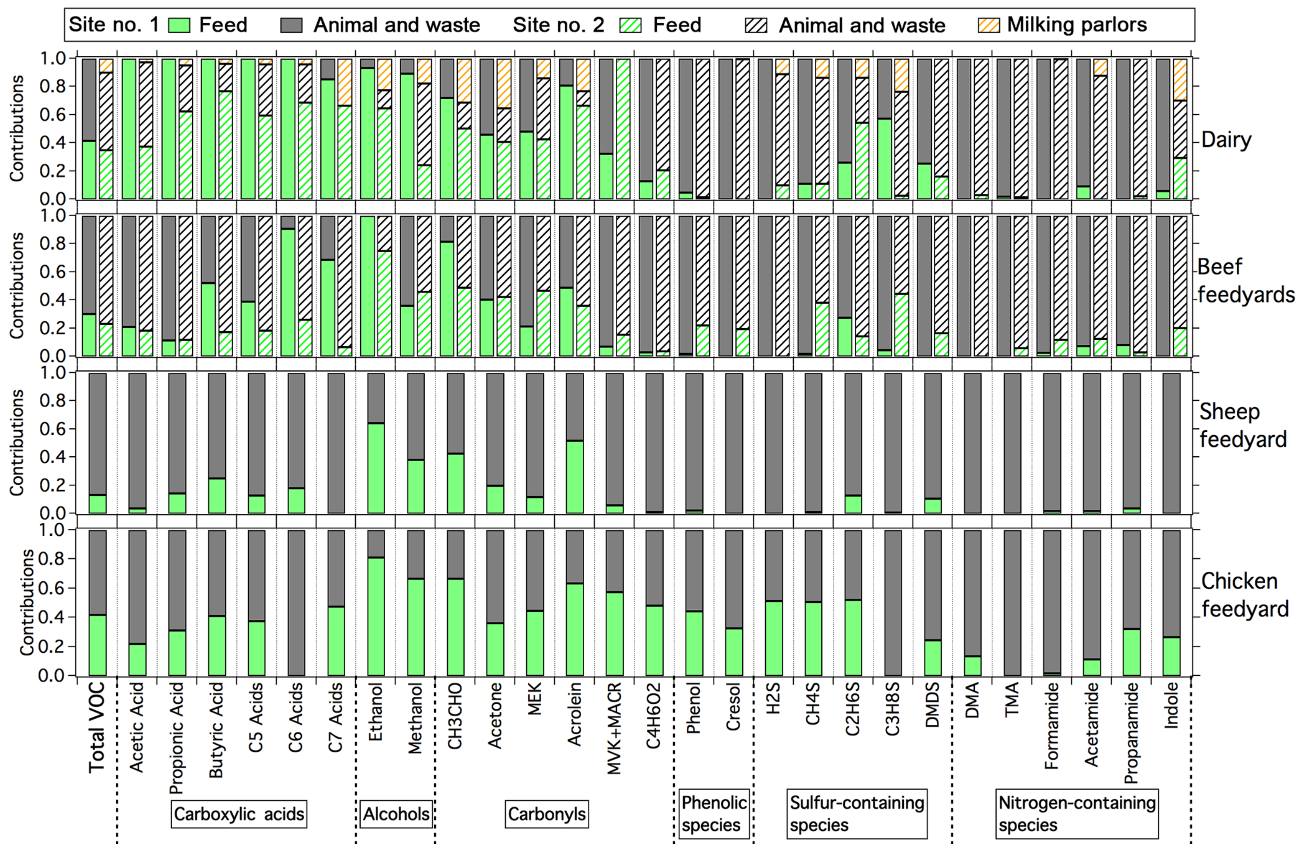

Figure 4. The relative contributions of feed storage+handling, animal+waste and milking parlors (only for dairy farm no. 2) to emissions of different VOC species and total VOC for the investigated CAFO sites. DMDS: dimethyl disulfide; DMA: dimethylamine; TMA: trimethylamine.

erally comparable or slightly smaller than those contributions to the total VOC concentrations.

In addition to the information on relative contributions from different sources, the multivariate fit analysis also provides the emissions ratios of VOCs to NH_3 for animal+waste and emission ratios of VOCs to ethanol for both feed storage+handling and milking parlors (see Tables S3–S8). These emission ratios represent chemical "fingerprints" of the emissions from various sources. The emission ratios are summed up for the VOC classes and the fractions of each VOC class in different source emissions are determined (Fig. 5). Overall, VOC emissions from both feed storage+handling and milking parlors are dominated by alcohols, whereas the contributions of carboxylic acids and other VOC classes are significantly larger for animal+waste emissions. The VOC compositional fractions shown in Fig. 3a for each site are the weighted average of the fractions for different sources in Fig. 5.

We acknowledge that there are some limitations in separating different sources inside each facility using measurements from the mobile laboratory, which may introduce some uncertainties to the results.

1. In this study, the relative fractions of different sources to VOC emissions are determined based on snapshots of measurements when the mobile laboratory passed by the CAFO sites. The relative fractions may change over time, and may be related to operation activities within the facilities, such as feed-mixing activities in feed mill area. Nevertheless, some encouraging evidence was observed: the determined relative fractions from different sources are reasonably similar between the two beef feed yards. The agreements between the two dairy farms are not as good as for the two beef feed yards. The abovementioned observations of the emissions from milking parlors and potential differences in feed ingredients for dairy cattle, which are reflected by the discrepancies in VOC compositions emitted from feed storage+handling (Fig. 5a), could be the reasons.

2. VOCs from various sources in a CAFO site are mostly emitted at the surface. VOCs were measured on the van at a single level near-ground (∼ 3 m). However, the plumes from CAFOs become deeper as they are transported downwind, and VOC concentrations are vertically diluted by background air due to turbulent mixing.

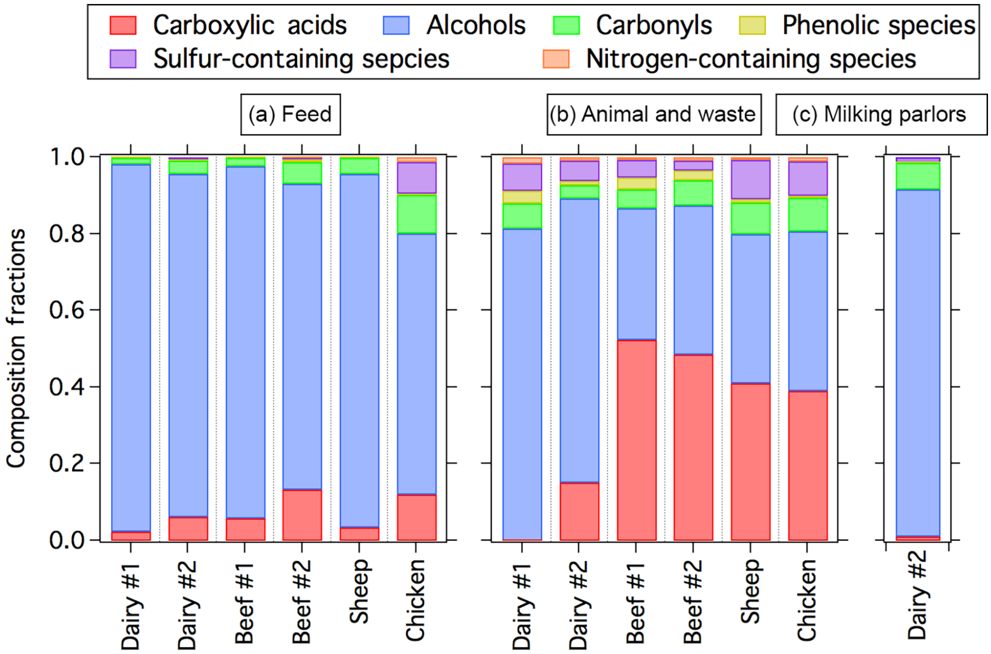

Figure 5. The relative contributions of each VOC class to emissions from feed storage+handling **(a)**, animal+waste **(b)** and milking parlors **(c)**.

As shown in Figs. 1–2 (and Figs. S2–S3), the feed mills and milking parlors at the sites studied in this work are located nearby public roads, and their contributions may be somewhat overestimated as a result.

3.4 Aircraft measurements

Time series of NH_3 and several VOCs inside two agricultural plumes in northeastern Colorado measured on 13 April 2015 from the NOAA WP-3D during the SONGNEX campaign are shown in Fig. 6. Large enhancements of NH_3 were observed in the two agricultural plumes, although the peak concentrations were a factor of ~ 10 lower than those from mobile laboratory measurements. VOC species, including acetic acid, propionic acid and ethanol, were also clearly elevated in the two plumes. As the aircraft was further away from the CAFOs, the emissions from different sources inside CAFO facilities have been well mixed prior to sampling. Thus, separation of the VOCs sources from different parts of the operations occurring within the facilities is not possible using aircraft measurements.

Figure 7a shows scatter plots of acetic acid versus NH_3 from the three flights over northeastern Colorado during the SONGNEX campaign. The correlation between acetic acid and NH_3 is strong for all of the three flights ($R =$ 0.81–0.87). Two different enhancement ratios of acetic acid to NH_3 were observed from aircraft measurements, which are close to the determined emission ratios from beef feed yards ($30.2 \pm 5.5 \times 10^{-3}$ ppb ppb^{-1}) and dairy farms ($6.4 \pm 0.6 \times 10^{-3}$ ppb ppb^{-1}) from mobile laboratory measurements, respectively. It implies that the enhancement ratios of acetic acid to NH_3 may be used as an indicator for emissions from different animal types. The relative contributions to NH_3 enhancements between dairy and beef cattle can be estimated based on data in Fig. 7a. The fractional contributions to NH_3 enhancements from beef cattle are estimated in the range of 0.71–0.98 based on the three SONGNEX flights (28 March: 0.98 ± 0.01; 29 March: 0.71 ± 0.11; 13 April: 0.96 ± 0.02). Combining the three SONGNEX flights in northeastern Colorado, beef cattle contribute 90 ± 4 % of measured NH_3 enhancements on these flights. This evidence suggests that beef cattle are more important for NH_3 emission from CAFOs in northeastern Colorado.

The enhancement ratios of other VOC species relative to NH_3 are also calculated from aircraft measurements and they are compared with those from mobile laboratory measurements in Fig. 7b. The determined enhancement ratios of carboxylic acids and alcohols compare well between aircraft and mobile laboratory measurements. The enhancement ratios of acetone and acetaldehyde to NH_3 are more scattered in aircraft measurements, as the agricultural plumes contributed only small enhancements of these species over a high background. The enhancement ratios of phenol, cresol, CH_3SH and DMS to NH_3 from aircraft measurements are lower than those from mobile laboratory measurements. The measured concentrations of these species from aircraft measurements were low. The signals of these species were only slightly higher than instrument noise levels at higher concentrations

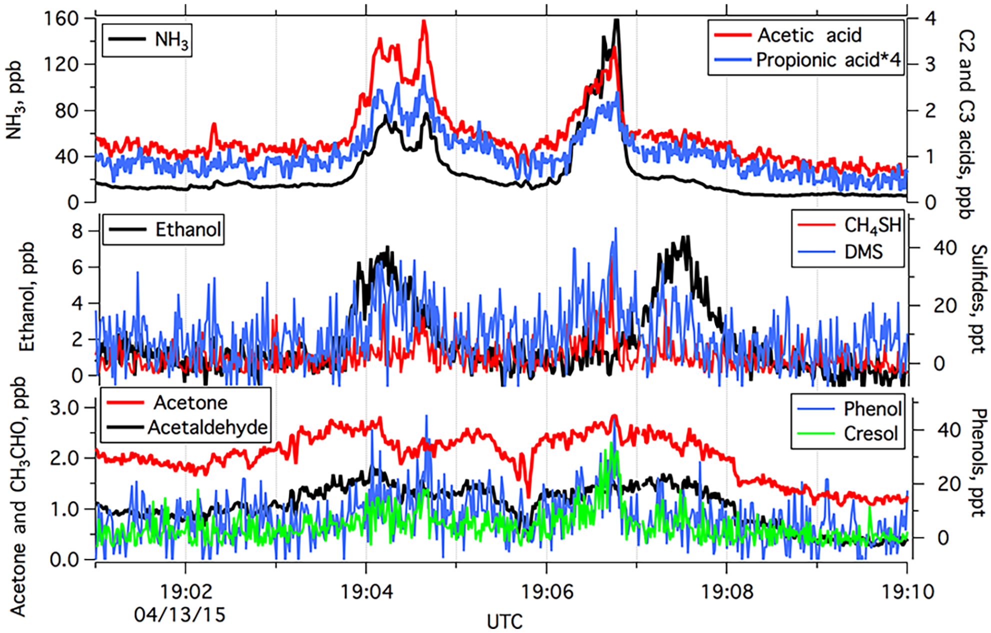

Figure 6. Time series of NH_3 and various VOC species of two agricultural plumes measured from NOAA WP-3D on 13 April 2015 during the SONGNEX campaign.

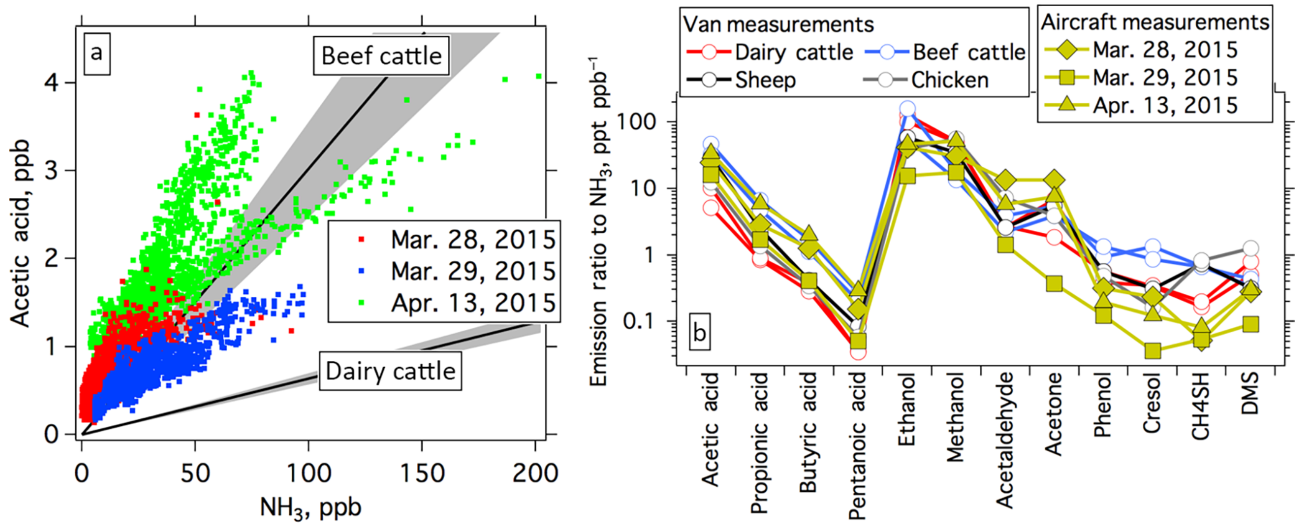

Figure 7. **(a)** Scatterplot of acetic acid versus NH_3 from the three SONGNEX flights in northeastern Colorado. The two black lines and gray-filled areas indicate emission ratios of acetic acid to NH_3 from beef feed yards and dairy farms determined from the mobile laboratory measurements, respectively. **(b)** Comparison of enhancement ratios of VOCs to NH_3 between mobile laboratory and aircraft measurements in northeastern Colorado.

range of NH_3 (~ 150 ppb; see example in Fig. 6), but not detectable in many plumes with lower NH_3 concentrations.

4 Conclusions

In this study, we measured downwind air to discern VOC emissions from CAFOs in northeastern Colorado using both mobile laboratory and aircraft measurements. We show that carboxylic acids and alcohols dominate VOC emissions from CAFOs, whereas sulfur-containing species and phenolic species are important to the odor activity values and NO_3 reactivity of CAFO emissions, respectively. VOC compositions of CAFO emissions determined from mobile laboratory and aircraft measurements are in good agreement. Based on mobile laboratory measurements of CAFO sites, NH_3 emissions are mainly from animals and their waste, whereas ethanol is predominately from feed storage and handling. We applied a multivariate linear regression method to apportion the relative fractions from the two sources using NH_3 and ethanol as tracers. The determined fractions between the two sources are different among various VOC species and animal types. In general, phenolic species and nitrogen-containing species are mainly associated with emissions from animals and their waste for the investigated CAFOs. Significant contributions from feed storage and handling are observed for carboxylic acids, alcohols and carbonyls. We also proposed that ambient enhancement ratios of acetic acid to NH_3 may be used as an indicator to separate CAFO emissions from different animal types.

Data availability. Data from measurements on the aircraft is available at https://www.esrl.noaa.gov/csd/groups/csd7/measurements/2015songnex/. Data from the mobile van is available upon request to the corresponding author (Bin Yuan).

The Supplement related to this article is available online at doi:10.5194/acp-17-4945-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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