Response to reviewers' comments

Reviewer #1:

Greetings, I have enjoyed reading this manuscript, and comparing it to previous publications in the field. Although the aircraft data were regional, the team has been successful discerning the CAFO emissions/VOCs from other sources. And although the road-passage measurements were only conducted once per site, good weather conditions were found (or selected!) and the results convincing. It is nice to see general agreement from the two approaches. There are several places in the ms where I would suggest careful re-editing to correct minor mistakes, grammar, and/or clarify. Some examples follow:

Reply: We would like to thank the reviewer for his/her work and nice comments. Please find the response to individual comments below.

line 28 'contributions to in the odor'

Reply: Corrected.

line 94 should clarify that measurements were only once per CAFO

Reply: Changed as the reviewer's suggestion. Please note that we performed downwind measurements twice for the dairy farm #2, beef feed yard #2 and the chicken house. The duplicated measurements usually agreed well. The last sentence of the paragraph is changed to: *We added a new VOC instrument to the payload, and performed mobile measurements in winter time (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.*

line 97 is a run-on sentence

Reply: Corrected. The sentence is changed to "*Here, we provide a brief description of the instrument (see details in Yuan et al., 2016).*"

line 128 provide formulas for chemicals at first mention

Reply: Chemical formulas are provided in the revised manuscript.

line 128 'around' is imprecise; 'along the downwind flanks' might be better

Reply: We decide to keep using "around", as measurements were conducted for the upwind flanks of the facility as well.

line 137 since there was no access to the facilities, 'waste may be largely' and near here it should be stated that 'waste cleaning time/practices are unknown'
Reply: Changed according to the comment.

line 147 'spatial distribution based on the variation observed (over a short time span of several minutes) while measuring along the downwind flanks' [I know this is 'wordy', but time variations implies watching a source as it varies over time (e.g. in the course of a day, from day to day, season to season, etc...)
Reply: Changed as the suggestion from the reviewer.

line 152 (although not known specifically here)
Reply: The statement is added in the revised manuscript.

line 166 needs a reference
Reply: A webpage is cited in the revised manuscript.

line 228 state estimated dilution(s), based on distance, and how much it varies across these data sets
Reply: We add a short sentence in the end of the paragraph: "(see example in section 3.4 for aircraft measurement results associated with a factor of ~10 lower concentrations than those from mobile laboratory)".

lines 263-4 plus or minus how much
Reply: The uncertainties from the multi-variate fits are shown in the revised manuscript.

line 269 provide wind speed means
Reply: The means of measured wind speeds are provided in this sentence.

line 291 separating
Reply: Corrected.

line 316 prior to sampling

Reply: Corrected.

line 321 'strong' should be enumerated

Reply: Correlation coefficients are provided in the revised manuscript.

lines 331-2 list numbers of each, as best as is known

Reply: The numbers for each flight are included in the revised manuscript.

lines 341-4 grammar hard to follow long sentence

Reply: The long sentence is divided into two sentences in the revised manuscript.

line 346 'measured downwind air to discern VOC...'

Reply: Changed in the revised manuscript.

Reviewer #2

In this study, Yuan and his colleagues measured the emissions of different VOCs, along with methane and ammonia, from CAFOs of northeastern Colorado through two methods: mobile laboratory and aircraft measurement. The high time-resolution measurements allowed the authors to identify different sources of VOCs within the CAFOs. They found ethanol was mainly from feed storage and handling while NH3 predominately came from animals and their waste. A multivariate regression analysis was conducted to determine the relative importance of these two sources for different VOC species. The contributions of different VOCs to odor activity, NO3 reactivity, and OH reactivity were also investigated. The study was interesting and the result was well presented. However, the reviewer would recommend the authors make the following edits before the manuscript can be reconsidered for publication:

Reply: We would like to thank the reviewer for his/her work and helpful comments. Please find the response to individual comments below.

Line 33-34 "emissions of ethanol concentrations". Concentrations can't be emitted. I would recommend changing it to "concentration of emitted ethanol" or "concentrations of ethanol emissions".

Reply: We change to "emissions of ethanol" in the revised manuscript.

Line 85-86 Should be "within the facilities that contribute to VOC emissions".
Reply: Corrected.

Figure 2 For the upper left figure, the number labeling of the time of measurement (1,2,3,4) should be on the same side of the road for easy reading. On the current figure, 1 was put on one side of the road, while 2 and 3 were put on the other. I had a hard time finding the location of time point 1 while first reading the manuscript.
Reply: The graph has been changed according to the reviewer's suggestion.

Line 226-228 The authors stated that "We note that OAV, OH and NO3 reactivity are measured along the fence line and they decrease rapidly with downwind distance and dilution." If the authors have data to support such a statement, please put them in the manuscript. Otherwise, please indicate "(data not shown)" at the end of the sentence.
Reply: Based on the comments from both reviewers, we add a short sentence in the end of the paragraph: "*(see example in section 3.4 for aircraft measurement results associated with a factor of ~10 lower concentrations) than those from mobile laboratory*".

Line 234 Is it possible to separate the VOCs from animal exhalation and animal waste?
Reply: The emissions from animal exhalation and animal waste should be able to be separated from measurements performed for a longer time period (e.g. days or weeks) in a CAFO facility, using potential different time variations of the two emissions (e.g. waste removal practices), as demonstrated in the study of Sintermann et al. (2014). However, this type of data is not available in this study. We added a sentence here to reflect this discussion: "*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).*"

Figure 4 On the top graph, there seem to be pretty high discrepancies on the sources of VOCs for the two dairy farms, especially for carboxylic acids, alcohols, and carbonyls. Are there any explanations for that?

Reply: We thank the reviewer for the comment. We notice that there are differences in the relative fractions of the sources for some VOCs between the two dairy farms, notably carboxylic acids, methanol and carbonyls (Figure 4). We do not know the exact reason for this.

There are some further observations that may help to understand this: (1) We did not observe an emission plume that can be clearly attributed to emissions from the milking parlor for the dairy farm #1. The emissions from the milking parlor may be well-mixed with those from feed before detection. Therefore, some of the fractions of feed emissions for the dairy farm #1 in Figure 4 may be contributed by emissions from milking parlor. Considering this, the differences for carbonyls would be not large, if the feed fractions in the dairy farm #1 with feed+milk parlor for the dairy farm #2 are compared. (2) We also observed some differences in the site-averaged VOC compositions (Figure 3A) and the determined VOC compositions of source emissions (Figure 5) between the two dairy farms. The differences in the determined VOC compositions from feed emissions imply that ingredients in cattle feed may be also different in the two dairy farms.

With the above discussion in consideration, we added a sentence in the fourth paragraph of section 3.1 in the revised manuscript:

It is worth noting that we did not distinctly observe emissions from the milking parlor in the dairy farm #1, which were potentially mixed with emissions from feed prior to sampling.

We also added a sentence in the last but one paragraph of section 3.3 in the revised manuscript:

The agreements between the two dairy farms are not as good as for the two beef feed yards. The above mentioned 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 (Figure 5A), could be the reasons.

Ling 265-268 The authors claimed that the reason for feed+handling played a major role in VOC emission of VOCs in Chicken farms was because "Chickens were raised in production houses and emissions of NH3 and VOCs may be treated when in-house air was ventilated out". Are there any supporting evidences for such a claim, like a detailed layout of the chicken farm to prove that such treatment does exist?

Reply: As mentioned in the manuscript, we had no access to the facility. The satellite images of the chicken house from Google Earth are not clear enough to locate potential odor mitigation

installations. Thus, we do not have evidence to prove that pollutant treatment does exist in this facility. However, we found through a news report that the chicken house uses a manure belt system to manage manure. For manure belt systems, chicken waste is frequently transported to a separated location for storage. The emissions of NH_3 from the chicken houses with manure belt systems were reported to be much lower than facility without manure belt system (Wood et al., 2015). We changed this paragraph to reflect this new information:

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 separated location for storage. The chicken houses with manure belt system 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, Figure S3) at this site compared to other 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) than others (4.7-5.5 m/s). It is also possible that emissions of NH_3 and VOCs were treated when in-house air was ventilated out (Wang et al., 2010).

Line 324-325 The authors stated that "the enhancement ratios of acetic acid to NH3 may be used as an indicator for emissions from different animal types" based on the observation on known beef feed yards and dairy farms. Have the authors tested this hypothesis on other CAFOs in the region that were covered by the aircraft measurement to support this claim, if the locations of other CAFOs in the region were known?

Reply: Identification of the plumes from individual facilities was difficult from aircraft measurements during SONGNEX, as the emissions have been mixed prior to sampling. We can only attribute three plumes to one single facility with known animal type, which happened to be the beef cattle feed yard #2 sampled by mobile laboratory as well. Note that the beef cattle feed yard #2 is one of the largest CAFO facilities in the area (Table S1). The enhancement ratio of acetic acid to NH_3 (33.2×10^{-3} ppb/ppb) derived from the three plumes agreed very well with that from mobile measurements (32.5×10^{-3} ppb/ppb). Unfortunately, we do not have information for other CAFO facilities in this region to validate our statement.

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References:

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Wang, L., Oviedo-Rondón, E. O., Small, J., Liu, Z., Sheldon, B. W., Havenstein, G. B., and Williams, C. M.: Farm-Scale Evaluation of Ozonation for Mitigating Ammonia Concentrations in Broiler Houses, Journal of the Air & Waste Management Association, 60, 789-796, 10.3155/1047-3289.60.7.789, 2010.

Wood, D., Cowherd, S., and Van Heyst, B.: A summary of ammonia emission factors and quality criteria for commercial poultry production in North America, Atmospheric Environment, 115, 236-245, 10.1016/j.atmosenv.2015.05.069, 2015.

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

Bin Yuan[1,2], Matthew M. Coggon[1,2], Abigail R. Koss[1,2,3], Carsten Warneke[1,2], Scott Eilerman[1,2], Jeff Peischl[1,2], Kenneth C. Aikin[1,2], Thomas B. Ryerson[1], Joost A. de Gouw[1,2,3]

1. NOAA Earth System Research Laboratory (ESRL), Chemical Sciences Division, Boulder, CO, USA

2. Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA

3. Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, CO, USA

Correspondence to: Bin Yuan (yuanbin501@gmail.com)

Manuscript prepared for ***Atmospheric Chemistry and Physics***

Deleted: bin.yuan@noaa.gov

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) that 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 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.

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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;Howard et al., 2010b;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, 2016) 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;Hobbs et al., 2004). *Ngwabie et al.* (2007;2008) reported that VOC concentrations in dairy, sheep and pig CAFOs were 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

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80 offline analytical methods (Filipy et al., 2006;Alanis et al., 2008;Sun et al., 2008;Chung

81 et al., 2010;Ni et al., 2012). VOCs were collected on filters, or in canisters and cartridges

82 and were quantified in the laboratory using various methods (see reviews in Ni et al.,

83 2012). These offline methods are labor-intensive, which limits the number of VOC

84 samples. Online fast measurement techniques (mainly proton-transfer reaction mass

85 spectrometers, PTR-MS) allow for more detailed investigation of CAFO facilities (Shaw

86 et al., 2007;Ngwabie et al., 2008;Sintermann et al., 2014). The previous online

87 measurements usually used a single stationary sampling inlet either inside a stall or at a

88 fence line, which does not provide spatial distribution information for VOCs in the

89 facilities.

90   In this study, we deployed a high time-resolution instrument on board a mobile

91 laboratory driven on public roads and a NOAA WP-3D research aircraft to measure

92 VOCs downwind of CAFO facilities. We will use this dataset to characterize chemical

93 compositions of VOC emissions and explore different sources within the facilities that

94 contribute to VOC emissions.

2. Experiments

96   Mobile laboratory measurements were conducted near Greeley in northeastern

97 Colorado, US. Six different CAFOs were studied, including two dairy farms, two beef

98 feed yards, one sheep feed yard and one egg-laying chicken farm (Table S1). Among the

99 six CAFOs, emissions of NH_3, N_2O and CH_4 in four facilities (the two dairy farms, one

100 beef cattle feed yard and the sheep feed yard) have been measured previously using an

101 instrumented van (Eilerman et al., 2016). We added a new VOC instrument to the

102 payload, and performed mobile measurements in winter time (February, 2016) for the six

103 CAFOs by sampling at their downwind flanks 1-2 times for each facility. Duplicated

104 measurements at the same facilities agreed well.

105   VOCs were measured using a hydronium ion time-of-flight chemical-ionization

106 mass spectrometer (H_3O^+ ToF-CIMS) instrument on the mobile laboratory. Here, we

107 provide a brief description of the instrument (see details in Yuan et al., 2016). VOCs are

108 ionized by H_3O^+ ions in a drift tube, similar to a PTR-MS (de Gouw and Warneke, 2007).

109 The protonated product ions are detected using a high-resolution time-of-flight (ToF)

110 analyzer (Tofwerk AG) (m/Δm=4000-6000). A number of VOC species were calibrated

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115 using either gravimetrically prepared gas cylinders or permeation tubes (see details in

116 Yuan et al., 2016). VOC background signals in the instrument were determined by

117 passing ambient air through a catalytic converter. The detection limits are compound-

118 dependent and range between 10-100 ppt for most VOC species at a time resolution of 1

119 s. Besides VOCs, two inorganic species, NH_3 and H_2S, were measured at m/z 18.034

120 (NH_4^+) and m/z 34.995 (H_3S^+) using the H_3O^+ ToF-CIMS, respectively (Li et al.,

121 2014;Müller et al., 2014).

122   In addition to the H_3O^+ ToF-CIMS, a cavity ringdown spectrometer (CRDS)

123 instrument (Picarro G1301m) measuring methane (CH_4) and carbon dioxide (CO_2) and an

124 off-axis integrated cavity output spectrometer (OA-ICOS, Los Gatos Research)

125 measuring nitrous oxide (N_2O) along with carbon monoxide (CO) were deployed during

126 the mobile laboratory measurements. Measurements of ambient temperature, relative

127 humidity, wind direction, wind speed and vehicle location were performed using

128 meteorological sensors (R.M. Young 85004 and AirMax 300WX) and a GPS compass

129 system (ComNav G2B). A summary of meteorological conditions during the mobile

130 laboratory measurements is shown in Table S2.

131   Measurements of agricultural plumes were also performed using the NOAA WP-3D

132 research aircraft in March-April, 2015 during the Shale Oil and Natural Gas Nexus

133 (SONGNEX) campaign. Data from three flights (March 28, March 29, April 13) over

134 northeastern Colorado are used in this study. VOCs were measured using the same H_3O^+

135 ToF-CIMS instrument as mobile measurements (Yuan et al., 2016). Another chemical

136 ionization mass spectrometer (CIMS) was used to detect NH_3 during SONGNEX (Nowak

137 et al., 2007). Due to background issues and lower concentrations, NH_3 signals were not

138 retrievable from H_3O^+ ToF-CIMS during the SONGNEX campaign.

3. Results and Discussions

3.1. Spatial distributions from mobile laboratory measurements

141   Figure 1 shows measured concentrations of NH_3, CH_4, CO_2, N_2O, ethanol (C_2H_5OH),

142 acetic acid (CH_3COOH) and acetone (CH_3COCH_3) around a beef feed yard (beef #1). The

143 concentrations of the seven species were enhanced and highly variable downwind of the

144 facility. Different time variations for the seven species were clearly observed. NH_3

145 concentrations peaked at around 13:46 local time (LT) and the peak location was

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146 northwest of this facility, directly downwind of the animal pens. This is consistent with

147 fresh waste of animals (urine and feces) as the main source of NH_3 within a CAFO

148 facility (Hristov et al., 2011). CO_2 and CH_4 are emitted from animal respiration and

149 eructation of the cattle (Shaw et al., 2007;Sintermann et al., 2014;Owen and Silver,

150 2015). CO_2 (R=0.77) and CH_4 (R=0.77) correlated well with NH_3 between 13:42-13:46

151 when NH_3 was high. These observations reflect the fact that animals and their fresh waste

152 may be largely co-located in the animal pens. But, waste cleaning time/practices in the

153 facility were unknown, owing to no access to the facility. Previous mobile and aircraft

154 measurements have also observed enhancements of NH_3 and CH_4 concentrations

155 downwind of animal pens in cattle feedlots (Miller et al., 2015;Hacker et al., 2016). The

156 time variations of two VOCs, acetic acid and acetone, followed reasonably well with both

157 NH_3 and CO_2, suggesting that animals and their waste contributed to the enhancements of

158 the two VOCs. Based on previous studies, the emissions from animal respiration should

159 dominate over waste for acetone, and vice versa for acetic acid (Ngwabie et al.,

160 2008;Sintermann et al., 2014). The similar time variations of NH_3, CO_2, acetone and

161 acetic acids (and less clearly for CH_4) imply that the co-located emissions from animals

162 and their waste may not be separated based on the variations observed (over a short time

163 span of several minutes) while measuring along the downwind flanks.

164   A single, narrow high concentration spike (up to 1 ppm) of ethanol was observed

165 around 13:44 LT (Figure 1). The hotspot of ethanol was located downwind of a feed mill

166 at the west side of the feed yard, indicating that the feed mill and its related activities can

167 emit large amounts of ethanol. Distillers grains, a fermented by-product from ethanol

168 production, are commonly used as an ingredient of feed in beef cattle feed yards (Raabe,

169 2012) (although not known specifically here). Therefore, it is not surprising to observe

170 large emissions of ethanol in the feed mill area. High concentrations of many other VOC

171 species (e.g. acetic acid and acetone) were observed in the feed mill plume, whereas NH_3,

172 CH_4 and N_2O were not enhanced. Combustion sources, possibly due to equipment

173 operation in the feed mill area, are likely responsible for the enhancement of CO_2 and CO

174 at ~13:44 LT. VOC emissions from these combustion plumes are negligible (see details

175 in SI, Figure S1).

176   Measurements downwind of a dairy farm (dairy #1) are shown in Figure 2. The

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180 highest concentrations of NH_3 and CO_2 were observed downwind of the animal pens,

181 similar to the beef feed yard shown in Figure 1. Interestingly, several high concentration

182 peaks of ethanol were observed along the drive track of the mobile laboratory. These

183 peaks were in close proximity or downwind of the feed lanes (white lines on the satellite

184 image, Figure 2B). As shown for beef #1, feed mills can be an important source of

185 ethanol and other VOCs. Different from the usage of distillers grains in beef cattle feed

186 yards, silage is more commonly used as fodder for dairy cattle (Raabe, 2012). Previous

187 studies showed that ethanol is the most abundant VOC species emitted from feed silage

188 (Hafner et al., 2013). It is expected that VOCs will continue evaporating from the feed

189 mixtures after the feed is delivered to the feed lanes. Time variations of acetic acid (and

190 acetone) correlated more closely with ethanol (R=0.72) than with NH_3 (R=-0.30) and CO_2

191 (R=-0.14), which differs from the beef feed yard. This suggests that the three VOCs were

192 mainly from emissions of feed lanes, rather than animals and their waste in this dairy

193 farm.

194   In addition to animals and their waste (referred to as animal+waste hereafter) and

195 feed storage and handling (referred to as feed storage+handling hereafter), we identified

196 another important VOC source from the other dairy farm studied (dairy #2, Figure S2).

197 High concentrations of ethanol, acetone, dimethyl sulfide (DMS, C_2H_6S) and CH_4 were

198 observed downwind of three milking parlors. Acetic acid was only moderately elevated,

199 whereas NH_3 was not enhanced. Compared to feed storage+handling, emission

200 compositions from the milking parlors are different. The emissions from milking parlors

201 might result from several sources, including animal exhalation and milking-related

202 activities. It is worth noting that we did not distinctly observe emissions from the milking

203 parlor in the dairy farm #1, which were potentially mixed with emissions from feed prior

204 to sampling.

205   The measurements downwind of three other CAFO sites (beef #2, the sheep feed

206 yard and the chicken house) are investigated in a similar way, as shown in Figure 1-2

207 (and Figure S2-S3). From this analysis, we identify three main VOC emission sources in

208 animal feeding facilities, namely animal+waste, feed storage+handling and milking

209 parlors. These measurements suggest that combustion sources are not important for VOC

210 emissions in these facilities.

3.2. VOC chemical compositions of different CAFOs

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212   The enhancements of VOCs downwind of each CAFO were integrated to determine

213   the averaged VOC compositions for each facility (Figure 3). The measured VOC species

214   are divided into six different groups, namely carboxylic acids, alcohols, carbonyls,

215   phenolic species, nitrogen- and sulfur-containing species. The averages of the sum of

216   measured VOC concentrations downwind of the sites are in the range of 22-139 ppb, with

217   higher concentrations at dairy farm #1 and the two beef feed yards (wind speeds during

218   the measurements were similar except at the chicken house, Figure 3E and Table S1). As

219   demonstrated in Figure 3A, alcohols (55-87%, mole fractions) and carboxylic acids (4-

220   32%) represent major classes of VOC from these CAFOs. Other VOC classes account for

221   8-21% of VOC concentrations in total.

222   As discussed in Section 1, VOC emissions from CAFOs can contribute to

223   unpleasant odor problems and ozone formation. We utilize odor activity value (OAV)

224   and the OH and NO_3 reactivity to evaluate the relative contribution of each VOC class to

225   the two environmental effects, respectively. The dimensionless OAV is estimated from

226   VOC concentrations divided by the species' single compound odor thresholds (SCOT)

227   ($OAV_i=C_i/SCOT_i$) (Feilberg et al., 2010;Parker et al., 2010;Woodbury et al., 2015). The

228   reported SCOT values in the literature are highly variable and we use the geometric

229   means of literature values for each compound, as compiled in Parker et al. (2010). The

230   averaged total OAVs from all measured VOCs are in the range of 0.8-5.5 at different

231   sites (Figure 3B). Sulfur-containing species contribute the largest fractions (51-91%) to

232   total OAVs at different sites, followed by phenolic species (6-37%) and carboxylic acids

233   (3-11%). The relative contributions of different species to OAV agree well with previous

234   estimates based on measurements from a beef feed yard (Woodbury et al., 2015).

235   OH reactivity (OHR) and NO_3 reactivity (NO3R) are determined as the products of

236   VOC concentrations and the respective reaction rate constants of VOCs with the two

237   oxidants (Atkinson et al., 2006) ($OHR_i= C_i \times k_{OH,i}$; $NO3R_i=C_i \times k_{NO3, i}$). The averaged OH

238   reactivities range between 1-10 s^{-1}, which is comparable or lower than the typical OH

239   reactivity observed in urban areas (a few s^{-1} to 50 s^{-1}) (Yang et al., 2016). Alcohols are the

240   largest contributors (40-75%) to OH reactivity at the sites, although the fractions from

241   carbonyls, phenolic and sulfur-containing species are also significant (Figure 3C). These

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242 results are generally consistent with the finding that ethanol accounts for the majority of

243 ozone formation potential of VOC emissions from a dairy farm (Howard et al., 2008).

244 The averaged NO_3 reactivities range from 0.02 to 0.26 s^{-1}, which are remarkably higher

245 than in urban areas (usually <0.01 s^{-1}) (Tsai et al., 2014;Brown et al., 2016). In contrast to

246 the OH reactivity, phenolic species account for the largest fractions (66-90%) of the NO_3

247 reactivity for all of the sites, with remaining contributions primarily from sulfur- and

248 nitrogen-containing species (Figure 3D). We note that OAV, OH and NO_3 reactivity are

249 measured along the fence line and they decrease rapidly with downwind distance and

250 dilution (see example in section 3.4 for aircraft measurement results associated with a

251 factor of ~10 lower concentrations than those from mobile laboratory).

252 **3.3. Relative importance of different sources for VOC emissions**

253   As shown in section 3.1, ethanol was primarily emitted from feed storage+handling

254 (and milking parlors), whereas NH_3 and CO_2 were attributed to emissions from animals

255 and their waste. This suggests that these species can be used as tracers to separate the

256 emissions from sources. However, there are two issues that need to be considered: (1)

257 Emissions of animal exhalation and waste are largely co-located in the animal pens. As

258 CO_2 is also emitted from combustion sources (see details in SI) and animal exhalation is

259 only important for a few species (e.g. acetone), NH_3 will be used as a tracer for the

260 emissions from animals and their waste. It is worth mentioning that long-term

261 measurements in CAFO facilities could permit separation of the two co-located sources

262 (see example in Sintermann et al., 2014). (2) There is some ethanol attributable to

263 animal+waste emissions that needs to be accounted for. Ethanol concentrations solely

264 from feed emissions ($[C_2H_5OH]_{Feed}$) can be calculated by subtracting the contribution of

265 ethanol by animal+waste from measured ethanol concentrations (see details in SI, Figure

266 S4).

267   After correcting ethanol for animal+waste emissions, the contributions of emissions

268 from feed storage+handling and animal+waste to measured VOC enhancements at each

269 individual site can be determined using multivariate linear fits to $[C_2H_5OH]_{Feed}$ and NH_3

270 concentration ($[NH_3]$).

271     $$[VOC] = ER_{C_2H_5OH} \times [C_2H_5OH]_{Feed} + ER_{NH_3} \times [NH_3] + [bg] \qquad Eq. (1)$$

272   Here, $[VOC]$ and $[bg]$ are measured concentrations of the VOC species and the

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273 background concentration outside the CAFO plumes, respectively. $ER_{C_2H_5OH}$ and ER_{NH_3}

274 are the emission ratios of the VOC species relative to ethanol and NH_3 from the

275 emissions of feed storage+handling and animal+waste, respectively. Along with $[bg]$, the

276 emission ratios are determined from the multivariate linear fits.

277   Based on the fitted parameters from Eq. 1 (and Eq. S3 for dairy farm #2), the relative

278 contributions of different sources to the enhancements of various VOC species can be

279 calculated for the investigated sites (Figure 4). In general, large differences in fractional

280 contributions to VOC enhancements exist among both different VOC species and

281 different animal types. The main findings from Figure 4 are:

282 (1)   Phenol, cresols, butanediones and many nitrogen-containing species are primarily

283 associated with animal+waste emissions for the investigated sites.

284 (2)   Both feed storage+handling and animal+waste account for significant fractions of

285 emissions of many oxygenated VOCs and sulfur-containing species.

286 (3)   Based on the results from the dairy farm #2, emissions from milking parlors

287 contribute significantly to the enhancements of a limited number of VOC species,

288 including ethanol ($23\pm1\%$), acetone ($35\pm3\%$), acetaldehyde ($31\pm3\%$), methanol ($18\pm3\%$),

289 MEK ($14\pm2\%$) and DMS ($14\pm2\%$).

290 (4)   Feed storage+handling plays important roles in the emissions of many VOC

291 species from the chicken farm. Based on a news report on the facility, a manure belt

292 system is used to manage manure in this facility. The manure belt system catches the

293 excreta from chicken to transport manure to a separate location for storage. The chicken

294 houses with manure belt usually lead to substantially lower emissions (e.g. NH_3) from

295 animal waste (Wood et al., 2015). It is consistent with significantly lower NH_3

296 concentrations (0-175 ppb, Figure S3) at this site compared to ruminant feed yards

297 measured in this study (0-1000 ppb), although wind speed was 36%-60% higher during

298 measurements of the chicken house (7.5 m/s) than others (4.7-5.5 m/s). It is also possible

299 that emissions of NH_3 and VOCs were treated when in-house air was ventilated out

300 (Wang et al., 2010).

301   We further determine the contributions of emissions from feed storage+handling,

302 animal+waste and milking parlors to the total VOC concentrations (first columns in

303 Figure 4, also Figure S5). Feed storage+handling emissions account for 35-41%, 23-30%,

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309 13% and 41% of the summed total VOC concentrations for the investigated dairy farms,

310 beef feed yards, the sheep feed yard and the chicken farm in this study, respectively. The

311 fractional contributions from the sources to odor activity value, OH reactivity and NO_3

312 reactivity are also calculated (Figure S5). The contributions from feed storage+handling

313 emissions to the three parameters are generally comparable or slightly smaller than those

314 contributions to the total VOC concentrations.

315   In addition to the information on relative contributions from different sources, the

316 multivariate fit analysis also provides the emissions ratios of VOCs to NH_3 for

317 animal+waste and emission ratios of VOCs to ethanol for both feed storage+handling and

318 milking parlors (see Table S3-S8). These emission ratios represent chemical

319 "fingerprints" of the emissions from various sources. The emission ratios are summed up

320 for the VOC classes and the fractions of each VOC class in different source emissions are

321 determined (Figure 5). Overall, VOC emissions from both feed storage+handling and

322 milking parlors are dominated by alcohols, whereas the contributions of carboxylic acids

323 and other VOC classes are significantly larger for animal+waste emissions. The VOC

324 compositional fractions shown in Figure 3A for each site are the weighted average of the

325 fractions for different sources in Figure 5.

326   We acknowledge that there are some limitations in separating different sources inside

327 each facility using measurements from the mobile laboratory, which may introduce some

328 uncertainties to the results.

329   (1) In this study, the relative fractions of different sources to VOC emissions are

330 determined based on snapshots of measurements when the mobile laboratory passed by

331 the CAFO sites. The relative fractions may change over time, and may be related to

332 operation activities within the facilities, such as feed mixing activities in feed mill area.

333 Nevertheless, some encouraging evidence was observed: the determined relative fractions

334 from different sources are reasonably similar between the two beef feed yards. The

335 agreements between the two dairy farms are not as good as for the two beef feed yards.

336 The above mentioned observations of the emissions from milking parlors and potential

337 differences in feed ingredients for dairy cattle, which are reflected by the discrepancies in

338 VOC compositions emitted from feed storage+handling (Figure 5A), could be the

339 reasons.

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343   (2) VOCs from various sources in a CAFO site are mostly emitted at the surface.

344   VOCs were measured on the van at a single level near-ground (~3 m). However, the

345   plumes from CAFOs become deeper as they are transported downwind, and VOC

346   concentrations are vertically diluted by background air due to turbulent mixing. As

347   shown in Figure 1-2 (and Figure S2-S3), the feed mills and milking parlors at the sites

348   studied in this work are located nearby public roads, and their contributions may be

349   somewhat overestimated as a result.

350   **3.4. Aircraft measurements**

351   Time series of NH_3 and several VOCs inside two agricultural plumes in northeastern

352   Colorado measured on April 13, 2015 from the NOAA WP-3D during the SONGNEX

353   campaign are shown in Figure 6. Large enhancements of NH_3 were observed in the two

354   agricultural plumes, although the peak concentrations were a factor of ~10 lower than

355   those from mobile laboratory measurements. VOC species, including acetic acid,

356   propionic acid and ethanol, were also clearly elevated in the two plumes. As the aircraft

357   was further away from the CAFOs, the emissions from different sources inside CAFO

358   facilities have been well mixed prior to sampling. Thus, separation of the VOCs sources

359   from different parts of the operations occurring within the facilities is not possible using

360   aircraft measurements.

361   Figure 7 (A) shows scatterplots of acetic acid versus NH_3 from the three flights

362   over northeastern Colorado during the SONGNEX campaign. The correlation between

363   acetic acid and NH_3 is strong for all of the three flights (R=0.81-0.87). Two different

364   enhancement ratios of acetic acid to NH_3 were observed from aircraft measurements,

365   which are close to the determined emission ratios from beef feed yards ($30.2\pm5.5\times10^{-3}$

366   ppb/ppb) and dairy farms ($6.4\pm0.6\times10^{-3}$ ppb/ppb) from mobile laboratory measurements,

367   respectively. It implies that the enhancement ratios of acetic acid to NH_3 may be used as

368   an indicator for emissions from different animal types. The relative contributions to NH_3

369   enhancements between dairy and beef cattle can be estimated based on data in Figure 7A.

370   The fractional contributions to NH_3 enhancements from beef cattle are estimated in the

371   range of 0.71-0.98 based on the three SONGNEX flights (March 28: 0.98±0.01; March

372   29: 0.71±0.11; April 13: 0.96±0.02). Combining the three SONGNEX flights in

373   northeastern Colorado, beef cattle contribute 90±4% of measured NH_3 enhancements on

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376 these flights. This evidence suggests that beef cattle are more important for NH_3 emission
377 from CAFOs in northeastern Colorado.
378   The enhancement ratios of other VOC species relative to NH_3 are also calculated
379 from aircraft measurements and they are compared with those from mobile laboratory
380 measurements in Figure 7B. The determined enhancement ratios of carboxylic acids and
381 alcohols compare well between aircraft and mobile laboratory measurements. The
382 enhancement ratios of acetone and acetaldehyde to NH_3 are more scattered in aircraft
383 measurements, as the agricultural plumes contributed only small enhancements of these
384 species over a high background. The enhancement ratios of phenol, cresol, CH_3SH and
385 DMS to NH_3 from aircraft measurements are lower than those from mobile laboratory
386 measurements. The measured concentrations of these species from aircraft measurements
387 were low. The signals of these species were only slightly higher than instrument noise
388 levels at higher concentrations range of NH_3 (~150 ppb, see example in Figure 6), but not
389 detectable in many plumes with lower NH_3 concentrations.

4. Conclusions

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

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Acknowledgement

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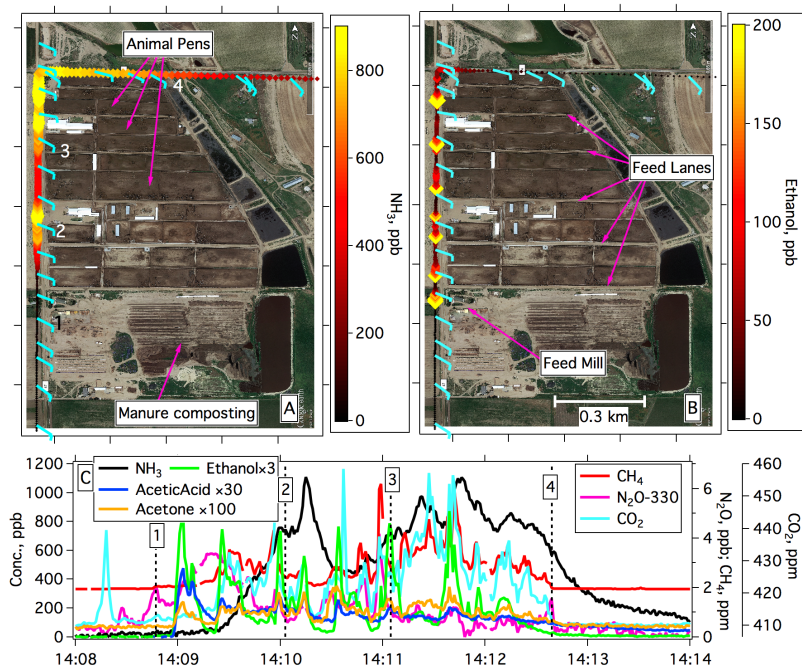
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Figures

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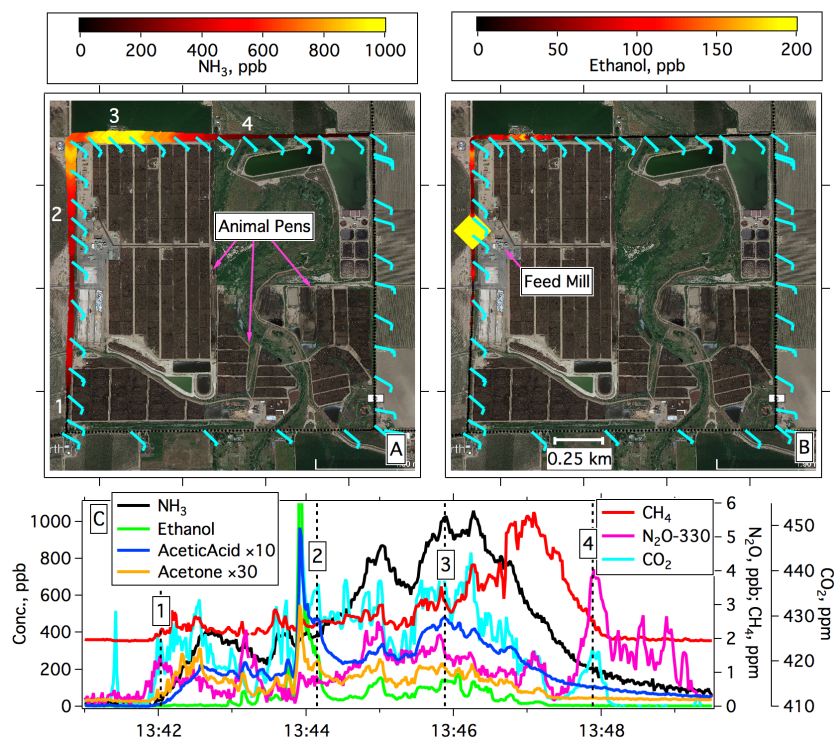
Figure 1. (A and B) Drive track of mobile laboratory color- and size-coded by NH$_3$ (A) and ethanol (B) concentrations around a beef feed yard (beef #1). The prevailing wind is shown by wind barbs (light blue flags) in the map. (C) Time series of NH$_3$, CH$_4$, CO$_2$, N$_2$O, ethanol, acetic acid and acetone measured downwind of the beef feed yard. Numbers (1-4) in (A) and (C) are used to allow alignment of the mobile laboratory locations on the map with the corresponding time series in panel C.

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Figure 2. (A and B) Drive track of mobile laboratory color- and size-coded by NH₃
(A) and ethanol (B) concentrations downwind of a dairy farm (dairy #1). The
prevailing wind is shown by wind barbs (light blue flags) in the map. (C) Time series
of NH₃, CH₄, CO₂, N₂O, ethanol, acetic acid and acetone measured downwind of the
dairy farm. Numbers (1-4) in (A) and (C) are used to allow alignment of the mobile
laboratory locations on the map with the corresponding time series in panel C.

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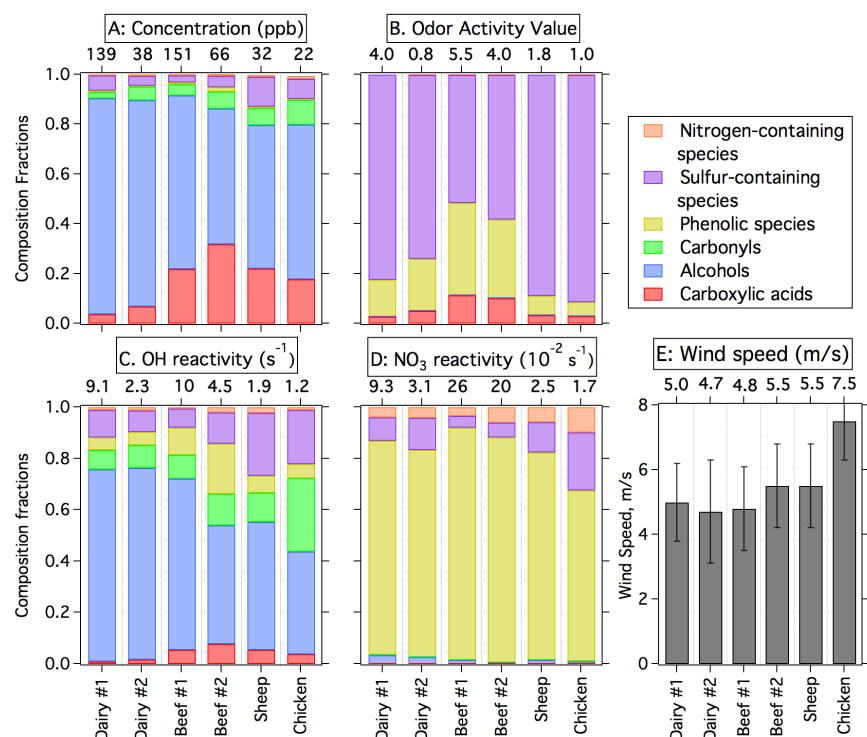
Figure 3. The fractional contributions of different VOC classes to the total VOC concentrations (A), odor activity values (B), OH reactivity (C) and NO$_3$ reactivity (D) for the six investigated CAFO sites. The mean wind speeds during the measurements of the CAFO sites are shown in (E). The mean values for the five parameters from each CAFO are shown at the top of each panel.
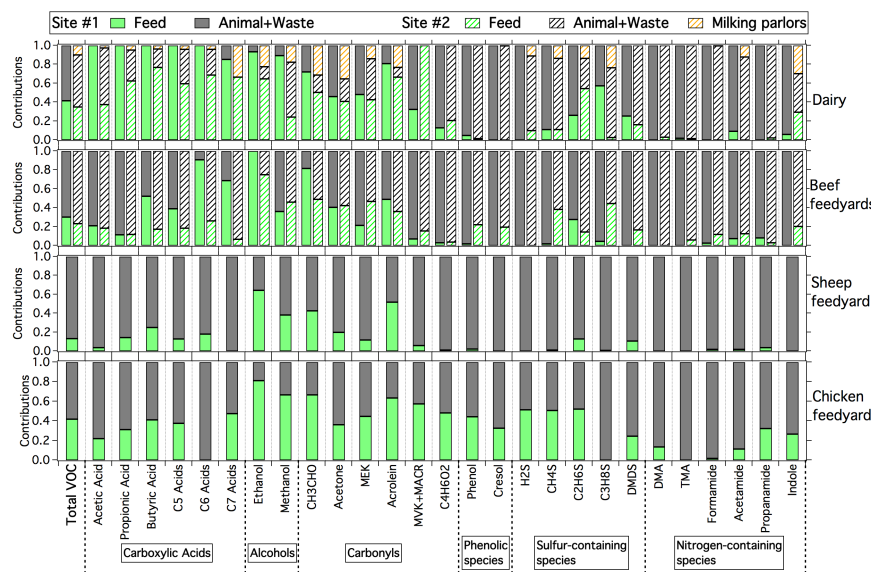
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Figure 4. The relative contributions of feed storage+handling, animal+waste and milking parlors (only for dairy farm #2) to emissions of different VOC species and total VOC for the investigated CAFO sites. DMDS: dimethyl disulfide; DMA: dimethylamine; TMA: trimethylamine.
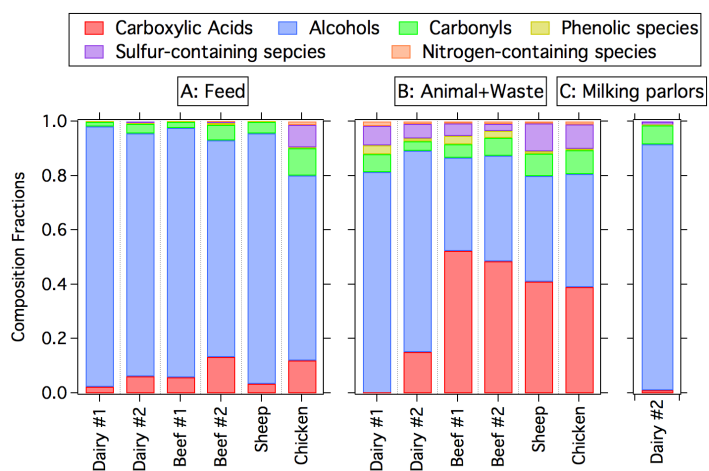
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Figure 5. The relative contributions of each VOC class to emissions from feed storage+handling (A), animal+waste (B) and milking parlors (C).
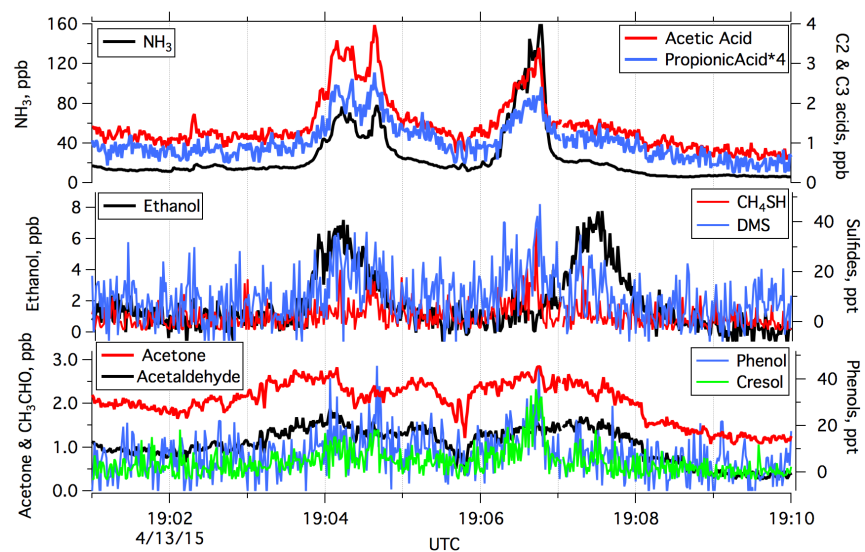
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Figure 6. Time series of NH$_3$ and various VOC species of two agricultural plumes measured from NOAA WP-3D on April 13, 2015 during the SONGNEX campaign.
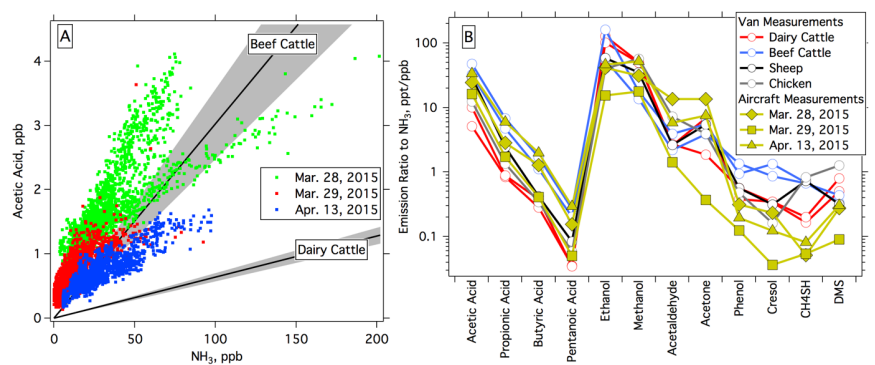
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Figure 7. (A) Scatterplot of acetic acid versus NH₃ from the three SONGNEX flights

in northeastern Colorado. The two black lines and gray-filled areas indicate

emission ratios of acetic acid to NH₃ from beef feed yards and dairy farms

determined from the mobile laboratory measurements, respectively. (B)

Comparison of enhancement ratios of VOCs to NH₃ between mobile laboratory and

aircraft measurements in northeastern Colorado.

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