1 **Emissions of volatile organic compounds (VOCs) from concentrated**

2 **animal feeding operations (CAFOs): chemical compositions and**

3 **separation of sources**

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

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.

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

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

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

75 2012). These offline methods are labor-intensive, which limits the number of VOC

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

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

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

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

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

81 facilities.

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

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

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

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

86 contribute to VOC emissions.

87 **2. Experiments**

88   Mobile laboratory measurements were conducted near Greeley in northeastern

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

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

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

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

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

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

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

96 measurements at the same facilities agreed well.

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

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

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

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

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

102 analyzer (Tofwerk AG) ($m/\Delta m=4000\text{-}6000$). A number of VOC species were calibrated

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

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

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

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

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

108   (NH_4^+) and m/z 34.995 (H_3S^+) using the H_3O^+ ToF-CIMS, respectively (Li et al., 2014;

109   Müller et al., 2014).

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

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

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

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

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

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

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

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

118   laboratory measurements is shown in Table S2.

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

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

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

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

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

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

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

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

127   **3. Results and Discussions**

128   **3.1. Spatial distributions from mobile laboratory measurements**

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

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

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

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

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

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

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

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

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

138 2015). CO_2 ($R=0.77$) and CH_4 ($R=0.77$) correlated well with NH_3 between 13:42-13:46

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

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

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

142 measurements have also observed enhancements of NH_3 and CH_4 concentrations

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

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

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

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

147 dominate over waste for acetone, and vice versa for acetic acid (Ngwabie et al., 2008;

148 Sintermann et al., 2014). The similar time variations of NH_3, CO_2, acetone and acetic

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

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

151 of several minutes) while measuring along the downwind flanks.

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

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

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

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

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

157 2012) (although not known specifically here). Therefore, it is not surprising to observe

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

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

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

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

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

163 in SI, Figure S1).

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

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

similar to the beef feed yard shown in Figure 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, Figure 2B). As shown for beef #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 #2, Figure 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 #1, which were potentially mixed with emissions from feed prior to sampling.

The measurements downwind of three other CAFO sites (beef #2, the sheep feed yard and the chicken house) are investigated in a similar way, as shown in Figure 1-2 (and Figure 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

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

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

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

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

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

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

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

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

205   32%) represent major classes of VOC from these CAFOs. Other VOC classes account for

206   8-21% of VOC concentrations in total.

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

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

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

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

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

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

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

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

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

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

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

218   (3-11%). The relative contributions of different species to OAV agree well with previous

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

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

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

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

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

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

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

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

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

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

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

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

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

232 NO_3 reactivity for all of the sites, with remaining contributions primarily from sulfur- and

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

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

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

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

237 **3.3. Relative importance of different sources for VOC emissions**

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

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

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

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

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

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

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

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

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

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

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

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

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

251 S4).

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

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

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

255 concentration ($[NH_3]$).

256 $$[VOC] = ER_{C_2H_5OH} \times [C_2H_5OH]_{Feed} + ER_{NH_3} \times [NH_3] + [bg] \qquad Eq.\,(1)$$

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

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

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

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

261 emission ratios are determined from the multivariate linear fits.

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

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

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

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

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

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

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

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

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

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

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

273 including ethanol (23±1%), acetone (35±3%), acetaldehyde (31±3%), methanol (18±3%),

274 MEK (14±2%) and DMS (14±2%).

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

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

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

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

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

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

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

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

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

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

285 (Wang et al., 2010).

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

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

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

289 13% and 41% of the summed total VOC concentrations for the investigated dairy farms,

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

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

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

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

294 contributions to the total VOC concentrations.

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

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

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

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

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

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

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

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

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

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

305 fractions for different sources in Figure 5.

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

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

308 uncertainties to the results.

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

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

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

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

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

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

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

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

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

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

319 reasons.

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

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

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

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

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

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

326 somewhat overestimated as a result.

3.4. Aircraft measurements

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

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

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

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

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

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

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

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

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

337 aircraft measurements.

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

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

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

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

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

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

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

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

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

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

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

349 29: 0.71±0.11; April 13: 0.96±0.02). Combining the three SONGNEX flights in

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

351 these flights. This evidence suggests that beef cattle are more important for NH_3 emission

352 from CAFOs in northeastern Colorado.

353   The enhancement ratios of other VOC species relative to NH_3 are also calculated

354 from aircraft measurements and they are compared with those from mobile laboratory

355 measurements in Figure 7B. The determined enhancement ratios of carboxylic acids and

356 alcohols compare well between aircraft and mobile laboratory measurements. The

357 enhancement ratios of acetone and acetaldehyde to NH_3 are more scattered in aircraft

358 measurements, as the agricultural plumes contributed only small enhancements of these

359 species over a high background. The enhancement ratios of phenol, cresol, CH_3SH and

360 DMS to NH_3 from aircraft measurements are lower than those from mobile laboratory

361 measurements. The measured concentrations of these species from aircraft measurements

362 were low. The signals of these species were only slightly higher than instrument noise

363 levels at higher concentrations range of NH_3 (~150 ppb, see example in Figure 6), but not

364 detectable in many plumes with lower NH_3 concentrations.

365 **4. Conclusions**

366   In this study, we measured downwind air to discern VOC emissions from CAFOs in

367 northeastern Colorado using both mobile laboratory and aircraft measurements. We show

368 that carboxylic acids and alcohols dominate VOC emissions from CAFOs, whereas

369 sulfur-containing species and phenolic species are important to the odor activity values

370 and NO_3 reactivity of CAFO emissions, respectively. VOC compositions of CAFO

371 emissions determined from mobile laboratory and aircraft measurements are in good

372 agreement. Based on mobile laboratory measurements of CAFO sites, NH_3 emissions are

373 mainly from animals and their waste, whereas ethanol is predominately from feed storage

374 and handling. We applied a multivariate linear regression method to apportion the

375 relative fractions from the two sources using NH_3 and ethanol as tracers. The determined

376 fractions between the two sources are different among various VOC species and animal

377 types. In general, phenolic species and nitrogen-containing species are mainly associated

378 with emissions from animals and their waste for the investigated CAFOs. Significant

379 contributions from feed storage and handling are observed for carboxylic acids, alcohols

380 and carbonyls. We also proposed that ambient enhancement ratios of acetic acid to NH_3

381 may be used as an indicator to separate CAFO emissions from different animal types.

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Acknowledgement

We thank Andy Neuman in NOAA for his assistance and guidance with mobile
laboratory measurements. M. Coggon acknowledges support from the CIRES Visiting
Postdoctoral Fellowship.

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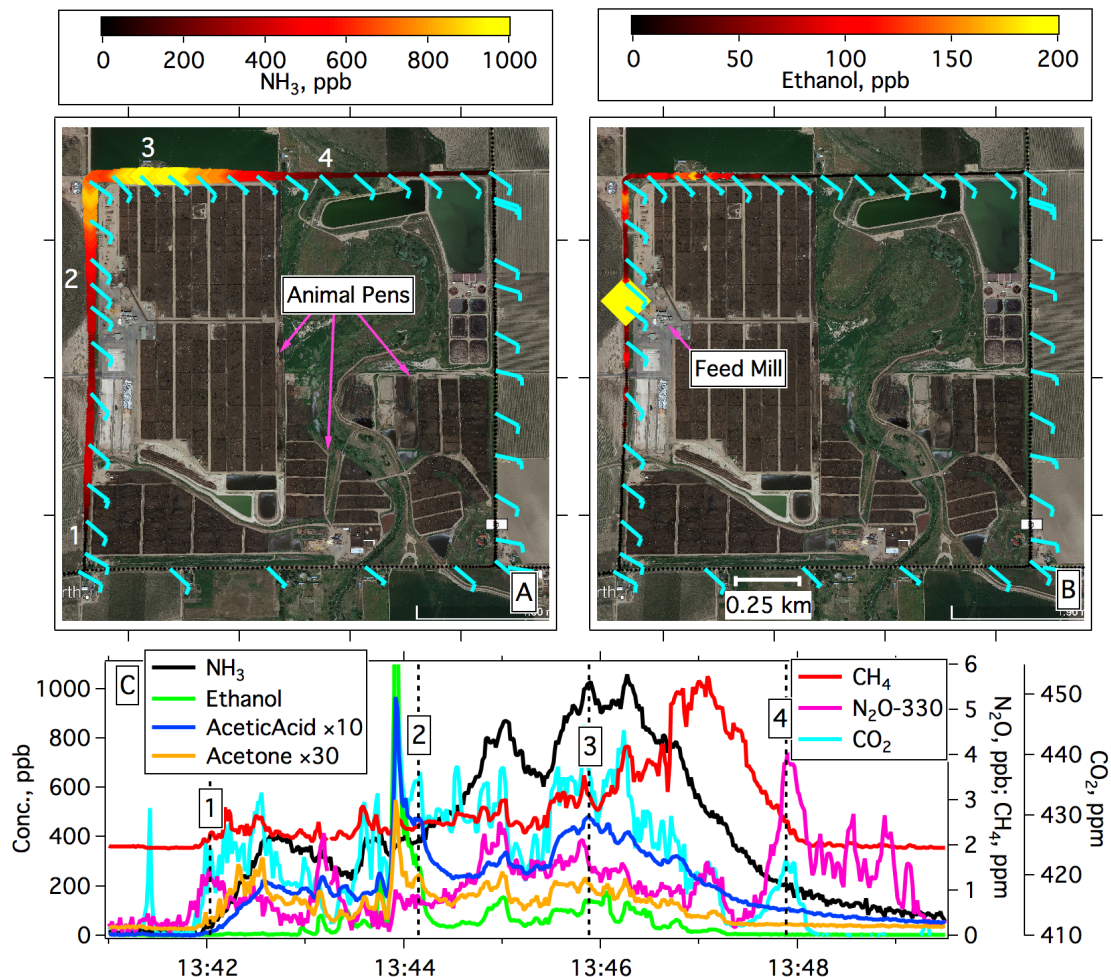
Figures

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.
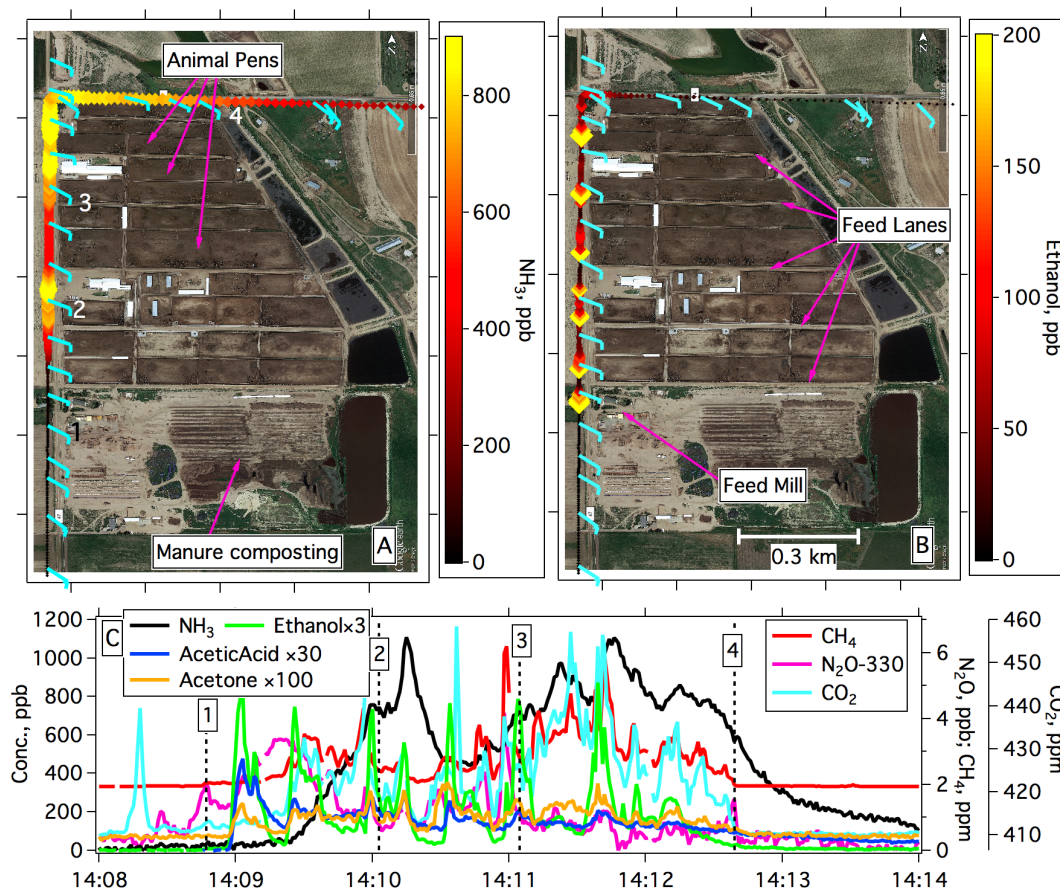
Figure 2. (A and B) Drive track of mobile laboratory color- and size-coded by NH$_3$ (A) and ethanol (B) concentrations downwind of a dairy farm (dairy #1). The prevailing wind is shown by wind barbs (light blue flags) in the map. (C) Time series of NH$_3$, CH$_4$, CO$_2$, N$_2$O, ethanol, acetic acid 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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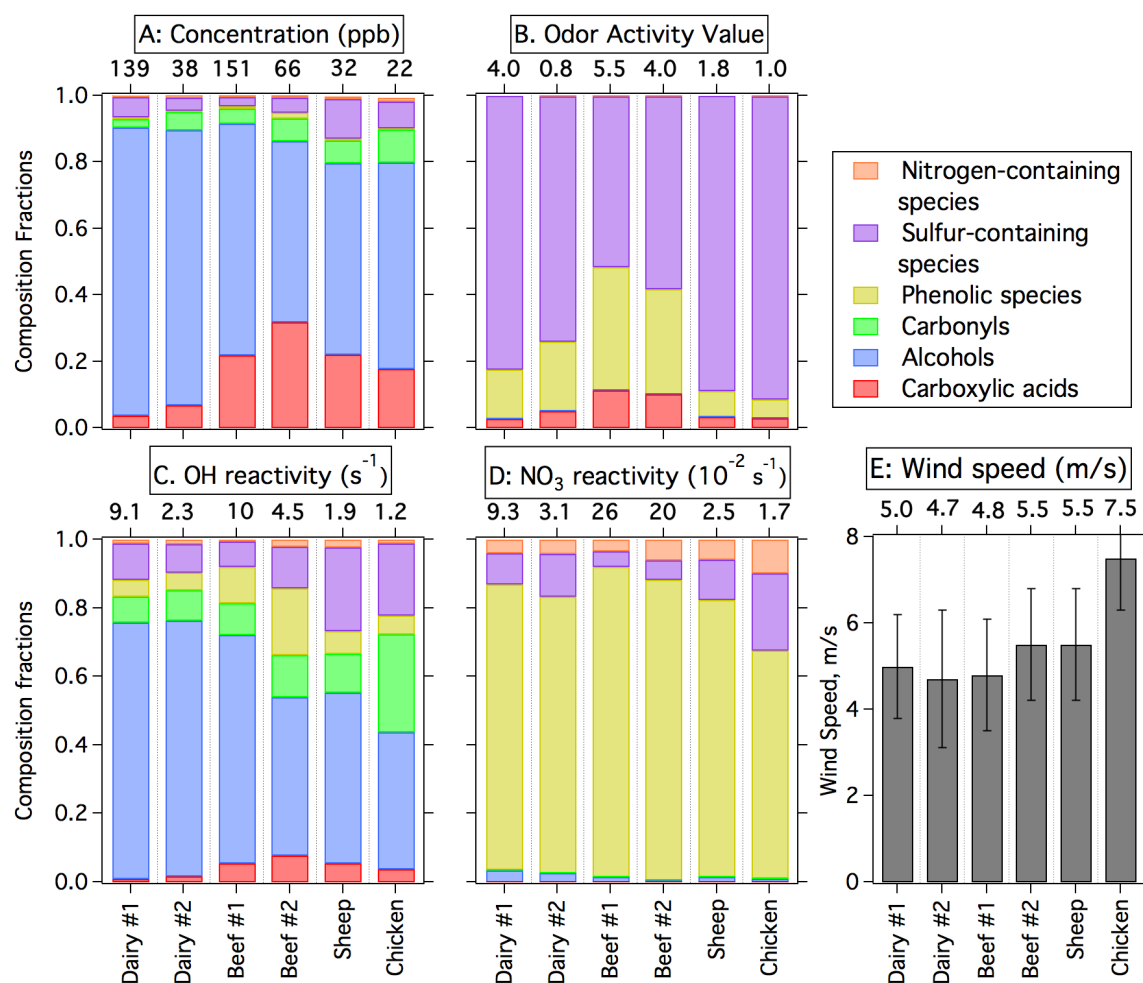
Figure 3. The fractional contributions of different VOC classes to the total VOC concentrations (A), odor activity values (B), OH reactivity (C) and NO$_3$ reactivity (D) for the six investigated CAFO sites. The mean wind speeds during the measurements of the CAFO sites are shown in (E). The mean values for the five parameters from each CAFO are shown at the top of each panel.

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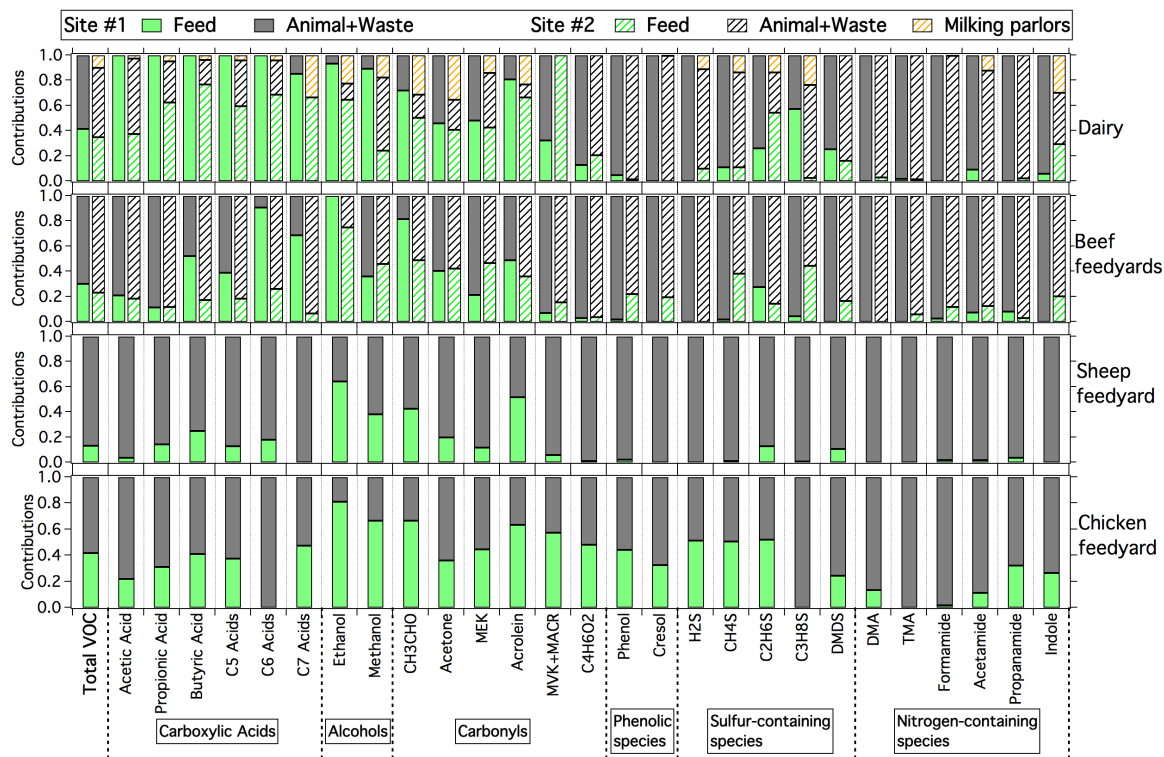
Figure 4. The relative contributions of feed storage+handling, animal+waste and milking parlors (only for dairy farm #2) to emissions of different VOC species and total VOC for the investigated CAFO sites. DMDS: dimethyl disulfide; DMA: dimethylamine; TMA: trimethylamine.

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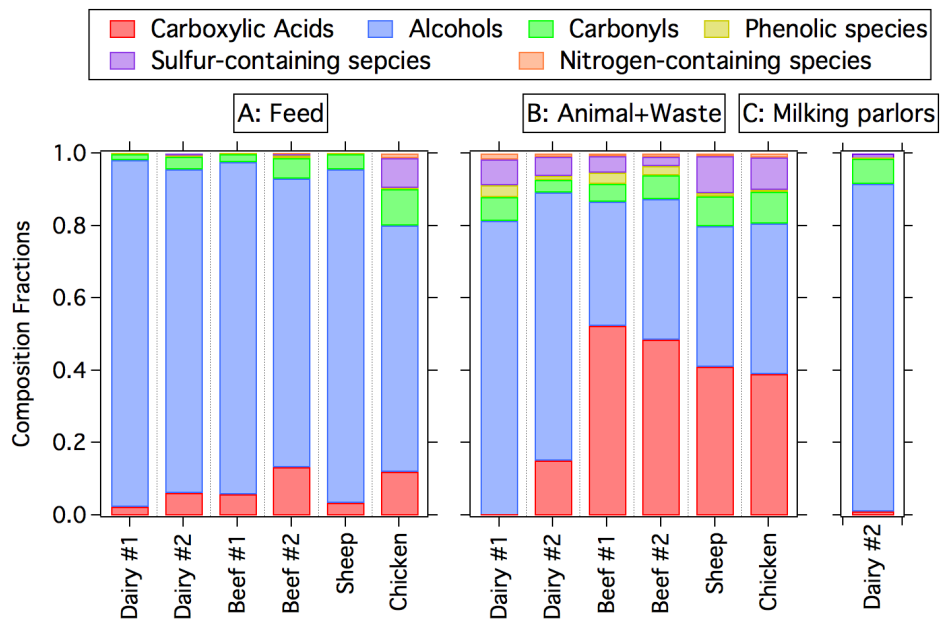
Figure 5. The relative contributions of each VOC class to emissions from feed

storage+handling (A), animal+waste (B) and milking parlors (C).

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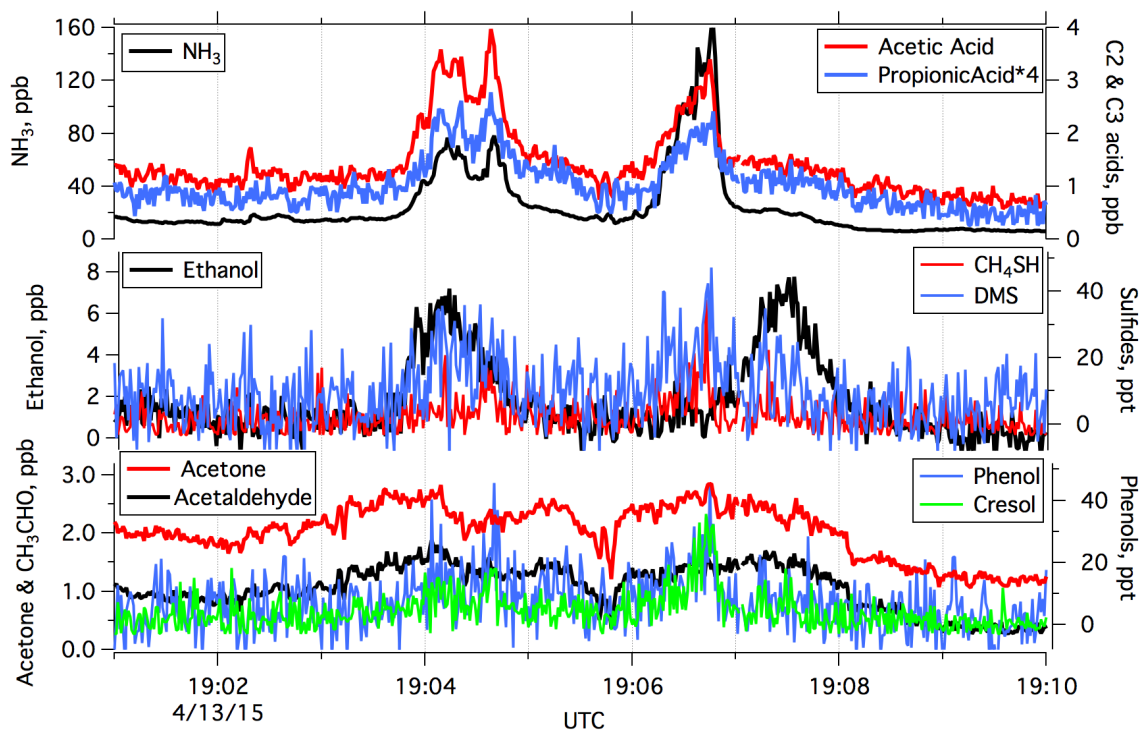
Figure 6. Time series of NH₃ and various VOC species of two agricultural plumes measured from NOAA WP-3D on April 13, 2015 during the SONGNEX campaign.

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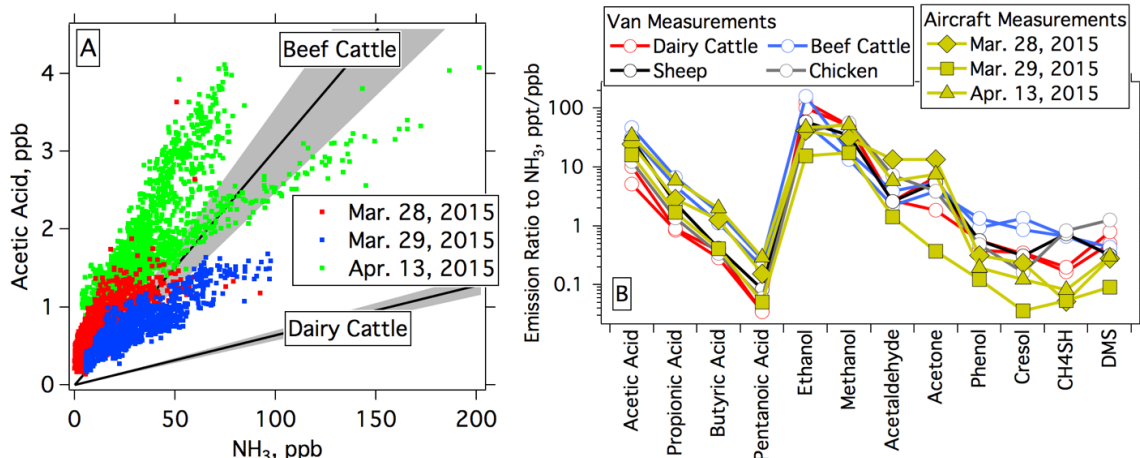
Figure 7. (A) Scatterplot of acetic acid versus NH$_3$ from the three SONGNEX flights in northeastern Colorado. The two black lines and gray-filled areas indicate emission ratios of acetic acid to NH$_3$ from beef feed yards and dairy farms determined from the mobile laboratory measurements, respectively. (B) Comparison of enhancement ratios of VOCs to NH$_3$ between mobile laboratory and aircraft measurements in northeastern Colorado.

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