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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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1. CAFO facilities and environmental conditions during measurements

Table S1. Animal types and maximum permitted livestock for investigated sites

Site type	Maximum permitted livestock capacity, head	Wind speed during measurements, m/s	Van speed downwind the facility, m/s
Dairy farm #1	6,100	5.0±1.2	4.7±0.7
Dairy farm #2	7,500	4.7±1.6	17±2.3
Beef feed yard #1	54,000	4.8±1.3	6.7±1.8
Beef feed yard #2	98,000	5.5±1.3	24±0.8
Sheep feed yard	95,000	5.5±1.3	4.3±0.5
Chicken house	>110,000	7.5±1.2	5.5±0.7

Table S2. Meteorological conditions during mobile measurements

Parameters	Average±standard deviation
Temperature, °C	10.7±0.6
Relative humidity, %	23.6±1.7
Wind speed, m/s	5.6±1.8
Wind direction, degree	120±14

2. Combustion sources

Mobile measurements of CAFOs in this study were mainly performed in rural regions with little traffic. The CAFO facilities were usually in the right-hand side of the driver for most of the measurements, which ensures that on-road vehicle traffic (if any) would not come between the mobile laboratory and CAFO facilities. Thus, we do not expect contributions of on-road vehicle emissions to our measurements shown in Figure 1-2 and Figure S2-S3.

However, carbon monoxide (CO), a tracer of combustion emissions, were significantly higher than background (~100 ppb) in several plumes sampled downwind of CAFOs (Figure S1). CO concentrations were up to 600 ppb in a plume downwind of the beef feed yard #1 (Figure S1A). This CO plume was from the feed mill area, implying that the plume might be as the result of operation of equipment used in the feed mill. The highest CO concentrations downwind of the CAFOs in this study were observed downwind of the sheep feed yard (up to 5 ppm, Figure S1B). This CO plume from the sheep feed yard was close to a narrow spike of ethanol as well. Ethanol was possibly due to emissions from a silage pile. In these CO plumes, we observed some enhancements of carbon dioxide (CO_2), whereas the enhancements of various VOCs were small (if any), compared to the enhancements as the results of emissions from other sources. Thus, we conclude that combustion sources were negligible for VOC emissions shown in this study.

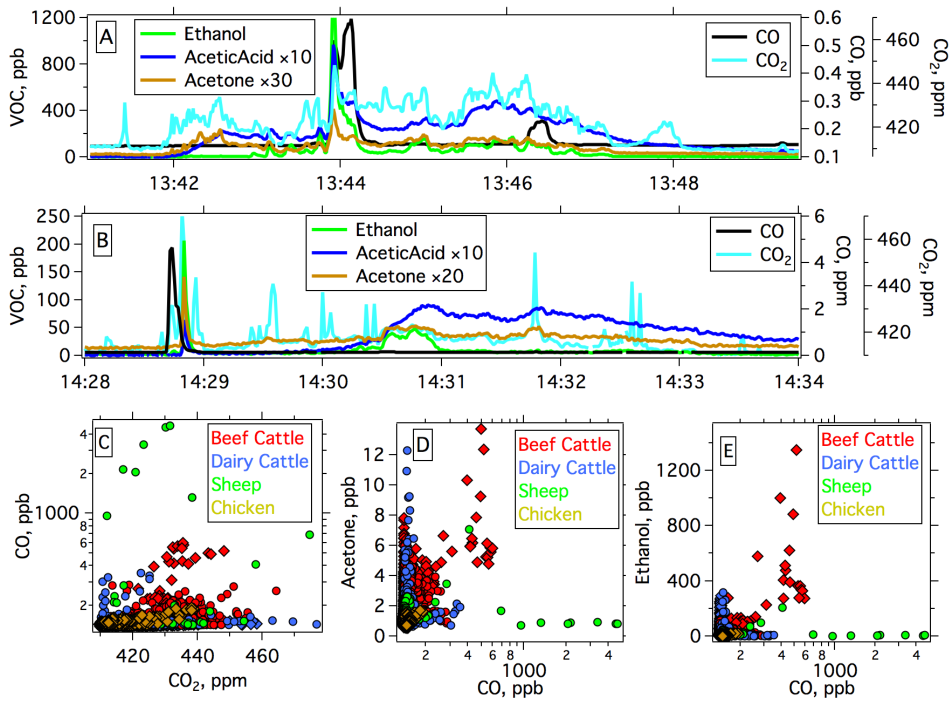

Figure S1. (A and B) Time series of CO, CO_2, ethanol, acetic acid and acetone downwind of the beef feed yard #1 (A) and the sheep feed yard (B). (C, D and E) Scatterplots of CO_2, acetone and ethanol versus CO from different CAFOs.

3. VOC distributions for dairy farm #2

Figure S2 shows measurements downwind of the other dairy farm (dairy #2). In addition to NH_3 emissions from animal+waste and ethanol emissions from the feed mill, high concentrations of ethanol were observed downwind of three milking parlors. CH_4, acetone and dimethyl sulfide (DMS) were also enhanced in these plumes, whereas acetic acid was only moderately elevated and NH_3 was not enhanced. Emission compositions from the milking parlors are clearly different from feed storage/handling.

Figure S3 shows measurements downwind of a chicken house. NH_3 concentrations measured downwind the chicken house were the lowest among the six CAFOs. An ethanol plume was observed downwind of the feed mill, similar to other CAFOs. CH_4 concentrations were not elevated, as chickens are not emitters for CH_4. The increase of acetone and acetic acid was clear in the feed mill plume, but the enhancements of the two VOCs were low when NH_3 concentrations were high.

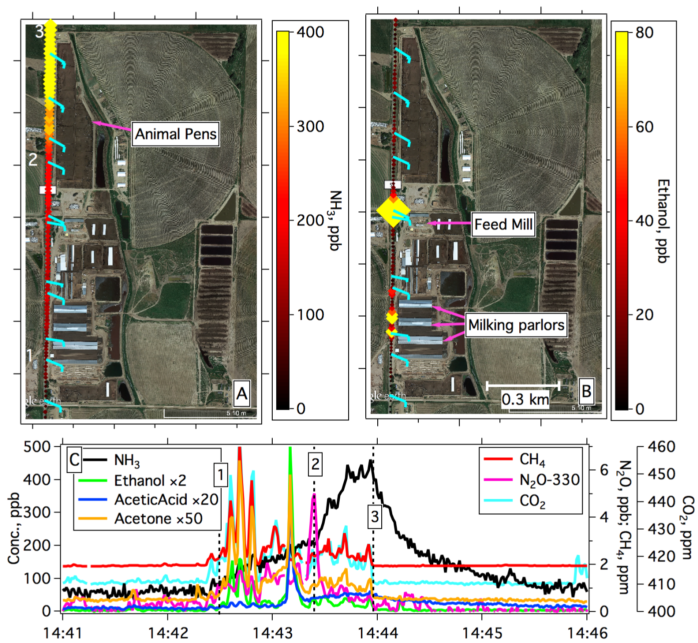

Figure S2. (A and B) Drive track of mobile laboratory color- and size-coded by NH_3 (A) and ethanol (B) concentrations downwind of a dairy farm (dairy #2). The prevailing wind is shown by wind barbs (light blue flags) in the map. (C) Time series of NH_3, CH_4, CO_2, N_2O, ethanol, acetic acid and acetone measured downwind of the dairy farm. Numbers (1-3) 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.

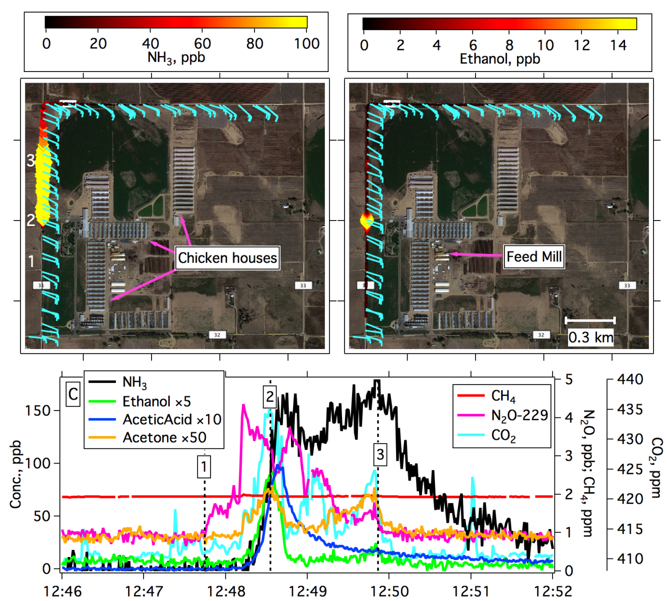

Figure S3. (A and B) Drive track of mobile laboratory color- and size-coded by NH_3 (A) and ethanol (B) concentrations downwind of a chicken house. The prevailing wind is shown by wind barbs (light blue flags) in the map. (C) Time series of NH_3, CH_4, CO_2, N_2O, ethanol, acetic acid and acetone measured downwind of the chicken house. Numbers (1-3) 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.

4. Calculation of ethanol from feed storage/handling and milking parlors

As shown in the main text, ethanol can be used as a tracer for emissions from feed storage+handling, but there is some ethanol attributable to animal+waste emissions that needs to be taken into account. Scatterplots of ethanol versus NH_3 from these CAFOs are shown in Figure S4A. The correlation between ethanol and NH_3 was low (*R*=0.24), indicating different sources for the two species. The data points that were clearly influenced by emissions of feed storage+handling and milking parlors are removed from the scatterplots and data points that are only influenced by animal+waste are shown in Figure S4B. The correlation coefficient between ethanol and NH_3 increases to 0.79. The emission ratio of ethanol to NH_3 ($ER_{C_2H_5OH/NH_3}$) can be estimated from the slope of the scatterplot in Figure S4B (0.017± 0.001 ppb/ppb).

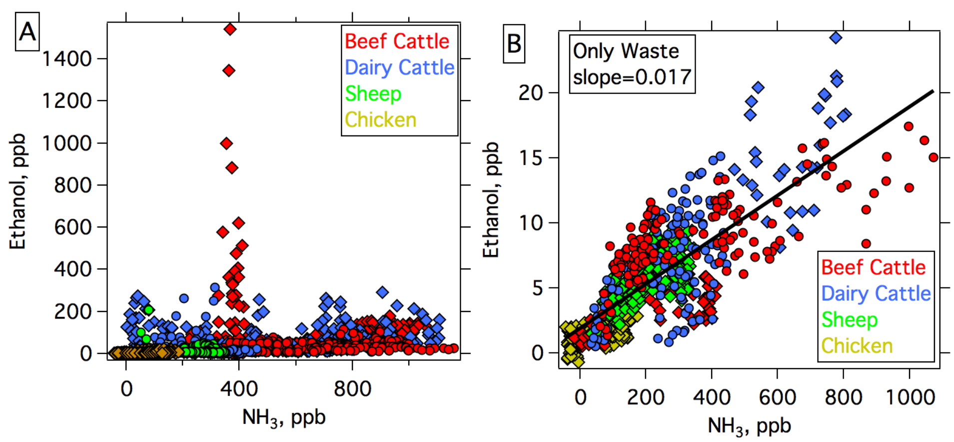

Figure S4. Scatterplots of ethanol versus NH_3 from mobile laboratory measurements: (A) all data; (B) only data when animal+waste emissions are large. The data points with clear influence from feed storage+handling and milking parlors are removed from (B), based on the spatial data shown in Figure 1-2 and Figure S2-S3.

Ethanol concentrations from feed emissions ($[C_2H_5OH]_{Feed}$) are calculated by subtracting the contribution of ethanol from animal+waste ($ER_{C_2H_5OH/NH_3} \times [NH_3]$) from measured ethanol concentrations ($[C_2H_5OH]$).

$$[C_2H_5OH]_{Feed} = [C_2H_5OH] - ER_{C_2H_5OH/_{NH_3}} \times [NH_3] \qquad Eq.(S1)$$

As shown in section 3.1 and (section 1 in SI), ethanol was elevated downwind of the milking parlors in one of the two dairy farm (dairy #2). For this dairy farm, ethanol concentrations that are not from animal+waste can be calculated as:

$$[C_2H_5OH]_{non-waste} = [C_2H_5OH] - ER_{C_2H_5OH/_{NH_3}} \times [NH_3] \qquad Eq.\ (S2)$$

We can further separate ethanol concentrations related to milking parlors and feed storage/handling for this facility. We assume that all of the enhancements of $[C_2H_5OH]_{non-waste}$ except those downwind of the milking parlors were due to feed storage+handling emissions (see Figure S1).

Using this information, a third term can be added in the multivariate linear fits for dairy farm #2 to obtain the relative fractions from emissions of milking parlors as well:

$$[VOC] = ER_{C_2H_5OH} \times [C_2H_5OH]_{Feed} + ER_{NH_3} \times [NH_3] + ER_{C_2H_5OH}' \times [C_2H_5OH]_{Milk} + [bg] \qquad Eq.\ (S3)$$

5. Contribution of different sources to total VOC concentrations, odor activity values, OH reactivity and NO_3 reactivity

In addition to total VOC concentrations, we also calculated the fractional contribution of different sources to odor activity value, OH reactivity and NO_3 reactivity (Figure S5).

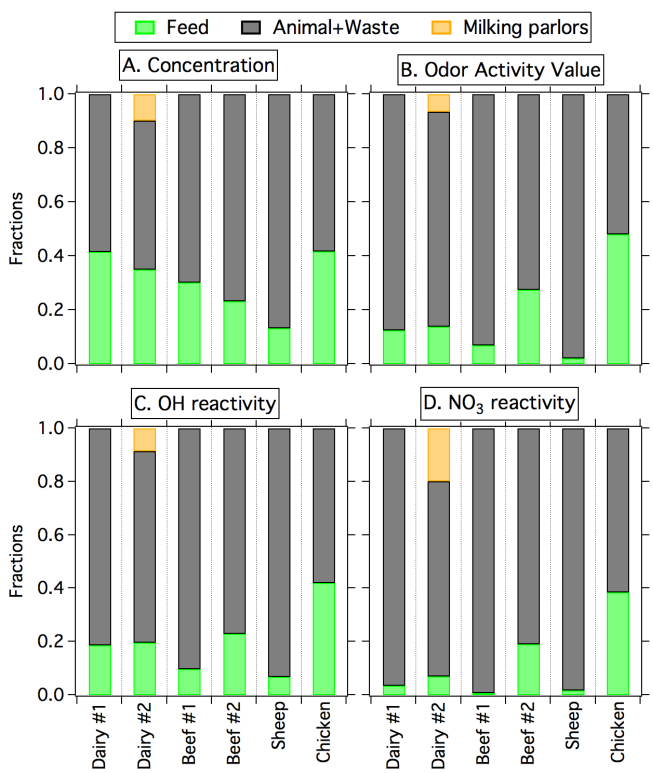

Figure S5. The relative contributions of emissions from feed storage+handling, animal+waste and milking parlors (only for dairy farm #2) to total VOC concentrations (A), odor activity values (B), OH reactivity (C) and NO_3 reactivity (D) for the investigated CAFOs.

6. Flight track of NOAA WP-3D on April 13, 2015

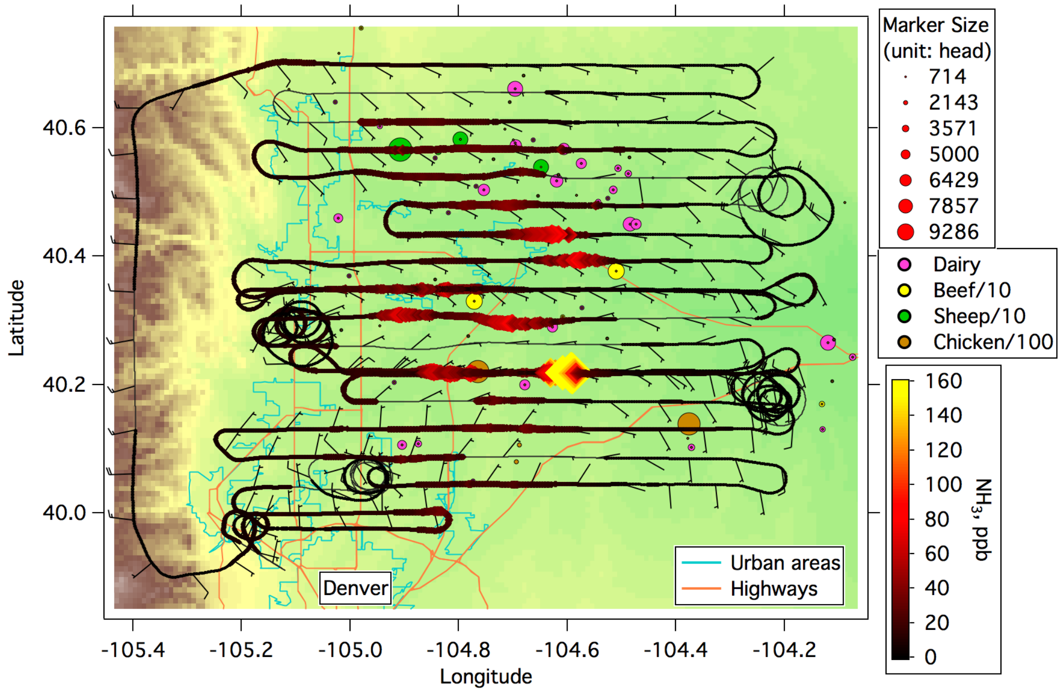

Figure S6. Flight track of NOAA WP-3D on April 13, 2015 during the SONGNEX campaign. The flight track is color- and size-coded using NH_3 concentrations. Wind directions at flight levels are also shown. The locations of CAFOs sites in northeastern Colorado are also shown in the graph.

7. Emission ratios and relative fractions from different sources

The obtained emission ratios and relative fractions from different sources for the investigated CAFO facilities in this study are tabulated in Table S3-S8.

Table S3. Emissions ratios (ER) from site-integration analysis and multivariate analysis, along with the relative fractions from feed storage+handling to different VOC species for dairy farm #1.

VOCs	Site-integrated ER to NH_3, ppt/ppb	ER from multivariate analysis		Percentage fractions from feed, %
		Animal+waste relative to NH_3, ppt/ppb	Feed relative to ethanol, ppt/ppb	
Acetic Acid	5.11	0.00±0.32	25.33±1.60	100
Propionic Acid	0.84	0.00±0.11	6.71±0.55	100
Butyric Acid	0.28	0.00±0.02	2.18±0.11	100
C5 Acid	0.04	0.00±0.00	0.16±0.01	100
C6 Acid	0.02	0.00±0.00	0.05±0.01	100
C7 Acid	0.00	0.00±0.00	0.01±0.00	85.3
Ethanol	127.92	17.05±0.49	1000±0.00	93.2
Methanol	50.48	4.04±2.32	308±11	89.3
CH_3CHO	2.69	0.69±0.08	16.16±0.37	72.0
Acetone	1.86	0.69±0.09	5.43±0.42	46.1
MEK	0.42	0.16±0.02	1.32±0.10	48.3
Acrolein	0.26	0.04±0.01	1.45±0.07	80.8
MVK+MACR	0.10	0.05±0.01	0.21±0.03	32.4
C4H6O2	0.16	0.10±0.01	0.14±0.04	12.8
Phenol	0.56	0.57±0.02	0.25±0.09	4.6
Cresol	0.34	0.31±0.01	0.00±0.05	0.0
H_2S	12.64	1.58±1.27	0.00±6.22	0.0
CH_4S	0.17	0.09±0.01	0.10±0.05	10.9
C_2H_6S	0.50	0.26±0.03	0.86±0.14	26.3
C_3H_8S	0.00	0.00±0.00	0.01±0.01	57.4
DMDS	0.01	0.00±0.00	0.01±0.01	25.3
DMA	0.01	0.01±0.00	0.00±0.01	0.0
TMA	0.18	0.19±0.01	0.03±0.03	2.0
Formamide	0.23	0.17±0.01	0.00±0.04	0.0
Acetamide	0.06	0.04±0.00	0.03±0.02	9.3
Propanamide	0.01	0.01±0.00	0.00±0.01	0.0
Indole	0.00	0.00±0.00	0.00±0.00	5.8

Table S4. Emissions ratios (ER) from site-integration analysis and multivariate analysis, along with the relative fractions from feed storage+handling and milking parlors to different VOC species for dairy farm #2.

VOCs	Site-integrated ER to NH_3, ppt/ppb	ER from multivariate analysis			Percentage fractions from feed, %	Percentage fractions from milking parlors, %
		Animal+waste relative to NH_3, ppt/ppb	Feed relative to ethanol, ppt/ppb	Milking parlors relative to ethanol, ppt/ppb		
Acetic Acid	10.11	6.06±0.32	70.39±0.96	13.19±2.40	37.4	2.4
Propionic Acid	0.89	0.23±0.05	8.27±0.16	1.79±0.39	62.6	4.7
Butyric Acid	0.38	0.09±0.02	6.63±0.08	0.89±0.19	76.8	3.6
C5 Acid	0.03	0.01±0.01	0.37±0.02	0.07±0.04	59.4	4.0
C6 Acid	0.02	0.00±0.00	0.12±0.01	0.02±0.02	68.9	4.0
C7 Acid	0.01	0.00±0.00	0.01±0.01	0.01±0.02	66.5	33.5
Ethanol	101.09	17.05±0.49	1000±0.00	1000±0.00	64.8	22.6
Methanol	49.59	12.5±3.8	96.8±11.6	203±29	24.2	17.7
CH_3CHO	2.60	0.20±0.15	10.40±0.45	18.52±1.11	50.3	31.2
Acetone	6.89	1.03±0.32	33.20±0.99	82.34±2.47	40.9	35.3
MEK	0.57	0.13±0.03	2.46±0.09	2.32±0.23	42.7	14
Acrolein	0.27	0.02±0.03	2.67±0.09	2.68±0.23	66.4	23.3
MVK+MACR	0.14	0.00±0.03	0.08±0.08	0.00±0.20	100	0.0
C4H6O2	0.16	0.03±0.02	0.15±0.05	0.00±0.13	20.4	0.0
Phenol	0.38	0.26±0.02	0.07±0.06	0.00±0.14	1.4	0.0
Cresol	0.35	0.28±0.01	0.00±0.04	0.08±0.09	0.0	0.5
H_2S	6.97	1.99±1.06	4.58±3.22	14.60±8.06	9.8	10.9
CH_4S	0.20	0.06±0.02	0.17±0.05	0.61±0.12	11.1	13.6
C_2H_6S	0.80	0.20±0.06	6.17±0.18	4.43±0.44	54.3	13.6
C_3H_8S	0.01	0.00±0.00	0.00±0.01	0.03±0.02	2.6	23.6
DMDS	0.02	0.00±0.00	0.02±0.01	0.00±0.03	16.3	0.0
DMA	0.02	0.03±0.01	0.02±0.02	0.00±0.04	2.8	0.0
TMA	0.14	0.08±0.01	0.03±0.03	0.00±0.07	1.6	0.0
Formamide	0.35	0.24±0.02	0.00±0.06	0.04±0.14	0.0	0.3
Acetamide	0.06	0.04±0.01	0.00±0.03	0.27±0.07	0.0	12
Propanamide	0.02	0.01±0.00	0.00±0.01	0.00±0.03	2.1	0.0
Indole	0.00	0.00±0.00	0.00±0.00	0.01±0.01	29.3	29.9

Table S5. Emissions ratios (ER) from site-integration analysis and multivariate analysis, along with the relative fractions from feed storage+handling to different VOC species for beef feed yard #1.

VOCs	Site-integrated ER to NH_3, ppt/ppb	ER from multivariate analysis		Percentage fractions from feed, %
		Animal+waste relative to NH_3, ppt/ppb	Feed relative to ethanol, ppt/ppb	
Acetic Acid	47.47	31.29±0.91	60.09±1.63	21.0
Propionic Acid	6.76	6.70±0.14	6.25±0.25	11.4
Butyric Acid	1.69	0.64±0.03	5.09±0.06	52.3
C5 Acid	0.27	0.13±0.01	0.62±0.02	39.1
C6 Acid	0.03	0.00±0.00	0.12±0.00	90.8
C7 Acid	0.01	0.00±0.00	0.03±0.00	68.6
Ethanol	161.45	17.05±0.49	1000±0.00	100
Methanol	17.80	8.82±0.49	35.8±0.87	35.9
CH_3CHO	3.90	0.54±0.10	17.49±0.18	81.7
Acetone	5.51	1.44±0.23	7.09±0.41	40.5
MEK	1.26	0.65±0.04	1.27±0.07	21.4
Acrolein	0.64	0.31±0.01	2.16±0.03	48.9
MVK+MACR	0.21	0.18±0.01	0.10±0.01	7.0
C4H6O2	0.42	0.38±0.01	0.08±0.02	3.0
Phenol	0.94	0.86±0.02	0.11±0.04	1.7
Cresol	1.34	1.47±0.03	0.00±0.05	0.0
H_2S	6.55	2.59±0.49	0.00±0.87	0.0
CH_4S	0.68	0.71±0.03	0.10±0.06	2.0
C_2H_6S	0.33	0.17±0.02	0.47±0.03	27.7
C_3H_8S	0.01	0.00±0.00	0.00±0.00	4.6
DMDS	0.04	0.04±0.01	0.00±0.01	0.0
DMA	0.01	0.01±0.00	0.00±0.00	0.0
TMA	0.08	0.10±0.00	0.00±0.01	0.0
Formamide	0.24	0.17±0.01	0.03±0.01	2.6
Acetamide	0.08	0.05±0.00	0.03±0.01	7.3
Propanamide	0.02	0.01±0.00	0.01±0.00	8.0
Indole	0.01	0.01±0.00	0.00±0.00	0.0

Table S6. Emissions ratios (ER) from site-integration analysis and multivariate analysis, along with the relative fractions from feed storage+handling to different VOC species for beef feed yard #2.

VOCs	Site-integrated ER to NH_3, ppt/ppb	ER from multivariate analysis		Percentage fractions from feed, %
		Animal+waste relative to NH_3, ppt/ppb	Feed relative to ethanol, ppt/ppb	
Acetic Acid	32.48	22.86±0.89	160.08±14.57	18.5
Propionic Acid	4.74	3.49±0.16	14.44±2.59	11.9
Butyric Acid	1.11	0.78±0.04	5.07±0.58	17.4
C5 Acid	0.20	0.13±0.01	0.93±0.10	18.5
C6 Acid	0.01	0.01±0.00	0.06±0.01	26.3
C7 Acid	0.00	0.00±0.00	0.00±0.01	6.5
Ethanol	54.91	17.05±0.49	1000±0.00	75.2
Methanol	13.53	5.07±0.39	132±6.0	45.8
CH_3CHO	2.21	0.92±0.05	27.14±0.88	48.9
Acetone	3.87	1.67±0.14	37.52±2.21	42.2
MEK	1.25	0.46±0.05	12.38±0.82	46.6
Acrolein	0.28	0.17±0.01	2.89±0.13	36.0
MVK+MACR	0.29	0.16±0.01	0.93±0.15	15.6
C4H6O2	0.50	0.28±0.02	0.34±0.26	3.8
Phenol	1.34	0.84±0.04	7.33±0.61	22.1
Cresol	0.86	0.60±0.03	4.43±0.42	19.4
H_2S	4.60	1.09±0.32	0.00±5.24	0.0
CH_4S	0.66	0.16±0.03	3.06±0.47	38.2
C_2H_6S	0.44	0.25±0.02	1.32±0.33	14.4
C_3H_8S	0.01	0.00±0.00	0.03±0.02	44.5
DMDS	0.02	0.01±0.00	0.07±0.04	16.5
DMA	0.02	0.01±0.00	0.00±0.04	0.0
TMA	0.16	0.14±0.01	0.26±0.09	5.8
Formamide	0.23	0.14±0.01	0.60±0.10	11.9
Acetamide	0.08	0.05±0.00	0.20±0.06	12.7
Propanamide	0.02	0.01±0.00	0.01±0.03	2.8
Indole	0.01	0.01±0.00	0.06±0.02	20.3

Table S7. Emissions ratios (ER) from site-integration analysis and multivariate analysis, along with the relative fractions from feed storage+handling to different VOC species for sheep feed yard.

VOCs	Site-integrated ER to NH_3, ppt/ppb	ER from multivariate analysis		Percentage fractions from feed, %
		Animal+waste relative to NH_3, ppt/ppb	Feed relative to ethanol, ppt/ppb	
Acetic Acid	29.76	33.61±1.13	35.83±5.42	3.6
Propionic Acid	2.43	2.44±0.10	11.63±0.48	14.4
Butyric Acid	0.42	0.33±0.02	3.08±0.08	24.8
C5 Acid	0.08	0.07±0.01	0.31±0.03	12.8
C6 Acid	0.01	0.01±0.00	0.04±0.02	17.9
C7 Acid	0.01	0.00±0.00	0.00±0.01	0.0
Ethanol	58.75	17.05±0.49	1000±0.00	64.2
Methanol	34.86	21.3±2.0	376±9.5	38.4
CH_3CHO	2.63	1.24±0.11	26.29±0.54	42.8
Acetone	5.46	4.00±0.13	27.82±0.64	19.7
MEK	2.46	2.05±0.08	7.79±0.39	11.8
Acrolein	0.22	0.13±0.02	3.80±0.08	51.8
MVK+MACR	0.20	0.17±0.02	0.30±0.10	5.9
C4H6O2	0.42	0.44±0.03	0.15±0.13	1.2
Phenol	0.57	0.55±0.02	0.36±0.09	2.2
Cresol	0.31	0.34±0.01	0.00±0.07	0.0
H_2S	19.59	9.40±1.94	0.00±9.28	0.0
CH_4S	0.73	0.49±0.04	0.15±0.21	1.1
C_2H_6S	0.32	0.17±0.02	0.69±0.10	12.9
C_3H_8S	0.01	0.01±0.00	0.00±0.01	0.7
DMDS	0.02	0.01±0.00	0.02±0.02	10.5
DMA	0.02	0.02±0.01	0.00±0.04	0.0
TMA	0.23	0.20±0.01	0.00±0.05	0.0
Formamide	0.45	0.26±0.02	0.12±0.10	1.7
Acetamide	0.07	0.07±0.01	0.04±0.05	1.9
Propanamide	0.03	0.03±0.01	0.03±0.03	3.6
Indole	0.01	0.00±0.00	0.00±0.01	0.0

Table S8. Emissions ratios (ER) from site-integration analysis and multivariate analysis, along with the relative fractions from feed storage+handling to different VOC species for chicken farm.

VOCs	Site-integrated ER to NH_3, ppt/ppb	ER from multivariate analysis		Percentage fractions from feed, %
		Animal+waste relative to NH_3, ppt/ppb	Feed relative to ethanol, ppt/ppb	
Acetic Acid	12.38	26.44±2.14	252.0±28.5	22.1
Propionic Acid	1.36	2.20±0.16	33.64±2.16	31.3
Butyric Acid	0.34	0.47±0.04	11.13±0.56	41.3
C5 Acid	0.06	0.09±0.01	1.80±0.14	37.6
C6 Acid	0.01	0.01±0.00	0.00±0.05	0.0
C7 Acid	0.01	0.00±0.00	0.02±0.04	47.6
Ethanol	40.12	17.05±0.49	1000±0.00	81.1
Methanol	56.63	18.6±2.29	1257±35	66.8
CH_3CHO	7.2	3.22±0.22	217.12±3.35	66.8
Acetone	3.9	1.86±0.17	35.52±2.57	36.3
MEK	2.49	1.14±0.12	30.91±1.83	44.6
Acrolein	0.34	0.29±0.03	17.11±0.39	63.5
MVK+MACR	0.36	0.21±0.03	9.36±0.41	57.3
C4H6O2	0.68	0.45±0.03	14.20±0.44	48.2
Phenol	0.48	0.33±0.03	8.76±0.41	44.4
Cresol	0.16	0.15±0.01	2.43±0.20	32.5
H_2S	10.59	6.53±0.81	233.09±12.41	51.5
CH_4S	0.83	0.50±0.04	17.40±0.62	50.7
C_2H_6S	1.26	0.62±0.08	22.88±1.24	52.2
C_3H_8S	0.01	0.00±0.00	0.00±0.05	0.0
DMDS	0.06	0.02±0.01	0.25±0.11	24.3
DMA	0.01	0.01±0.01	0.04±0.11	13.5
TMA	0.03	0.03±0.00	0.00±0.07	0.0
Formamide	0.5	0.27±0.02	0.18±0.38	1.9
Acetamide	0.12	0.06±0.01	0.25±0.19	11.4
Propanamide	0.02	0.01±0.01	0.23±0.09	32.3
Indole	0.01	0.01±0.00	0.08±0.02	26.6