

Direct Measurements of the Ozone Formation Potential from Livestock and Poultry Waste Emissions

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The global pattern of expanding urban centers and increasing agricultural intensity is leading to more frequent interactions between air pollution emissions from urban and agricultural sources. The confluence of these emissions that traditionally have been separated by hundreds of kilometers is creating new air quality challenges in numerous regions across the United States. An area of particular interest is California's San Joaquin Valley (SJV), which has an agricultural output higher than many countries, a rapidly expanding human population, and ozone concentrations that are already higher than many dense urban areas. New regulations in the SJV restrict emissions of reactive organic gases (ROGs) from animal sources in an attempt to meet Federal and State ozone standards designed to protect human health. The objective of this work is to directly measure the ozone formation potential (OFP) of agricultural animal plus waste sources in representative urban and rural atmospheres using a transportable "smog" chamber. Four animal types were examined: beef cattle, dairy cattle, swine, and poultry. Emissions from each animal plus waste type were captured in a 1 m³ Teflon bag, mixed with representative background NO_x and ROG concentrations, and then exposed to UV radiation so that ozone formation could be quantified. The emitted ROG composition was also measured so that the theoretical incremental reactivity could be calculated for a variety of atmospheres and directly compared with the measured OFP under the experimental conditions. The results demonstrate that OFP associated with waste ROG emissions from swine (0.39 ± 0.04 g-O₃ per g-ROG), beef cattle (0.51 ± 0.10 g-O₃ per g-ROG), and dairy cattle (0.42 ± 0.07 g-O₃ per g-ROG) are lower than OFP associated with ROG emissions from gasoline powered light-duty vehicles (LDV) (0.69 ± 0.05 g-O₃ per g-ROG). The OFP of ROG emitted from poultry waste (1.35 ± 0.73 g-O₃ per g-ROG) is approximately double the LDV OFP. The measured composition of ROG emitted from animal plus

waste sources is nine times less reactive than the current regulatory profiles that are based on dated measurements. The new animal waste ROG OFP measurements combined with adjusted animal waste ROG emissions inventory estimates predict that actual ozone production in the SJV from livestock and poultry (5.7 ± 1.3 tons O₃ day⁻¹) is 40 ± 10% of the ozone produced by light duty gasoline vehicles (14.3 ± 1.4 tons O₃ day⁻¹) under constant NO_x conditions.

1. Introduction

Global meat production has nearly tripled in the last 50 years reflecting an increase in world population and improved standards of living (1). Progress within the United States during this half century has increased livestock production within the same acreage through the adoption of concentrated animal feeding operations (CAFOs). At the same time, urban areas have expanded into traditional agricultural regions bringing the air pollutant emissions from fossil fuel combustion into close proximity to agricultural livestock emissions. This new mixture of pollutants from sources that were historically separated by hundreds of kilometers has resulted in new air pollution challenges across the United States.

California's San Joaquin Valley (SJV) represents a prime example of a region where the confluence of urban and agricultural air pollutant emissions results in poor air quality. The SJV has regional ozone concentrations that rival those of Los Angeles (2) even though the average population density in Los Angeles is twenty times higher. In 2008, agricultural production in the SJV was estimated at \$24 B, which is ~67% of California's total agricultural production and ~9% of the United States total (3). More than half of this output came from livestock and poultry operations, with the SJV currently containing roughly 2 million dairy cattle, 300 000 beef cattle, 40 million chickens, and 127 000 swine (4). Many of the urban centers in the SJV are rapidly expanding, bringing them into close proximity to these livestock and poultry production regions.

It is virtually impossible to measure the detailed chemical composition from every emissions source within California and so emissions characteristics are often measured for one class of sources and then extrapolated to similar sources, sometimes with many years between measurements. In the case of ROG emissions from animal waste sources, the California Air Resources Board (CARB) first estimated that the ratio of ROG/TOG (total organic gases, which includes non-ozone-forming methane) equals 8% for dairy cattle based on historical measurements (5, 6). It was then assumed that this ROG/TOG ratio could be used for all animal types and the ROG emissions could be calculated using TOG emissions estimates. Based on this methodology, the San Joaquin Valley Air Pollution Control District (the local agency directly responsible for enforcement of CARB policies in the SJV) has approved a plan to decrease ROG emissions from CAFOs in the SJV by 26% (15.8 tons day⁻¹) (7) to reduce ozone concentrations.

Recent studies have shown that the actual ozone production caused by animal waste ROG emissions may be lower than estimated values (8, 9). Shaw et al. (9) demonstrated that the ratio of ROG/TOG in the emissions from dairy cattle waste is 6–10 times lower than the estimates used by CARB. Furthermore, Howard et al. (8) directly measured that the ozone formation potential (OFP) of the ROG emitted by dairy cattle and their fresh waste is significantly less than previously estimated. The purpose of the current paper is to expand on

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these direct measurements to include the other major livestock and poultry operations prevalent in California and the United States. ROG emissions from beef cattle, swine, and chickens were evaluated in a transportable atmospheric “smog” chamber to directly measure OFP under various conditions of background NO_x and ROG. Model calculations were then performed to determine if the measured ROG emissions explained the observed ozone formation (or if unidentified ROG produced more ozone formation than expected). Finally, ozone formation estimates and total contributions to statewide ozone production were calculated for each animal waste type.

2. Materials and Methods

2.1. Field Experiments. Direct measurements of the ROG OFP from livestock and poultry waste emissions were carried out using two mobile ozone chamber assays (MOChAs). Each MOChA was designed to be a transportable “smog chamber” that could be taken directly to sources that are too complicated to simulate in a laboratory (8). The chamber consists of a wooden box mounted on top of a modified trailer for easy transportation to a sampling site. The inner surface of the chamber is coated with reflective aluminum sheeting. One side of the chamber contains banks for up to 26 ultraviolet (UV) lamps (model no. F40BL, Sylvania), which are used to simulate the desired intensity of sunlight. Twenty-four lamps were used in the current study to produce $50 \pm 2 \text{ W/m}^2$ of UV, which is representative of conditions on a clear summer day in central California (note the uncertainty ranges presented throughout the manuscript represent one standard deviation unless otherwise noted). A 1 m^3 Teflon (PFA) bag is placed inside the UV exposure chamber. At the start of each experiment the bag is filled with air extracted from the target source using inert Teflon tubing and a Teflon diaphragm pump. Particles are removed from the input air using an inline quartz fiber filter. After filling the Teflon bag with source air, additional NO_x is injected from a high pressure cylinder to simulate NO_x concentrations in either polluted urban or rural background environments. A ROG mini-surrogate representative of SJV background conditions during stagnation events can also be added to the chamber as necessary to simulate the desired environment. The representative mini-surrogate used in the current study consisted of $55 \pm 1\%$ ethene, $33 \pm 1\%$ hexanes, and $12 \pm 1\%$ xylenes by volume (10). Once the chamber is filled, the inlet valves are closed and an initial grab sample is collected for ROG analysis using passivated SUMMA stainless steel canisters (either SilcoCan model no. 24178, Restek U.S., Bellefonte, PA or Aerosphere canisters, Labcommerce Inc., San Jose, CA). The UV lights are then turned on and three hour irradiation experiments are performed. During the course of an experiment, measurements are made for NO_x concentrations (model no. ML9841A, Teledyne Monitor Laboratories, Englewood, CO), ozone concentrations (model no. 450, Teledyne Instruments Advanced Pollution Instrumentation, Inc., San Diego, CA), and temperature/humidity (model no. HMP50-L, Campbell Scientific, Logan, UT) between the times 0–5 min, 20–30 min, 55–65 min, 85–90 min, 115–120 min, 145–150 min, and 175–180 min. Concentrations are measured more extensively during the first hour to capture transient behavior during the initial phase of each experiment. Measurement times during subsequent hours are shortened slightly to prolong the length of each experiment given the instrument flow rate and the volume of the reaction chamber. All measurements are logged using National Instruments measurement and automation software (National Instruments, Austin, TX). Light intensity is also recorded before and after each experiment using a UV photometer (model no. PMA-2111, Solar Light Co. Inc., Glenside, PA). Finally at the end of the three hour period another grab sample is

collected using SUMMA canisters. The bag is then evacuated and flushed with clean air produced by a zero air generator (model no ZA-750–12, Perma Pure Inc., Toms River, NJ). The clean air generator is designed to produce particle-free and ROG-free air that can be used as a calibration standard. Experiments conducted with clean air produce negligible concentrations of ozone and tests showed that a single air exchange could be used for cleaning in the present study (8). Two identical MOChAs can be used to make replicate measurements or to check the OFP of background air during each experiment. Further details of the MOCHA experimental apparatus, standard operating procedures and initial validation are available elsewhere (8).

Sixteen poultry experiments were conducted at an operating farm near Davis, California in the current study. Eight of these experiments were conducted using no additional ROG while the other eight were conducted using 125 ppb of additional ROG mini-surrogate to represent conditions influenced by urban emissions. During every experiment, a second MOChA was used to measure the OFP of the background air. The poultry farm is home to approximately 80 000 laying hens that are housed in a 800 m^2 naturally ventilated steel barn. The chickens are kept in elevated wire cages so that manure passes through the bottom of each cage and accumulates on the floor of the barn where it is removed every ~ 2 months. Poultry were typical adult-sized egg-laying chickens weighing approximately 6 lbs. The specific breed is a trade secret developed from common American and South American poultry breeds. During the present study, air samples were drawn into the MOChA from the interior of the barn using a Teflon inlet line with a total length of 4 m. The exact concentration of ROG collected during each experiment is used to calculate ozone formation potential (the amount of ozone formed per unit of initial ROG) but these measurements were not used to estimate ROG emissions fluxes.

Thirty two beef and 12 swine experiments were performed at the UC Davis Department of Animal Science Swine Research Facility. Once again, half of these experiments employed additional ROG mini-surrogate to represent conditions influenced by urban emissions. Separate experiments were conducted using several subcategories of beef cattle, including four experiments each for 1200 lbs/750 lbs/150 lbs Holsteins and 750 lbs Black Angus and eight experiments each for 1200 lbs Black Angus and 300 lbs Holsteins. Swine were a variation of the Yorkshire breed with a weight of approximately 200 lbs. The animals were housed in a 129 m^3 chamber that was maintained at $\sim 18^\circ\text{C}$ using a mechanically ventilated water-evaporation HVAC system. The total air flow rate through the chamber was $3.0 \times 10^3 \text{ L min}^{-1}$ giving an air residence time of ~ 6 min. Individual experiments used three beef cattle or six swine in the chamber. Animals were sealed inside the chamber with air only exchanged through the ventilation system (except during feedings when the cattle were fed an 80% corn-based ration). The animals were housed in the chamber for a 48 h period during which the manure was allowed to accumulate on the floor. OFP experiments were performed after animals had acclimated in the chamber for 24 hrs. The animals were removed after the 48 h and the chamber was cleaned before the start of the next experiment. MOChA air samples were drawn from a port on the outlet ventilation duct using a Teflon inlet line with a total length of 10 m.

NO_x was added to each animal waste emissions sample as a 95% NO_2 /5% NO blend to achieve an initial NO_x concentration of 50 ppb, which is a typical reactive nitrogen concentration measured in the SJV during the summer months (2). Additional ROG sampling was performed during each experiment to compliment the MOChA standard operating procedures. Extra SUMMA canister grab samples

were collected from the ventilation exhaust port during beef and swine experiments and from the middle of the barn during poultry experiments. SUMMA canisters were pre-cleaned and evacuated (0.05 mmHg) prior to sample collection as recommended by U.S. Environmental Protection Agency method TO-15 (11). SUMMA canisters were filled to +10 psig during sample collection. Samples collected with SUMMA canisters were analyzed within 48 h by gas chromatography–mass spectrometry (GC–MS) connected with automatic high performance cryofocusing units (Lotus Consulting, Long Beach, CA) using standard analysis methods (11, 12). ROG samples were also collected at various locations during each experiment using charcoal sorbent tubes (Orbo 32, Sigma-Aldrich, St. Louis, MO). The sorbent tube samples complement the canister grab samples because they are better suited to collect less volatile compounds which may have low recovery from canisters. Sorbent tubes were extracted in CS₂ solvent, followed by GC–MS analysis. Additionally, DNPH–Silica cartridges (model no. 037500, Waters Corp, MA) were collected during the swine experiments to measure the concentration of reactive carbonyl compounds. DNPH cartridges were analyzed through acetonitrile elution followed by high performance liquid chromatography (HPLC) (see refs 13, 14).

2.2. Model Implementation. A modified version of the Caltech Atmospheric Chemistry Mechanism (CACM) (15) was used to predict ozone formation potential during each experiment based on the initial NO_x and ROG concentration/composition. Reasonable agreement between predicted and measured OFP builds confidence that the major components of the ROG emitted from each animal waste source have been quantified. Under-predictions of measured ozone formation would indicate the presence of an uncharacterized subcomponent of ROG with high OFP (no such results were detected in the current study). Modifications were made to the standard CACM mechanism to more exactly represent the UV spectrum emitted by the MOChA lamps and to implement an explicit lumping scheme for ethanol and acetylaldehyde reactions in order to more accurately predict the OFP of these chemical species. Further details of the CACM model used to reproduce MOCHA measurements are presented elsewhere (8).

3. Results and Discussion

Figure 1 displays the predicted NO₂, NO, and O₃ concentrations at the end of each 180 min CACM simulation versus the measured concentrations of those species. Examples of predicted and measured concentrations throughout each experiment are provided in the Supporting Information (SI). Each CACM simulation was initialized with the concentrations measured in the MOChA after the bag had been filled with air emissions from the animal plus waste source. The dark line in each panel of Figure 1 illustrates perfect agreement between model predictions and measurements while the dotted lines represent ±5% deviation from the 1:1 line.

Figure 1a illustrates that the maximum final NO concentrations during each experiment ranged between 1 and 12 ppb. Model predictions for the final NO concentrations generally agree with measurements (regression slope = 1.08 ± 0.05, R² = 0.97), but final NO concentrations are slightly overpredicted at the high end of the concentration range (+10%).

Figure 1b shows that the final NO₂ concentrations during each MOChA experiment ranged between 20 and 90 ppb. A linear regression analysis of measurements and model predictions yields a regression slope = 0.92 ± 0.08 and correlation coefficient (R²) = 0.91. Model predictions are within 5% of measured values above 35 ppb. However, at

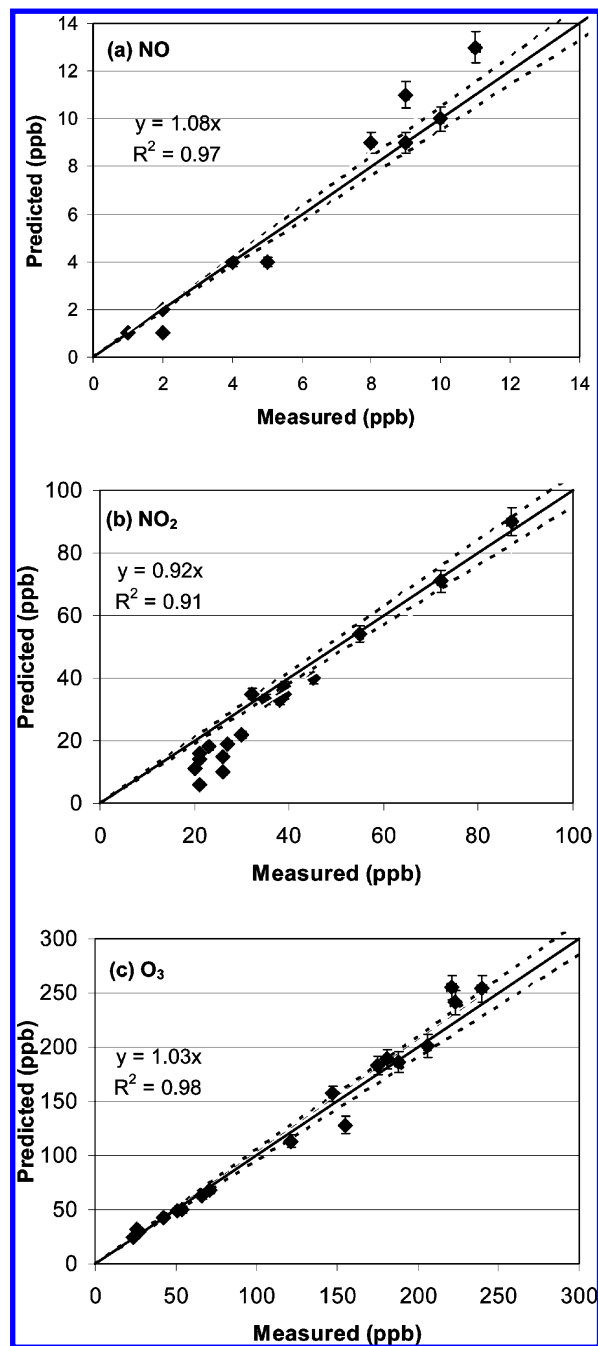


FIGURE 1. Predicted vs measured concentrations of (a) NO, (b) NO₂, and (c) O₃ during experiments to measure the OFP of ROG emissions from animal sources. Uncertainty bars represent the 95% confidence interval of the measurement.

lower final NO₂ concentrations the model under-predicts measured values by 20–70%. Part of this discrepancy is caused by the mis-classification of NO_y compounds as NO₂ by the measurement device (model no. ML9841A, Teledyne Monitor Laboratories, Englewood, CA). The chemiluminescence monitor measures NO concentrations in an unperturbed air sample and then, through the use of a molybdenum catalyst, converts all reactive nitrogen compounds to NO for a second measurement. NO₂ is calculated as the difference between the first and second measurement under the assumption that NO and NO₂ account for the majority of the reactive nitrogen in the system. The monitor inherently measures NO_y species (HONO, HNO₃, etc) as NO₂. When model results for total NO_y–NO concentrations are compared to measured NO₂ concentrations (that include NO_y–NO) the

TABLE 1. Composition of ROG Emissions from Animal Sources. Units Are ($\mu\text{g Compound}/\mu\text{g ROG}$) \times 100%^a

ROG	animal type					
	beef cattle		swine		poultry	
	% total	std dev	% total	std dev	% total	std dev
alkanes and cyclic alkanes						
butane	0.03	0.06				
isobutane	0.05	0.14				
2-methyl butane	0.15	0.26	0.27	0.13		
<i>n</i> -pentane			0.05	0.08		
<i>n</i> -heptane			0.11	0.09		
2-methyl hexane			0.18	0.18		
3-methyl hexane			0.28	0.21		
<i>n</i> -octane			0.30	0.43		
3-methyl heptane	0.19	0.10	0.72	1.02		
isopropylcyclobutane			0.23	0.03		
alkenes						
2-methyl 1-propene			0.13	0.19		
2-butene	0.01	0.02				
2-methyl 1-pentene	1.17	1.82				
dienes						
isoprene	0.06	0.06	0.13	0.18		
1,2-pentadiene	0.14	0.16				
hexadiene	0.01	0.01				
alpha-pinene	0.29	0.39	1.31	0.24		
beta-pinene	0.15	0.43				
camphene			2.77	0.00		
hexachlorobutadiene					5.47	9.48
alcohols and phenols						
ethanol	81.91	10.13	52.82	1.91		
allyl alcohol	1.05	2.97				
methyl butanol	1.68	1.58				
1-hexanol			2.39	1.28		
heptanol	0.08	0.12				
2-ethyl hexanol	0.15	0.18				
phenol	0.06	0.08	1.79	0.28		
2-phenyl 2-propanol			17.96	9.79		
ketones						
methyl isobutyl ketone	0.08	0.17			0.96	0.42
3-hexanone	0.15	0.13				
methyl <i>n</i> -butyl ketone	0.48	1.23	0.09	0.13		
cyclohexanone	0.32	0.26	0.27	0.09		
aldehydes						
ethanal (acetaldehyde)			1.55	0.45		
2-methyl butanal	0.23	0.49				
hexanal	1.29	0.51	1.64	0.93	33.29	11.29
furfural			0.13	0.18		
heptanal	0.93	0.86	0.96	0.22	21.40	10.33
benzaldehyde	0.08	0.16	1.11	0.11		
octanal	1.50	1.25	1.61	0.69	16.40	6.03
nonanal	3.14	2.32	6.59	2.41		
decanal	0.69	0.87	3.03	1.17		
aromatics						
benzene	0.01	0.02	0.35	0.22		
toluene	1.10	1.78	0.47	0.38		
methyl-ethyl benzene isomers	0.23	0.21			0.24	0.42
trimethylbenzene isomers	0.15	0.10	0.75	0.28	0.43	0.75
chlorobenzene	0.01	0.03				
1,4 dichlorobenzene	0.13	0.23			0.69	1.19
1,3 dichlorobenzene	0.09	0.18			0.55	0.96
1,2 dichlorobenzene	0.11	0.20			0.79	1.36
1,3,5 trichlorobenzene	2.01	2.04			19.05	17.24
other compounds						
<i>n</i> -propyl amine	0.02	0.05				
chloropicrin	0.08	0.11				
dimethyl disulfide					0.73	1.27
total ROG concentration ($\mu\text{g}/\text{m}^3$)	233.38	30.27	357.00	12.73	36.43	26.57

^a The standard deviation represents variability across multiple sets of animals. Missing values represent measurements that were below instrument detection limits or indistinguishable from background concentrations.

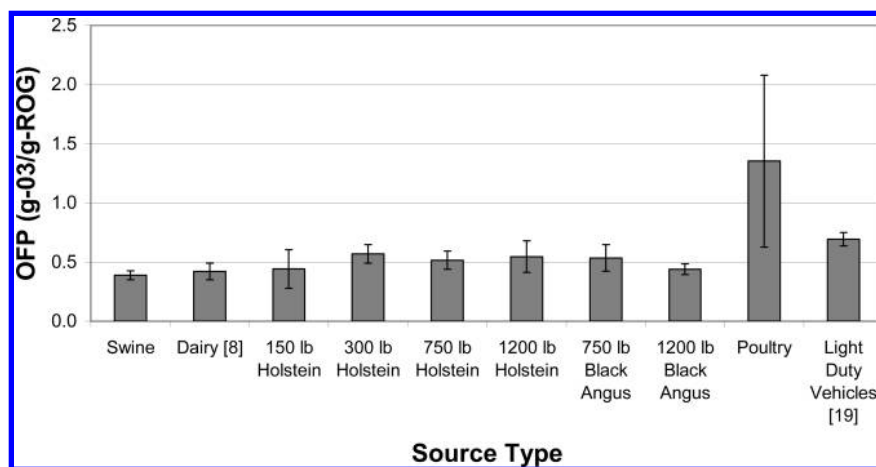


FIGURE 2. Average OFP of the ROG emissions from animal sources (see (8) for dairy cattle) and light duty gasoline-powered vehicles (19) expressed as g-O₃ produced/g-ROG emitted. Uncertainty bars represent the range of conditions considered (see text).

two results agree within 10%. A comparison between Figure 1a vs 1b shows that NO concentrations at the end of an experiment were typically 10–20 times lower than the NO₂ concentration.

Predicted vs measured final ozone concentrations during livestock and poultry experiments are plotted in Figure 1c. Individual experiments were performed with and without a ROG mini-surrogate background atmosphere inside the smog chamber leading to a broad range of final ozone concentrations. The CACM model was able to predict the measured ozone concentrations across the entire range of observations (regression slope = 1.033 ± 0.04 , $R^2 = 0.98$).

The detailed ROG composition (compound mass/total ROG mass $\times 100\%$) measured using GC–MS analysis of SUMMA canister/sorbent tube samples, and HPLC analysis of DNPH cartridges during beef cattle, swine, and poultry experiments is listed in Table 1. Total ROG concentrations (in $\mu\text{g}\cdot\text{m}^{-3}$) for each source type are reported at the bottom of Table 1. Uncertainty in the reported values can stem from numerous sources: analytical uncertainty, sample collection uncertainty, and uncertainty caused by variability in the source itself. The overall uncertainty of the current measurements is dominated by the source variability. The uncertainty ranges listed in Table 1 therefore reflect one standard deviation of the measurements from similar animal types. Total ROG emissions are also summarized for each animal waste category. Ethanol ($82 \pm 10\%$) accounted for the majority of the ROG measured from beef cattle, with numerous other compounds making up the balance. Ethanol ($52 \pm 2\%$) also dominated swine emissions, followed by 2-phenyl-2-propanol ($18 \pm 13\%$), aldehydes ($16 \pm 6\%$), other alcohols ($4 \pm 2\%$), terpenes ($4 \pm 1\%$), and various other minor compounds. Ethanol was not detected in poultry waste emissions. Aldehydes accounted for $71 \pm 29\%$ of the identified ROG mass from poultry barns, with another $20 \pm 17\%$ attributed to trichlorobenzene, and the remainder accounted for by various compounds. These results compare favorably with results of ROG concentrations from animal waste sources published previously (16–18). The chlorinated compounds, as well as the methyl-substituted benzenes, plausibly arise from the feed (or the facility) rather than from the animal waste. Various pesticides and/or pesticide solvents are used in and around the poultry barn or in feed production, which could account for the high trichlorobenzene concentration. These results demonstrate that ROG composition varies substantially for different animal waste sources and ROG profiles from one source should only be applied to other sources with caution.

After validating the CACM model versus experimental data, model simulations were used to determine OFP of the ROG emissions from agricultural sources under a wide range of conditions. Figure 2 plots the OFP (grams of O₃ produced per gram of ROG) for livestock and poultry waste emissions. The OFP of dairy cattle (8) and light duty gasoline-powered vehicles (LDV) (19) were added to Figure 2 for comparison to the animal waste sources characterized in the current study. The livestock and poultry waste OFP was predicted for two reference systems spanning the range of rural conditions in the SJV (NO_x = 50 ppb; ROG mini-surrogate = 62.5 ppb) and urban conditions in the SJV (NO_x = 75 ppb; ROG mini-surrogate = 125 ppb) (20). These reference systems happen to lie on the ozone isopleth at the point where ROG and NO_x controls would contribute equally to ozone reduction. Hence, the calculated OFP conforms to the equal benefit incremental reactivity method (EBIR) (21). The OFP (g-O₃/g-added ROG) is defined as the additional ozone formed when a small amount of source ROG is added to the reference mixture. The range of OFP calculated for each reference system is shown as the uncertainty bars about the mean value in Figure 2. The OFP of livestock ROG emissions (including dairy cows) ranged between 0.4 and 0.6 g-O₃/g-ROG. Animal breed and size influenced OFP by less than 6%. The poultry waste ROG emissions had a significantly higher OFP value of 1.35 ± 0.73 g-O₃ per g-ROG. The uncertainty in the OFP measurement for poultry waste emissions is largely due to the variability in the trichlorobenzene concentration. A more detailed analysis of the pesticide use at the poultry farm would help to narrow the uncertainty for poultry OFP. For reference, the calculated OFP of the ROG emitted from light duty gasoline-powered vehicles is approximately 0.69 ± 0.05 g-O₃ per g-ROG (see ref 19 for ROG emissions from LDV).

Figure 3 depicts the OFP for livestock and poultry waste emissions based on direct measurements (including previous dairy measurements (8)) versus the OFP predicted by the ROG source profile in the official CARB emissions inventory (4). CARB employs a single ROG profile for all animal waste sources. The approach that CARB used to develop this approximate animal waste ROG profile and the errors associated with it have been discussed previously in the literature (8, 9). The direct OFP measurements for livestock waste are 40–60% lower than CARB estimates. The direct measurements of poultry waste OFP are 50% higher than CARB estimates. Comparing across all direct measurements, swine, dairy cattle, and beef cattle all have similar OFP (an average of 0.44 ± 0.07 g-O₃ per g-ROG),

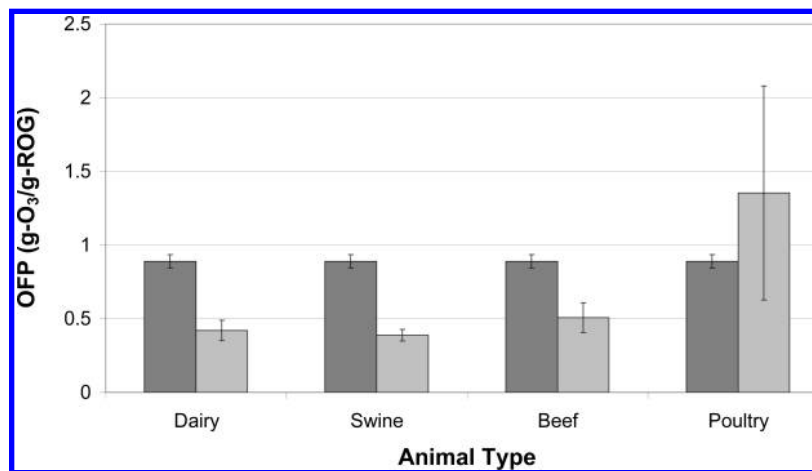


FIGURE 3. Comparison of OFP for livestock and poultry emissions based on the present study (light bars) and the official CARB emissions inventory (dark bars). Uncertainty bars represent the range of conditions considered (see text).

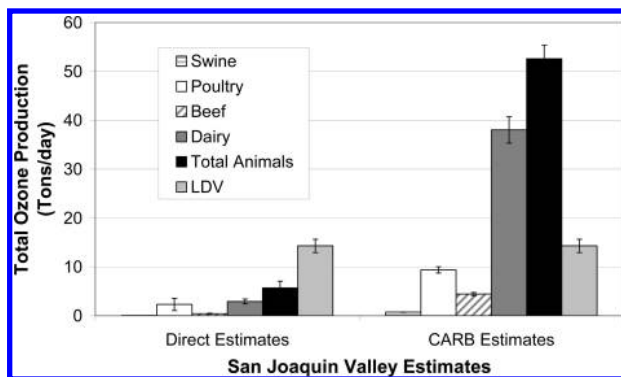


FIGURE 4. Total ozone production for animal plus waste sources based on two ozone formation estimates and light duty passenger vehicles calculated as the product of total ROG emissions (22) and the OFP for each ROG source assuming equal benefit incremental reactivity conditions. Uncertainty bars represent the range of conditions considered (see text).

whereas the OFP of poultry waste is 3 times higher than the other sources.

Total ozone formation from a source can be approximately calculated as the product of the OFP and the total ROG emissions from that source. Figure 4 shows the estimated total ozone production (tons-O₃/day) attributed to the various animal waste sources and light duty vehicles using the total ROG emissions (tons-ROG/day) from CARB's inventory (19) along with the direct OFP (bars) measured in the current study (see Figure 3) in the SJV. Ozone production totals calculated using direct measurements of OFP were combined with animal waste ROG emissions that were reduced by a factor of 6 to correct an error in the ROG/TOG ratio used in the official emissions inventory (see ref 9). This methodology produces an updated estimate of total ozone production from animal waste sources that can then be compared to official estimates.

The results illustrated in Figure 4 show that LDV emissions are the dominant source of ozone production for the SJV based on the new estimates of ozone formation predicted in this study. LDV emissions account for 14.3 ± 1.4 tons day⁻¹ of ozone production compared to only 5.70 ± 1.8 tons day⁻¹ of ozone production associated with livestock and poultry waste emissions. Estimates for total ozone production from animal waste sources using the official emissions inventory are approximately 9 times larger than the values calculated using the updated methodology due to an overestimation of the ROG emissions rate (factor of 6) and an overestimation of the OFP of those emissions (factor of 1.5). More accurate

studies of agricultural ozone formation potential within the SJV are needed to develop accurate emissions inventories for livestock and poultry waste sources.

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Supporting Information Available

Figure S1 compares the time sequence of predicted vs measured O₃, NO, and NO₂ concentrations during beef, poultry, and swine experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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