Volatile Organic Compound Emissions from Dairy Cows and Their Waste as Measured by Proton-Transfer-Reaction Mass Spectrometry

STEPHANIE L. SHAW,*,† FRANK M. MITLOEHNER,‡ WENDI JACKSON,‡ EDWARD J. DEPETERS,‡ JAMES G. FADEL,‡ PETER H. ROBINSON,‡ RUPERT HOLZINGER,†,§ AND ALLEN H. GOLDSTEIN†

Department of Environmental Science, Policy, and Management, University of California, Berkeley, Hilgard Hall, Berkeley, California 94720, and Department of Animal Science, University of California, Davis, Davis, California 95616

California dairies house approximately 1.8 million lactating and 1.5 million dry cows and heifers. State air regulatory agencies view these dairies as a major air pollutant source, but emissions data are sparse, particularly for volatile organic compounds (VOCs). The objective of this work was to determine VOC emissions from lactating and dry dairy cows and their waste using an environmental chamber. Carbon dioxide and methane were measured to provide context for the VOCs. VOCs were measured by proton-transfer-reaction mass spectrometry (PTR-MS). The compounds with highest fluxes when cows plus waste were present were methanol, acetone + propanal, dimethylsulfide, and *m*/*z* 109 (likely 4-methyl-phenol). The compounds with highest fluxes from fresh waste (urine and feces) were methanol, *m*/*z* 109, and *m*/*z* 60 (likely trimethylamine). Ethanol fluxes are reported qualitatively, and several VOCs that were likely emitted (formaldehyde, methylamine, dimethylamine) were not detectable by PTR-MS. The sum of reactive VOC fluxes measured when cows were present was a factor of 6−10 less than estimates historically used for regulatory purposes. In addition, ozone formation potentials of the dominant VOCs were ∼10% those of typical combustion or biogenic VOCs. Thus dairy cattle have a comparatively small impact on ozone formation per VOC mass emitted.

Introduction

The San Joaquin Valley (SJV) in central California is in extreme nonattainment of current state and federal ozone (O_3) standards (*1*). O_3 is formed by the interaction of sunlight with volatile organic compounds (VOCs) and nitrogen oxides. VOC emissions reductions are required at the air district level to achieve O_3 standard attainment. Agricultural processes, notably animal operations, are no longer exempt from emission controls as a result of California Senate Bill 700. The proposed SJV Air District Rule 4570 intends to reduce VOC emissions from dairies, cattle feedlots, poultry ranches, and other operations by 14 Mg VOC day^{-1} (26%; *2*). Rule 4570 development is ongoing, includes the adoption of VOC emission factors, and is scheduled to be implemented in January 2007.

California is home to the largest dairy industry in the world, with ∼2100 dairies that produce ∼23% of the nation's milk supply. Within the last 10 years the number of lactating cows per dairy has more than doubled to an average of 825. In 2004 California dairy cattle and their waste were estimated to contribute as much reactive organic gases (ROGs) to the atmosphere as light/medium duty trucks or light passenger vehicles (*2*). ROGs are defined as the subset of VOCs that are reactive enough to contribute substantially to atmospheric photochemistry (*1*). The relevant 183 μg ROG cow^{-1} s^{-1} emission factor was based on a 67-year-old study of what is now known to be total organic gas emissions from adult Holstein and Jersey cows (*3*). ROG emissions were then calculated by applying an 8% factor as determined by the Environmental Protection Agency (*4*). Compound-specific VOC analysis techniques have improved dramatically in recent years, and new measurements of dairy emissions are required to create accurate inventories.

This article reports the results of controlled chamber experiments designed to identify and quantify VOC emissions from dairy cows and their waste at various stages of the lactation cycle (SLC). Emissions were measured with a proton-transfer-reaction mass spectrometer (PTR-MS). In contrast to traditional gas chromatography−mass spectrometry, this technique uses 'soft' chemical ionization which results in minimal compound fragmentation. Therefore no separation is required, resulting in high frequency measurements and rapid response times (s) (*5*). In addition, simultaneous detection of a variety of VOC types that traditionally required multiple instruments is possible.

Methods

Site Description. Experiments were conducted at the University of California, Davis, Department of Animal Science Swine Research Facility. Groups of three cows each were housed in an environmentally controlled chamber (4.4 m × 2.8 m × 10.5 m) at 18 °C, which simulated representative commercial freestall conditions. Fresh air was provided by forced ventilation at 3.8×10^4 L min^{-1}, resulting in a chamber residence time of ∼6 min. Tests of smoke release with complete dispersal throughout the chamber prior to execution of the experiments showed the air was completely cleared in <10 min. Feed and water troughs were provided to allow ad libitum consumption. The cows excreted urine and feces, which accumulated on the concrete floor until the chamber was cleaned. Therefore all reported cow measurements also include waste. All waste only measurements are applicable for fresh day-old wastes.

Teflon diaphragm (oil-less) pumps (KNF) pulled air at a controlled rate (MKS Instruments) from inlet and outlet vents on the chamber ceiling to analytical instrumentation in an adjacent chamber. All sampling lines were approximately 20 m long 1/8 in. ID Teflon tubes with inline Teflon particulate filters. A 1 L min^{-1} flow was pulled from the chamber to a proton-transfer-reaction mass spectrometer (Ionicon Analytik) channel, of which a minor fraction was analyzed. A 4

* Corresponding author phone: (510)642-9732; fax: (510)643-5098; e-mail: slshaw@alum.mit.edu.
† University of California, Berkeley.
‡ University of California, Davis
§ Current address: Institute for Marine and Atmospheric Research (IMAU), Utrecht, The Netherlands.

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TABLE 1. Diet Composition (in % of Dry Matter (DM)), DM Ingested, Milk Yield, and Body Weight for Cows in Various Stages of Lactation Cycle

ingredient	far off	close up	early lactation	mid lactation 1[a]	mid lactation 2[a]	late lactation
grain mix[b]	0	23.1	34.8	34.8	33.3	33.3
alfalfa	31.0	29.7	39.2	39.2	48.2	48.2
oat hay	61.0	0	0	0	0	0
whole cottonseed meal	0	0	11.3	11.3	5.4	5.4
almond hulls	0	10.7	8.1	8.1	11.6	11.6
soybean meal	0	0	4.0	4.0	0	0
milk mineral	0	0	1.6	1.6	1.2	1.2
energy II	0	0	0.6	0.6	0	0
salt	0	0	0.3	0.3	0.3	0.3
oats	0	21.4	0	0	0	0
niacin pellet	0	1.1	0	0	0	0
nutri-chlor	0	9.1	0	0	0	0
dry cow pellet[c]	8.0	4.9	0	0	0	0
total DM ingested (DMI; kg cow^{-1} $time^{-1}$ [d])	7.6	11.4	NA	NA	9.1	6.5
average milk yield (kg cow^{-1} day^{-1})	0	0	47.8	31.6	44	32.7
average body weight (kg cow^{-1})	747.3	791.8	724.7	618.3	560.5	540.8

[a] Mid lacation 1 fed the same diet as early lactation; mid lactation 2 fed the same diet as late lactation. [b] The grain mix contained (% DM) barley (41.5), corn (41.5), beet pulp (13.8), and tallow (3.2). [c] The dry cow pellet contained (% DM) minerals (*27*), soybean meal (36.5), and wheat meal run (36.5). [d] DMI for lactating cows is calculated for the 6 h enclosure time and is only a portion of the daily intake. DMI for dry cows is per 24 h enclosure time.

L min^{-1} flow was pulled to a second channel and split between a LICOR 6262 infrared gas analyzer, to measure CO_2, and a cavity-enhanced-absorption spectrometer (Los Gatos Research, Inc.), to measure CH_4.

Animal Management. Both dry (nonlactating) and lactating Holstein dairy cows were used. Dry cows were pregnant and either 'far off' (45−60 days) or 'close up' (≤14 days) from calving. Lactating cows were categorized as early, mid, or late based on the days from calving and milk yield. Diet composition and consumption are listed in Table 1 and were intended to represent diets fed on commercial dairies in California. The far off diet was predominately forage based and provided sufficient energy and nutrients for cow maintenance and fetal development. The close up diet included forage and concentrate, which provided additional energy and nutrients for fetal development, as well as starch and sugar to increase the amylolytic microorganisms. This prepared the cows to later receive the early lactation diet (high concentrate). The late lactation diet contained more forage and less fat since the energy requirements for milk synthesis decline as yield decreases. Mid lactation cow groups were split in two and fed either early or late lactation diets to determine if composition influenced emissions. Cow groups were selected according to one of these six SLC. Three dry cows entered the empty chamber at approximately 08:30, and they remained for two consecutive 24 h sampling periods. The chamber was cleaned with a pressure hose at hour 24 to remove accumulated waste while the cows remained inside. Cows were removed after 48 h, but the accumulated waste from hours 24−48 h remained and was sampled for another 24 h. Alternatively, three lactating cows were milked before entry into the chamber at 08:30, where they remained for 6 h before removal for a second milking. Two to four consecutive days of lactating cows were tested. These consecutive days each had either different cow groups or replicate testing of the same group. Accumulated waste from the previous day was sampled for a 24 h period after some of the lactating cow groups exited. All measurements were repeated at least twice. Animal care was reviewed and approved by the Institutional Animal Care and Use Committee at the University of California, Davis.

Gas Analysis. The PTR-MS uses chemical ionization with H_3O^+ as a reactant and proton donor. If the target VOC has a proton affinity (PA) greater than that of H_2O, the proton is transferred to the VOC, which is detected by a mass spectrometer. Proton transfer occurs on every collision of a H_3O^+ ion with a VOC molecule, whenever $PA_{VOC} > PA_{H2O}$, thus defining the reaction rate. An applied electrical field defines the ion reaction time. VOC concentrations are calculated by combining these with measured count rates of H_3O^+ and the protonated VOC, which are modified by experimentally determined mass spectrometer transmissions at each m/z ratio (*5*). Therefore the PTR-MS allows estimation of mixing ratios for species which are unidentified or for which calibration standards were not available (*5*), which is an important benefit for these measurements. Many VOC types, including alcohols, aldehydes, aromatics, ketones, alkenes, amines, nitriles, sulfides, and acids, have $PA > PA_{H2O}$. Alkanes, some alkenes, and halogenated compounds are not detected. The PTR-MS also provides much more accurate measurements for polar VOC (e.g., aldehydes or ketones) than any technique requiring sample storage (e.g., canisters (*6*)). Compound detection limits are extremely low at 30−50 pptv, even in complex gas mixes.

Tentative identifications of protonated VOC masses were made by comparison with published ambient or dairy measurements (e.g., *5*, *7*−*10*). Confirmation occurred through analysis of fragmentation, water cluster, and isotope patterns in the context of each experiment, as few masses are unique to a single compound. As with all analyses, VOCs that tend to adsorb or condense onto surfaces can be difficult to detect. Analytical capabilities for such VOC (i.e., trimethylamine (TMA), volatile fatty acids (VFA), phenols) must be determined on an instrumentation basis. As calibration standards with which to test for TMA and VFA losses were not available, the observed fluxes of these compounds must be considered lower limits. They are included for relative comparisons across cow groups. Previous work with the identical PTR-MS showed good sensitivity and negligible memory effects for acetic acid (*7*). Expected compounds that typically cannot be quantified with the PTR-MS are hydrogen sulfide (H_2S), carbon disulfide, and formaldehyde due to low PA, and methylamine (MA) and dimethylamine (DMA) due to high instrument background at their masses. In addition, a large fraction of sampled ethanol is fragmented and converted to

TABLE 2. Average $\pm$ 1σ of All Hourly Averaged Compound Fluxes (μg cow^{-1} s^{-1}) from the First 6 h of Enclosure for All Replicate Days (n)

cow groups[a]	CO_2 $\times 10^{-4}$	TOG[b]	CH_4	ROG[c]	methanol[d]	DMS[d]	m109[d]	acetic acid[d]	acetone + propanal[e]
far off 21, $n = 4$	12.2 $\pm$ 1.2	NA	NA	10.6	5.3 $\pm$ 2.8	1.3 $\pm$ 1.0	0.56 $\pm$ 0.25	0.78 $\pm$ 0.60	4.5 $\pm$ 1.0
far off [f]86, $n = 4$	12.1 $\pm$ 1.5	NA	NA	10.3	5.9 $\pm$ 2.3	1.0 $\pm$ 1.0	0.47 $\pm$ 0.29	0.42 $\pm$ 0.51	4.5 $\pm$ 1.4
far off WASTE[f,g] 50, $n = 2$	0.17 $\pm$ 0.46	NA	NA	6.1	3.8 $\pm$ 1.0	0.07 $\pm$ 0.26	0.49 $\pm$ 0.38	0.09 $\pm$ 0.21	0.4 $\pm$ 1.0
close up 25, $n = 4$	18.6 $\pm$ 2.7	3650	3610 $\pm$ 860	37.4	23 $\pm$ 18	7.9 $\pm$ 9.6	1.4 $\pm$ 1.2	1.0 $\pm$ 2.0	4.7 $\pm$ 2.2
close up[f] 83, $n = 4$	17.1 $\pm$ 3.2	2950	2920 $\pm$ 960	23.6	12 $\pm$ 12	3.1 $\pm$ 6.1	2.6 $\pm$ 1.8	1.0 $\pm$ 1.5	4.1 $\pm$ 1.8
close up WASTE[f,g] 27, $n = 2$	0.27 $\pm$ 0.20	16.6	1.7 $\pm$ 3.6	14.5	4.96 $\pm$ 0.71	0.06 $\pm$ 0.04	5.6 $\pm$ 3.1	0.87 $\pm$ 0.38	0.29 $\pm$ 0.19
early lactating 24, $n = 2$	21.2 $\pm$ 2.1	NA	NA	22.5	13.5 $\pm$ 2.9	1.53 $\pm$ 0.87	0.68 $\pm$ 0.25	1.2 $\pm$ 1.5	8.0 $\pm$ 2.0
mid lactating 1 38, $n = 4$	18.1 $\pm$ 2.3	NA	NA	16.4	7.1 $\pm$ 3.2	1.2 $\pm$ 1.1	0.74 $\pm$ 0.27	2.0 $\pm$ 1.2	4.0 $\pm$ 1.8
mid lactating 2 17, $n = 2$	20.5 $\pm$ 4.7	4190	4160 $\pm$ 1150	30.8	15.3 $\pm$ 6.5	5.0 $\pm$ 3.0	1.19 $\pm$ 0.46	2.7 $\pm$ 1.4	4.8 $\pm$ 1.3
mid lactating 2 WASTE[g] 12, $n = 2$	0.16 $\pm$ 0.18	17.	2.6 $\pm$ 8.2	14.2	6.1 $\pm$ 1.3	0.43 $\pm$ 0.13	2.05 $\pm$ 0.72	1.19 $\pm$ 0.52	0.22 $\pm$ 0.07
late lactating 14, $n = 2$	17.3 $\pm$ 3.2	3590	3560 $\pm$ 770	24.4	12.2 $\pm$ 5.5	3.9 $\pm$ 3.0	1.08 $\pm$ 0.38	1.57 $\pm$ 0.82	4.84 $\pm$ 0.64
late lactating WASTE[g] 13, $n = 2$	0.22 $\pm$ 0.24	19	6 $\pm$ 33	12.8	5.3 $\pm$ 1.2	0.33 $\pm$ 0.24	1.70 $\pm$ 0.40	1.09 $\pm$ 0.42	0.38 $\pm$ 0.25

[a] Number of data points (first number) was identical for all individual ROGs within a cow group except m109 and m60 ($\sim$50%) and CO_2 and CH_4 ($\sim$200%). [b] TOG = CH_4 + ROG + acetone + propanal. [c] ROG = sum of all PTR-MS VOCs (except acetone + propanal, ethanol, and TMA). [d] Masses included in ROG (and thus TOG) with highest fluxes. [e] NOT included in ROG (but is a TOG). [f] Data from all 24 h were used. [g] Fluxes relevant for day-old waste.

ethene, which is undetectable due to low PA. This results in very low signal-to-noise for ethanol.

The PTR-MS was operated continuously, alternating between single ion mode (SIM) and scan mode (SCAN) at the start of each sampling hour. SIM monitored 50 specified masses and was used to obtain better precision than was possible when monitoring masses 20−175 amu in SCAN mode (Table S1). SCAN mode was useful for detecting all compounds in that mass range with PA > PA_{H2O}. All masses observed by the PTR-MS are reported here unless noted otherwise. Twenty minutes each of chamber inlet air, outlet air, and inlet air redirected through a catalytic converter to remove all VOC and create an instrument blank (*7*) were sampled hourly.

Gaseous calibration mixes (Apel-Riemer Environmental, Inc.) were available for a subset of the observed VOCs. Mixes were added by dynamic dilution to the blank for the last 10 min of each sampling hour. Uncertainties for calibrated compounds, determined as the difference between expected and measured concentrations, were <±20% (Table S1). Measurement uncertainties for unidentified or uncalibrated compounds were larger (<±40%), as they were determined by propagating reaction rate and transmission uncertainties through the concentration calculation.

CO_2 concentrations in chamber inlet air were measured during minutes 12−15 and 27−30 of each sampling half hour, while outlet air was measured during the remaining time. CO_2 was calibrated three times daily for 2 min each against two standards (2500 $\pm$ 50 ppm, and either 386 ppm or 90 ppm). The cavity-enhanced-absorption gas analyzer measured CH_4 concentrations on this same schedule. This instrument works in real time, with ppbv detection limits, and only occasional factory calibration is required (*11*).

Fluxes were calculated as the concentration difference between the chamber outlet and inlet air streams, multiplied by the air density and flowrate, and reported in units of μg compound cow^{-1} s^{-1}. For this paper VOCs were defined as all the individual volatile compounds detected by PTR-MS. Reactive organic gases (ROGs) are the subset of VOCs that contribute substantially to atmospheric photochemistry and form O_3 (*1*). This was calculated as the sum of all PTR-MS VOCs except acetone (exempt for regulatory purposes (*1*)), TMA (uncalibrated), and ethanol (low signal-to-noise). Total organic gases (TOGs) were calculated as the sum of CH_4, ROGs, and acetone + propanal. VOC and ROG data were hourly averages ($\sim$10−15 points), and all other data were half-hourly averages ($\sim$100 points).

Statistical Analysis. The most abundant compound fluxes from the different experiments were statistically analyzed with two models using PROC MIXED of SAS Version 9 (SAS Institute; Cary, NC). Model A compared different SLC when the cows plus waste were in the chamber and included cow groups as random within SLC. The contrasts tested for model A were as follows: (1) all lactating vs all dry, (2) far off vs close up, and (3) early vs late lactation diet groups. Model B included all the terms of model A plus chamber status (empty chamber, cows plus waste, and waste only) and the interaction of SLC and chamber status. Chamber status was compared only through the interaction term. The contrasts tested for model B were as follows: (1) waste for lactating cows vs empty chamber, (2) waste for dry cows vs empty chamber, (3) cows plus waste vs waste for lactating cows, and (4) cows plus waste vs waste for dry cows.

Results and Discussion

CO_2 and CH_4 Fluxes. CO_2 fluxes for the cow groups and statistical comparisons between them are reported in Tables 2 and 3. Dry cows plus waste emitted significantly less CO_2 than lactating cows plus waste. Far off cows plus waste emitted significantly less CO_2 than close up cows plus waste. However, the fluxes from various lactating cow groups were not significantly different from each other, even though two different diets were used depending on the SLC. The fluxes averaged across all dry and all lactating cows plus waste were (15.7 $\pm$ 3.9) $\times$ 10^4 and (19.4 $\pm$ 3.4) $\times$ 10^4 μg CO_2 cow^{-1} s^{-1}, respectively. The corresponding dry and lactating cow plus waste CH_4 fluxes were 3610 $\pm$ 860 and 3900 $\pm$ 1000 μg cow^{-1} s^{-1}. CH_4 fluxes from lactating cows are usually larger than those from dry cows because of greater feed consumption (*3*, *12*). There was no statistical difference between CH_4 fluxes in this study ($P = 0.13$; 95% significance) as determined with Student's t-test. This is likely due to the limited amount of available CH_4 data. Fluxes were not measured for far off or early lactation cows, the former of which consumed substantially less feed than other cows (Table 1). This also prohibited CH_4 inclusion into the statistical models (Table 3).

CO_2 fluxes from waste were not significantly different from those in the empty chamber; both were smaller than those from the cows plus waste (Table 3). CH_4 fluxes from the waste

TABLE 3. Probability (*P*) Values of the Differences between Average Fluxes of Selected Comparisons

	CO_2	ROG	methanol	DMS	m109	acetic acid	acetone + propanal	isoprene
model A: cows + waste comparisons								
lactating vs dry	**0.020**[a]	0.893	0.796	0.602	0.989	0.067[b]	0.313	**0.007**
far off vs close up	**0.014**	0.061[b]	0.075[b]	0.110	0.161	0.658	0.754	0.313
early vs late lactation diet groups	0.664	0.417	0.575	0.311	0.399	0.323	0.399	0.242
model B: waste comparisons								
waste vs empty (lactating)	0.753	**0.003**	**0.007**	0.682	**<0.0001**	**0.005**	0.468	0.188
waste vs empty (dry)[c]	0.761	**0.024**	**0.038**	0.948	**<0.0001**	0.174	0.418	0.677
cows + waste vs waste (lactating)	**<0.0001**	**0.001**	**0.001**	**0.002**	**0.004**	**0.008**	**<0.0001**	**<0.0001**
cows + waste vs waste (dry)[c]	**<0.0001**	0.168	0.115	0.208	**0.002**	0.277	**<0.0001**	**0.016**

[a] Bold type signifies statistical differences with $P < 0.05$ (95% confidence). [b] Statistical differences exist with $P < 0.10$ (90% confidence). [c] Comparisons within groups of dry cows used average fluxes from all 24 h. All other comparisons were between dry and lactating cows. As the latter were only in the chamber for 6 h per day, only the first 6 h of data were used (even when more existed).

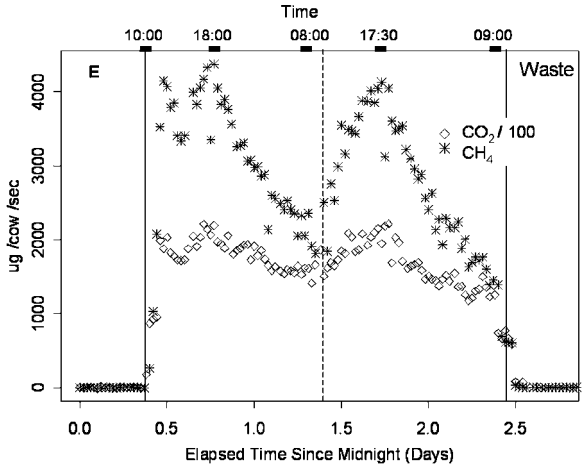

FIGURE 1. CO_2 and CH_4 fluxes from close up cows and their waste averaged over both replicate 2.5 day periods. Cow entry and exit times are denoted by solid lines, cleaning by a dashed line, and a clean and empty chamber by 'E'. Pooled standard errors are smaller than the symbols.

of lactating cows were not different from ($P = 0.27$; 95% significance) those of the empty chamber as determined using Student's *t*-test, but fluxes from the waste of dry cows were ($P < 0.001$). Therefore CO_2 and CH_4 were dominantly derived from the cows through respiration and enteric fermentation, respectively. This assumes the waste fluxes were representative of those on the previous day when the waste was excreted. The exception was CH_4 emission from the waste of dry cows.

The average CH_4 fluxes observed in this study were 1.8 times greater than the 2123 μg cow^{-1} s^{-1} previously determined for adult Holstein and Jersey cows (*3*, *4*). Several more recent measurements were summarized by Williams et al. (*13*), who noted 2662 μg CH_4 cow^{-1} s^{-1} was typical for dairy cows. This corresponds well with our 24-h-averaged fluxes from close up cows plus waste. Furthermore, our CH_4 to CO_2 mass flux ratio (2.0%) was 44% lower than that previously measured for lactating Holstein cows (3.6%; (*14*)).

Daily CO_2 and CH_4 Patterns. Figure 1 shows daily patterns of CO_2 and CH_4 fluxes from close up cows and their waste. Fluxes of both compounds increased immediately after the cows entered the chamber around 10:00 on the first day. CH_4 fluxes peaked about 17:00 to 18:00 depending on the day, and then they decreased until 08:00 or 09:00 on subsequent mornings. Peaks in CH_4 fluxes are commonly observed several hours after feeding (*13*). Thus the evening maxima for close up cows plus waste imply their primary meals were in the afternoons. The CO_2 pattern was more subtle than that for CH_4, but still evident. However the CO_2 fluxes for far off cows plus waste (not shown) were constant over each enclosure. This implies daily patterns may change with SLC. Patterns for lactating cows plus waste are unknown as they were in the chambers for only 6 h per day. However, Kinsman et al. (*14*) reported that CO_2 and CH_4 fluxes from lactating Holsteins increased at 07:00 and decreased at 21:00.

VOC Fluxes Measured by PTR-MS. The VOCs or protonated masses measured by the PTR-MS with highest fluxes from the cows plus waste are reported in Table 2 and were as follows: methanol (m/z 33 + 51), acetone + propanal (m/z 59 + 77), dimethylsulfide (DMS; m/z 63), m/z 109 (likely 4-methyl-phenol), m/z 60 (likely TMA), and acetic acid (m/z 61 + 43; possible minor contribution from propanol). There were many VOCs with small but clearly positive fluxes when the cows were present. The most abundant of these were the following: m/z 41, acetaldehyde (m/z 45), ethanol (m/z 47), m/z 49 (possibly methanethiol), m/z 58, m/z 64, isoprene (m/z 69), m/z 75 + 57 (likely propionic acid), monoterpenes (m/z 81 + 137), m/z 83 (possibly hexanal and/or hexenol), m/z 87 (likely sum of pentanones), m/z 89 + 71 (likely butyric acid + isobutyric acid + ethyl acetate), dimethyldisulfide + phenol (m/z 95), m/z 101 (likely oxygenated aldehydes or ketones), m/z 103 + 85 (likely valeric acid + isovaleric acid), m/z 107 (possibly benzaldehyde + xylenes), m/z 121 (likely acetophenone), m/z 122, and m/z 123.

Dairy cow emissions of similar suites of VOCs have been previously observed. Dewhurst et al. (*8*) used a variation of the PTR-MS technique to measure VOC in the rumen headspace of Holstein−Friesian cows. They detected ppmv amounts of DMS and ppbv amounts of ethanol, methanol, acetone, acetaldehyde, acetic acid, propionic acid, butyric acid, and propanol. These measurements were often the same order of magnitude as our chamber air concentrations when cows were present. The average DMS fluxes reported here compared well to previously published fluxes (2.4 μg cow^{-1} s^{-1} (*13*)). Some of the most abundant VOCs we observed (methanol, ethanol, and acetone) are also the primary VOCs emitted in human breath (*15*).

The ROG fluxes averaged across all dry and all lactating cows plus waste were 25 and 23 μg cow^{-1} s^{-1}, respectively. While ethanol was not quantitative, it was so abundant its flux could be estimated as equal to, or slightly larger than, that of methanol for all experiments. Including this minimum ethanol estimate increased the ROG fluxes to 40 and 35 μg cow^{-1} s^{-1}, for dry and lactating cows plus waste, respectively. Regardless of ethanol inclusion, TOG fluxes from both dry and lactating cows plus waste were overwhelmingly dominated by CH_4 (>98%).

After the cows were removed from the chamber their waste remained. The VOCs with largest fluxes emitted from all wastes were methanol, m/z 109, and m/z 60. Acetic acid fluxes from the waste of lactating cows were also large (Table 2). Hobbs et al. (*9*) measured VOCs emitted from cattle

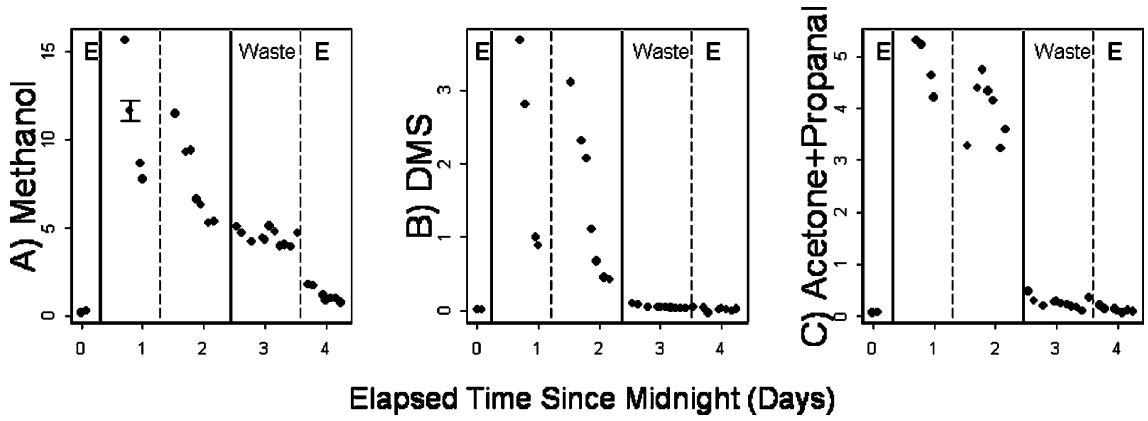

FIGURE 2. VOC fluxes in μg cow^{-1} s^{-1} from dry cows averaged over two replicate far off and two replicate close up cow periods. Cow entry and exit times are denoted by solid lines, cleaning times by dashed lines, and a clean and empty chamber by 'E'. Pooled standard errors are smaller than the symbols except for methanol, which is depicted on one point in panel A.

manure and similarly found acetic acid and 4-methyl-phenol (likely m/z 109) fluxes larger than those of other VFAs. No DMS, isoprene, or acetone + propanal fluxes were emitted from any waste as there was no significant difference from the empty chamber fluxes (Table 3). Therefore these compounds were likely derived only from the cows, assuming the waste only fluxes are representative of those from the previous day. DMS was previously reported to be derived from cows and not their waste (*13*).

The m/z 109 fluxes from waste were statistically larger than those from the empty chamber. Interestingly, fluxes from the cows plus waste were statistically smaller than those from waste alone (Table 3). It is therefore not clear if m/z 109 was derived in part from the cows, or solely from the waste. Previous work has shown that 4-methyl-phenol (likely m/z 109) is directly excreted as a fermentation product of the protein tyrosine, but it can also be emitted after later transformation within the waste (*16*, *17*).

The fluxes of ROGs, methanol, and acetic acid from the lactating cows plus waste were statistically larger than the corresponding fluxes from waste alone. The waste fluxes were in turn larger than those from the empty chamber (Tables 2 and 3). This implies these VOCs were primarily derived from cows, and emitted in comparatively small quantities from the waste. This once again assumes the waste only fluxes are representative of those from the previous day. In contrast there was no such difference for dry cows (Table 3), implying the entirety of these VOC emissions were derived from the waste alone. The average TOG fluxes from the wastes of all dry and all lactating cows were 12 and 18 μg cow^{-1} s^{-1}, respectively, and were dominated by ROGs (74 and 77%).

Daily VOC Patterns. Figure 2 shows daily patterns of methanol, DMS, and acetone + propanal fluxes from dry cows and their waste. All fluxes increased immediately after cows entered the chamber and on subsequent mornings after cleaning. Methanol and DMS fluxes were highest initially then decreased, while acetone + propanal remained comparatively constant. Once the cows were removed, methanol fluxes continued while the others ceased. Methanol and DMS can be created during rumen fermentation of the feed. Methanol derives from carbohydrate and proteins, while DMS derives from the amino acid cysteine (*16*). DMS fluxes are known to peak several hours after feeding (*8*, *13*), implying our dry cows fed at chamber entry. Acetone is released in the lungs of many living organisms as a result of metabolic fat burning and was thus detected whenever the cows were present. Despite the fact Figure 2 shows that larger DMS and methanol fluxes occurred from dry cows plus waste as compared to waste alone, the range of fluxes when cows were present was so large that these apparent differences were not statistically significant (Table 3).

Interpretation of the emissions sources may be confounded by time, as the waste was excreted 1 day before it was sampled alone. The statistics previously discussed implied the cows alone were responsible for most of the emissions of several compounds. However, it is possible those emissions were in part due to the waste, if they were emitted with a high initial flux that decreased over the 2 day enclosure. It is much more likely this occurred for compounds which did not have clear flux decreases when the cows exited the chamber (i.e., methanol, m/z 109) than for compounds which did (i.e., CO_2, CH_4, DMS, acetone + propanal; Figures 1 and 2). Longer enclosure periods could result in very different VOC emissions patterns. For example, it can often take a month or more in liquid manure storage lagoons to see large VOC increases (*18*). Therefore, while the reported fluxes from day-old waste can be compared to those measured when cows were present, they are likely inaccurate for waste stored longer than several days.

SLC Affects Fluxes. Dry cows undergo significant transition as they prepare for calving. That was exhibited by larger CO_2, ROG, and some individual VOC fluxes (e.g., methanol) for close up cows plus waste than for far off cows plus waste. These differences could be due to increased feed consumption, changes in diet composition, or changes in cow physiology, but it was not possible to deconvolute these factors. Previous work has shown that increasing the amount of dietary protein provided to close up cows resulted in increased urinary phenols (*16*, *17*). The average m/z 109 (likely 4-methyl-phenol) fluxes from the waste of close up cows reported here were larger than those from all other wastes. If a lactating cow does not eat sufficient feed to sustain milk production, she undergoes ketosis (i.e., metabolizes excessive amounts of body fat to produce energy). This results in increased production of ketones, including acetone, and is most common in early lactation phase. Early lactation cows plus waste in this study had the largest average acetone + propanal fluxes. Isoprene was included in the statistical analysis as an example of a VOC whose emissions from mammals are typically correlated with general metabolic rates (*5*). Dry cows plus waste emitted significantly less isoprene than lactating cows plus waste (Table 3 and unpublished data). Acetic acid fluxes were also significantly larger for lactating than dry cows plus waste. This was likely due to the larger amount of nonfibrous carbohydrates present in their feed, which are typically fermented faster and more completely than the forage fed to dry cows.

The largest compound fluxes observed were generally emitted from either close up or lactating cows plus waste.

TABLE 4. Normalized Ozone Formation Potential (OFP) for ROGs Emitted from Dairy Cows in Mid Lactation Phase

VOC	OFP	fluxes (μg cow^{-1} s^{-1})
isoprene	1.26 ± 0.18	0.28 ± 0.08
m-xylene	1.09 ± 0.04	0.2 ± 0.8[a]
ethene	1.00 ± 0	NA
formaldehyde	0.60 ± 0.17	NA
acetaldehyde	0.50 ± 0.35	0.61 ± 0.19
toluene	0.45 ± 0.16	0.08 ± 0.45[a]
ethanol	0.34 ± 0.07	≥ methanol flux
m109 (4-methyl-phenol)	0.32	0.97 ± 0.36
propionic acid	0.15	0.43 ± 0.25
methanol	0.11 ± 0.03	11.2 ± 4.8
acetic acid	0.10	2.4 ± 1.3

[a] Fluxes not significantly different from 0.

Additionally, compounds whose fluxes were statistically larger for the cows plus waste than for the waste alone were more numerous for lactating than for dry cows. An average flux would clearly be insufficient to represent all SLC, despite the fact all experiments were performed with the same breed and physical factors that can affect emission. Therefore we recommend that future studies group cows by their SLC.

O_3 Formation Potential of Dairy Cow ROGs. Determining the effects of dairy emissions on air quality requires including not just the fluxes but also the O_3 formation potential (OFP) of each individual ROG into an atmospheric model simulation. The OFP itself is also defined through modeling as the amount of O_3 produced as a result of adding a small amount of an individual ROG to an initial emissions mix, divided by the amount of ROG added. Modeling was beyond the scope of this work, but it was possible to qualitatively assess the impact of dairy ROG emissions on O_3 formation in regions with significant anthropogenic air pollution. We normalized the results of three independent OFP calculations (*19*−*21*) for all ROGs for which OFP were available to those of ethene and averaged them (Table 4). The ROGs we observed with the highest fluxes, ethanol and methanol, had OFPs ∼33 or 10% those of typical combustion (ethene) or biogenic (isoprene) ROGs. The ROGs with highest OFPs had fluxes that often were not significantly different from 0. We qualitatively conclude that dairy cows have a much smaller impact on ozone formation per VOC mass emitted than combustion or biogenic sources.

The ROG emitted as a percent of TOG when cows were present in the chamber was 0.8 ± 0.2%. Including a rough estimate of the ethanol flux (= methanol flux) brings this to 1.3%. This is a factor of 6−10 lower than the 8% historically used by California regulatory agencies for development of cow ROG emission inventories (*4*). The PTR-MS does not measure alkanes and alkenes, but large fluxes are not expected (*10*). Additionally, their OFPs are similar to, or less than, that of ethene (*19*−*21*). We do not report quantitative data for formaldehyde and methylamines. VFAs $>C_4$, and large molecular weight phenols, sulfur, and nitrogenous compound fluxes may be lower limits. Except for formaldehyde, OFP are not available for these compounds as their photochemistry has not been thought to produce large amounts of O_3. Even if we are only capturing a third of the ROG emissions, which we believe is a considerable underestimate based on relative emission fluxes from other published work (i.e., *8*−*10, 13*), ROG would still be only a third of the 8% estimate.

Our major findings, that (1) the OFP of ROGs emitted by dairy cows are a fraction of those for typical combustion or biogenic ROGs and (2) that the ROG/TOG ratio measured was a factor of 6−10 lower than that used historically, suggest that ROG emissions from dairy cows provide a much smaller contribution to O_3 formation than currently estimated for regulatory purposes in California.

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Supporting Information Available

PTR-MS accuracy and precision are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Schwehr, B. Definitions of VOC and ROG. California Air Resources Board, Planning and Technical Support Division, Emission Inventory Branch: Sacramento, CA, 2004. http://www.arb.ca.gov/ei/speciate/ROG_DFN_9_04.pdf.
(2) San Joaquin Valley Air Pollution Control District. 1-hour extreme ozone attainment demonstration plan. 2006. http://www.valleyair.org/Air_Quality_Plans/AQ_plans_Ozone_Final.htm.
(3) Ritzman, E. G.; Benedict, F. G. *Nutritional physiology of the adult ruminant*; Carnegie Institute: Washington, DC, 1938.
(4) U.S. Environmental Protection Agency. Volatile Organic Compound (VOC) Species Data Manual, Second Edition; EPA-450/4-80.-015; July 1980.
(5) Lindinger, W.; Hansel, A.; Jordan, A. On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS): Medical applications, food control, and environmental research. *Int. J. Mass. Spec. Ion. Proc.* **1998**, *173*, 191−241.
(6) Ochiai, N.; Tsuji, A.; Nakamura, N.; Daishima, S.; Cardin, D. B. Stabilities of 58 volatile organic compounds in fused-silica-lined and SUMMA polished canisters under various humidified conditions. *J. Environ. Monit.* **2002**, *4*, 879−889.
(7) Holzinger, R.; Millet, D. B.; Williams, B.; Lee, A.; Kreisberg, N.; Hering, S. V.; Jimenez, J.; Allan, J.; Worsnop, D. R.; Goldstein, A. G. Emission, oxidation, and secondary organic aerosol formation of volatile organic compounds as observed at Chebogue Pt, Nova Scotia. Submitted.
(8) Dewhurst, R. J.; Evans; R. T., Mottram, T. T.; Spanel, P.; Smith, D. Assessment of rumen processes by selected-ion-flow-tube mass spectrometric analysis of rumen gases. *J. Dairy Sci.* **2001**, *84*, 1438−1444.
(9) Hobbs, P. J.; Webb, J.; Mottram, T. T.; Grant, B.; Misselbrook, T. M. Emissions of volatile organic compounds originating from UK livestock agriculture. *J. Sci. Food Agric.* **2004**, *84*, 1414−1420.
(10) Filipy, J.; Rumburg, B.; Mount, G.; Westberg, H.; Lamb, B. Identification and quantification of volatile organic compounds from a dairy. *Atmos. Environ.* **2006**, *40* (8), 1480−1494.
(11) Baer, D.; Paul, J. P.; Gupta, M.; O'Keefe, A. Sensitive absorption measurements in the near-infared region using off-axis integrated-cavity-output spectroscopy. *Appl. Phys. B.* **2002**, *75*, 261−265.
(12) Wilkerson, V. A.; Casper, D. P.; Mertens, D. R. The prediction of methane production of Holstein cows by several equations. *J. Dairy Sci.* **1995**, *78*, 2402−2414.
(13) Williams, J.; Wang, N. Y.; Cicerone, R. J.; Yagi, K.; Kurihara, M.; Terada, F. Atmospheric methyl halides and dimethylsulfide from cattle. *Global Biogeochem. Cyc.* **1999**, *13* (2) 485−491.
(14) Kinsman, R.; Sauer, F. D.; Jackson, H. A.; Wolynetz, M. S. Methane and carbon dioxide emissions from dairy cows in full lactation monitored over a six-month period. *J. Dairy Sci.* **1995**, *78*, 2760−2766.
(15) Fenske, J. D.; Paulson, S. E. Human breath emissions of VOCs. *J. Air Waste Manage. Assoc.* **1999**, *49*, 594−598.
(16) Mackie R. I.; Stroot, P. G.; Varel, V. H. Biochemical identification and biological origin of key odor components in livestock waste. *J. Anim. Sci.* **1998**. *76*, 1331−1342.
(17) Willig, S.; Losel, D.; Claus, R. Effects of resistant potato starch on odor emission from feces in swine production units. *J. Agric. Food Chem.* **2005**, *53*, 1173−1178.
(18) Zhang, R. H.; Ma, Y.; Mitloehner, F.; McGarvey, J. Reducing Gas Emissions from Manure Storages by Anaerobic Digestion and

Aeration Technologies. Paper presented at ASAE Annual International Meeting, Tampa, FL, July 17−20, 2005.
(19) Russell, A.; Milford, J.; Bergin, M. S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W. R. T.; Croes, B. Urban ozone control and atmospheric reactivity of organic gases. *Science* **1995**, *269*, 491−495.
(20) Derwent, R. G.; Jenkin, M. E.; Saunders, S. A.; Pilling, M. J. Photochemical ozone creation potentials for organic compounds in Northwest Europe calculated with master chemical mechanism. *Atmos. Environ.* **1998**, *32* (14), 2429−2441.
(21) Hakami, A.; Harley, R. A.; Milford, J. B.; Odman, M. T.; Russell, A. G. Regional, 3-dimensional assessment of the ozone forming potential of organic compounds. *Atmos. Environ.* **2004**, *38*, 124−134.

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