# Alcohol, Volatile Fatty Acid, Phenol, and Methane Emissions from Dairy Cows and Fresh Manure

**Huawei Sun** University of California–Davis

**Steven L. Trabue and Kenwood Scoggin** USDA-ARS

**Wendi A. Jackson, Yuee Pan, Yongjing Zhao, and Irina L. Malkina** University of California–Davis

**Jacek A. Koziel** Iowa State University

**Frank M. Mitloehner\*** University of California–Davis

There are approximately 2.5 million dairy cows in California. Emission inventories list dairy cows and their manure as the major source of regional air pollutants, but data on their actual emissions remain sparse, particularly for smog-forming volatile organic compounds (VOCs) and greenhouse gases (GHGs). We report measurements of alcohols, volatile fatty acids, phenols, and methane ($CH_4$) emitted from nonlactating (dry) and lactating dairy cows and their manure under controlled conditions. The experiment was conducted in an environmental chamber that simulates commercial concrete-floored freestall cow housing conditions. The fluxes of methanol, ethanol, and $CH_4$ were measured from cows and/or their fresh manure. The average estimated methanol and ethanol emissions were 0.33 and 0.51 g $cow^{-1}$ $h^{-1}$ from dry cows and manure and 0.7 and 1.27 g $cow^{-1}$ $h^{-1}$ from lactating cows and manure, respectively. Both alcohols increased over time, coinciding with increasing accumulation of manure on the chamber floor. Volatile fatty acids and phenols were emitted at concentrations close to their detection limit. Average estimated $CH_4$ emissions were predominantly associated with enteric fermentation from cows rather than manure and were 12.35 and 18.23 g $cow^{-1}$ $h^{-1}$ for dry and lactating cows, respectively. Lactating cows produced considerably more gaseous VOCs and GHGs emissions than dry cows ($P < 0.001$). Dairy cows and fresh manure have the potential to emit considerable amounts of alcohols and $CH_4$ and research is needed to determine effective mitigation.

CALIFORNIA is the leading dairy state in the USA, producing 21% of the nation's milk supply. The highest concentration of dairies is in the San Joaquin Valley in Central California (Agricultural Statistics Board, 2005), a region with the worst air quality in the nation that is in extreme nonattainment of state and federal ozone standards. Smog-forming volatile organic compound (VOC) and greenhouse gas (GHG) emissions from dairies are believed to contribute to the impairment of health and well-being of humans and animals and to affect the regional and global environment (IPCC, 2001; California Air Resources Board, 2005).

Ozone is formed through the interaction of VOCs and oxides of nitrogen in the presence of sunlight. There are limited data on emission rates of VOCs emitted from dairy cows and manure. Rabaud et al. (2003) identified 35 different VOCs from a small dairy farm in California with alcohols as a main compound group. Filipy et al. (2006) identified and quantified VOCs from a lactating cow open stall on a commercial dairy in Washington. They determined an emission rate of ethanol and dimethyl sulfide of 3693.6 ± 1846.8 mg $cow^{-1}$ $h^{-1}$ and 49.68 ± 37.08 mg $cow^{-1}$ $h^{-1}$, respectively, using an atmospheric tracer method. Miller and Varel (2001) measured volatile fatty acids (VFAs) and alcohol concentrations in fresh and aged cattle slurries under laboratory conditions. A high concentration of ethanol (25–40 m$M$) was found in both slurries. Aged cattle manure produced twice the concentration of VFAs compared with fresh manure during anaerobic incubation. Martensson et al. (1999) monitored VFAs in dairy barns and detected acetic, butyric, lactic, and formic acids in the air. Sonesson et al. (2001) identified 70 different VOCs on eight dairy farms in Sweden. They found $p$-cresol, 2-butanone ethyl acetate, α-pinene, and $\Delta^3$–carene at levels well below the occupational exposure level (ACGIH, 1999). With respect to ozone-forming

H. Sun, Dep. of Biological & Agricultural Engineering, Univ. of California, Davis, 3060 Bainer Hall, One Shields Avenue, Davis, CA 95616. S.L. Trabue and K. Scoggin, United State Department of Agriculture, Agricultural Research Service, 2150 Pammel Dr. Ames, IA 50011. W.A. Jackson, Y. Pan, I.L. Malkina, and F.M. Mitloehner, Dep. of Animal Science, Univ. of California, Davis, 2151 Meyer Hall, One Shields Avenue, Davis, CA 95616. Y. Zhao, Dep. of Mechanical and Aeronautical Engineering, Univ. of California, Davis, One Shields Avenue, Davis, CA 95616. J.A. Koziel, Dep. of Agricultural and Biosystems Engineering, Iowa State Univ., Ames, IA 50011. Disclaimer: Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and use of the name by the USDA implies no approval of the product to the exclusion of others that may be suitable.

**Abbreviations:** EPA, Environmental Protection Agency; GHG, greenhouse gases; LOQ, limit of quantification; LU, livestock unit (500 kg live weight animal); VFAs, volatile fatty acids; VOC, volatile organic compounds.

**Table 1. Feed components and chemical feed composition for dry and lactating cows.**

|  | Dry cow | Lactating cow |
|---|---|---|
| **Feed components (g kg⁻¹)** |  |  |
| Corn | 0 | 349 |
| Alfalfa | 310 | 392 |
| Oat hay | 610 | 0 |
| Cottonseed meal | 0 | 113 |
| Almond hulls | 0 | 81 |
| Soybean meal | 0 | 40 |
| Milk mineral | 0 | 16 |
| Energy mix | 0 | 6 |
| Salt | 0 | 3 |
| Dry cow pellet† | 80 | 0 |
| **Chemical composition (g kg⁻¹)** |  |  |
| Dry matter | 860 |  |
| Crude protein | 144 |  |
| Ash | 104.5 |  |
| P | 2.5 |  |
| Ca | 9.7 |  |
| Mg | 2.7 |  |
| K | 21.3 |  |

† The dry cow pellet contained (%DM) minerals (27), soybean meal (36.5), and wheat meal run (36.5).

VOCs, no comprehensive research that characterizes emissions from dairy cows and their fresh manure has been conducted.

The Intergovernmental Panel on Climate Change (IPCC) reported that since the year 1750, the atmospheric concentration of the greenhouse gases carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) has increased by 31, 150, and 16%, respectively (IPCC, 2001). The IPCC estimated that agriculture contributes 21 to 25% of global $CO_2$ emissions, 55 to 60% of global $CH_4$ emissions, and 65 to 80% of global $N_2O$ emissions (IPCC, 2001). Processes and sources generating GHGs include the burning of fossil fuels, deforestation, rice paddies, biomass burning, enteric fermentation of ruminants, fermentation of animal manure, and application of nitrogenous fertilizers. Dairy cows and their manure are considered to be important contributors to $CH_4$ and to a lesser extent $N_2O$ emissions (IPCC, 2001; Jarvis and Pain, 1994; Phetteplace et al., 2001). Considering that the 100-yr global warming potentials of $CH_4$ and $N_2O$ are 20 and 300 times higher than $CO_2$, respectively (IPCC, 2001; Kuczynski et al., 2005), the effect of cows and their manure on the global GHG emissions becomes even more important. Methane and $N_2O$ can be produced from enteric fermentation in the cow and decomposition of manure (Kaspar and Tiedje, 1981; Jungbluth et al., 2001). Previous studies predicted $CH_4$ emissions from dairy cows based on the physiology and feed energy consumption of the animal (Crutzen et al., 1986; Holter and Young, 1992; IPCC, 2001). Methane emission factors of 5.79 g LU⁻¹ h⁻¹ (livestock unit [LU] = 500 kg live weight animal) for dry cows and 11.17 g LU⁻¹ h⁻¹ for lactating cows were obtained (Holter and Young, 1992). Direct measurement of $CH_4$ emissions from cows and dairy facilities were conducted in previous studies but not under controlled conditions (Jungbluth et al., 2001; Kinsman et al., 1995; Kirchgessner et al., 1991; Sneath et al., 1997). Many factors, such as feed intake, animal size, growth rate, milk production, and particularly energy consumption, can

affect $CH_4$ emissions from dairy cows (Jungbluth et al., 2001). Compared with studies of $CH_4$ emissions, there is a scarcity of literature on $N_2O$ emissions from dairy cows (Jungbluth et al., 2001). Generally, ruminant animals are considered as a small source of $N_2O$ emissions (IPCC, 2001). The direct measurements of $N_2O$ emissions from dairy facilities had yielded emission factors in the range of 0.01 to 0.08 g LU⁻¹ h⁻¹ (Amon et al., 2001; Jungbluth et al., 2001; Sneath et al., 1997). No studies have quantified $N_2O$ emissions from cow enteric fermentation.

The objective of the present study was to quantify VOC and GHG emissions from dry (not lactating) and lactating cows (enteric fermentation) and fresh manure under environmental chamber conditions.

# Materials and Methods

## Environmental Chambers

Experiments were conducted inside of an environmentally controlled chamber (4.4 m × 2.8 m × 10.5 m) at the Department of Animal Science, University of California, Davis, California. The chamber (142 m³ volume) has a continuous ventilation rate of 2219 m³ h⁻¹ (at 20°C and 1 atm), resulting in a chamber residence time of approximately 6 min and equivalent to 15.8 air exchanges per hour. A balometer (TSI Inc., Shoreview, MN) was used to check the ventilation rate before and after the experiment. The chamber temperature was maintained at 20°C and controlled via air conditioning. The relative humidity of air in the chamber was 56 ± 11%. Typical dairy freestall housing conditions for three cows were simulated by assembling three steel freestall stanchions at the west end of the chamber where animals could rest. Head gates were installed at the east end of the chamber where cows accessed feed ad libitum. Animals had ad libitum access to water by a water trough. Ambient temperature and relative humidity were measured in 10-min intervals using two HOBO sensors (Onset Computer, Bourne, MA) located inside the chamber. Cow excreta (urine and feces slurry mix) accumulated on the concrete floor until the chamber was cleaned. The environmental chamber facility is certified by the Association for Assessment and Accreditation of Laboratory Animal Care International, and the Institutional Animal Care and Use Committee approved the project to certify the health and welfare of the animals.

## Animals

The present work describes emission rates on a per-cow basis. The average body weights of dry and lactating cows were 770 and 656 kg, respectively, and the feed intake levels (on a dry matter basis) were 17.7 and 19.1 kg d⁻¹, respectively. The average milk yield was 31 kg cow⁻¹ d⁻¹. A total of nine dry (pregnant but not lactating) and nine mid-lactating Holstein dairy cows from the UC Davis dairy herd were used for the experiments in groups of three cows. Cows were fed a total mixed ration (Table 1) diet ad libitum, which was formulated to meet the 2001 National Research Council requirements for dry or lactating cows. Both diets were analyzed for crude protein (AOAC, 1997a), total digestible nutrients (AOAC, 1997b), acid detergent fiber (AOAC, 1997b), neutral detergent fiber

(Van Soest et al., 1991), and minerals (Ca, P, Mg, K) (Sah and Miller, 1992). The chemical composition is listed in Table 1.

## Gas Sampling and Analysis

The environmental chamber had one incoming and one outgoing air duct. Analytical instruments located in the attic space above the chamber pulled air through Teflon tubing (12.7 mm ID, 0.25 m long) from each air duct immediately above the ceiling. Background samples of the "empty chamber" were collected during the first day of each 2-d experimental period to assess the VOC and GHG concentrations in the incoming and outgoing air. After 2 h of empty chamber measurement, three cows were placed inside the chamber. The first 2 h after cows entered the chamber were used to measure air emissions in the "cows only" phase (enteric fermentation; no manure). In the following "cows and manure" phase, the animals were kept inside the chamber for an additional 22 h, and manure accumulated over time. The lactating cows were milked with a mobile milking unit before placement in the chamber and a second time inside the chamber at 1900 h. After 24 h, cows were taken out of the chamber, but the accumulated animal manure was left undisturbed on the chamber floor for second-day measurements (24 h; "manure only" phase).

Ethanol, methanol, $N_2O$, and $CH_4$ from dairy cows and their excreta were continuously measured using an INNOVA model 1412 Field Gas Monitor (INNOVA AirTech Instrument, Ballerup, Denmark). This gas analyzer can selectively measure up to five component gases and water vapor simultaneously through the use of optical filters. The detection limits of the INNOVA 1412 are 0.08 $\mu$g $L^{-1}$ for methanol, 0.10 $\mu$g $L^{-1}$ for ethanol, 0.21 $\mu$g $L^{-1}$ for $CH_4$, and 0.04 $\mu$g $L^{-1}$ for $N_2O$. The INNOVA is approved as a reference method for alcohol measurements by the California Air Resource Board (CARB, MSO 2000-08) and by the Environmental Protection Agency (EPA) for the measurement of ethanol and chlorinated VOC (EPA-VS-SCM-28). In the present study, the INNOVA analyzer was calibrated monthly by the instrument manufacturer. The sampling interval for inlet and outlet air was 20 min. To avoid the responding error, only data logged between minute 5 and 17 of each sampling interval was used for later analysis. Data corresponding to the short interval of time when the chamber door was opened to allow entry and exit of cows (at 0700 h on the first day and 0900 h on the second day, respectively) were omitted for calculation of emission fluxes.

Emissions of VFAs and phenolic compounds were measured using a modified sorbent tube EPA TO-17 method (Woolfenden and McClenny, 1997). Measured VFAs were acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic. Phenols and cresol compounds were phenol, 2-methylphenol, 2-ethylphenol, 3-methylphenol, 4-methylphenol, indole, and 3-methylindole. Four sorbent tube gas samplers (GS 301, Gerstel, Muehlheim, Germany) were connected to the inlet and outlet air ducts from the air handling system for the environmental chamber, respectively, using quick-connect fittings and flexible Teflon tubing. Samples were collected in duplicate on glass sorbent tubes (178 × 6 mm diameter) containing a multi-bed sorbent packing of Carbopack C and Carbopack X (Supelco, Bellefonte, PA) (1:2 ratio v/v) at flow rate of 100 mL $min^{-1}$, for a total volume of 12 L.

Samples were taken at 0, 6, 12, 18, and 24 h after cows entered the chamber for dry cows and at 0, 3, 6, 9, and 24 h for lactating cows. More samples for "manure only" phases were taken at 0, 6 12, 18, and 24 h after cows left the chamber. During the lactating cow experiments, sorbent tube sampling was not conducted during night time. All samples were refrigerated and analyzed within 14 d of the time they were sampled in the field.

Sorbent tubes were analyzed by thermal desorption–gas chromatography–mass spectrometry. The thermo-desorption system was a Gerstel TDSA (Gerstel, Muehlheim, Germany) interfaced to a 6890 GC (Agilent Technologies, Wilmington, DE) and 5973N inert mass selective detector (Agilent Technologies). Thermal desorption parameters were as follows: splitless mode; initial temperature, 60°C; final temperature, 300°C; initial time, 0.5 min; final hold time, 3 min; ramp, 60°C $min^{-1}$; with a transfer line temperature of 320°C. The 6890 GC was equipped with programmed temperature vaporizer inlet (CIS 4; Gerstel) and a 30 m × 0.25 mm × 0.25 $\mu$m free fatty acid phase column (J&W Scientific, Inc., Wilmington, DE). The programmed temperature vaporizer inlet used the following parameters: solvent vent mode; initial temperature, −30°C, final temperature, 320°C, initial time, 0.2 min, final time, 3 min; ramp, 12°C $s^{-1}$, vent flow 20 mL $min^{-1}$, and purge split flow 20 mL $min^{-1}$. This method is essentially a 20:1 split injection from thermo-desorption system to analytical column. Helium was used as the carrier gas in constant flow mode at 1.4 mL $min^{-1}$. The 6890 GC oven temperature program was (i) initial temperature, 80°C hold 0.05 min; (ii) ramp 10°C to 220°C; and (iii) ramp 50°C to 240°C and hold 5 min. The mass spectrometer transfer line and source temperatures were maintained at 240 and 150°C, respectively. The mass spectrometer was operated under Single Ion Monitoring mode using the following monitoring ions: (i) VFA compounds monitored 43, 57, 60, 73, 74, and 87, 94, and 101 m/z from 3 to 14.1 min and (ii) phenolic compounds monitored 39, 66, 77, 94, 107, 108, and 122 m/z.

A stock standard solution for VFAs including acetic, propionic, isobutyric, butyric, 2-methylpropanoic, isovaleric, valeric, and hexanoic acids was prepared in high-perormance liquid chromatography–grade water (Burdican and Jackson, Mustegon, MI). A reference standard stock solution for seven aromatic compounds, including phenol, 2-methylphenol, 2-ethylphenol, 3-methylphenol, 4-methylphenol, indole, and 3-methylindole, was prepared in methanol (Capillary GC Grade; Sigma-Aldrich, St. Louis, MO). All chemicals were 99% pure or higher (GC grade) and provided by Aldrich (Sigma-Aldrich).

Calibration curves were generated using external standards loaded onto sorbent tubes using the ATIS system (Supelco, Inc., Bellefonte, PA). The ATIS system was maintained at 110°C and purged with nitrogen at 100 mL $min^{-1}$ for a minimum total volume loading of 250 mL for each sorbent tube. The limit of quantification (LOQ) for the VFAs ranged from 0.8 to 3.8 $\mu$g $m^{-3}$ air for acetic acid and 2-methylpropanoic acid. The LOQ for phenolic compounds ranged from 0.38 ng (2-methylphenol) to 5.43 ng (4-methylphenol), which corresponded to 0.02 (2-methylphenol) to 2.7 $\mu$g m-3 air for 2-methylphenol and 4-methylphenol, respectively.
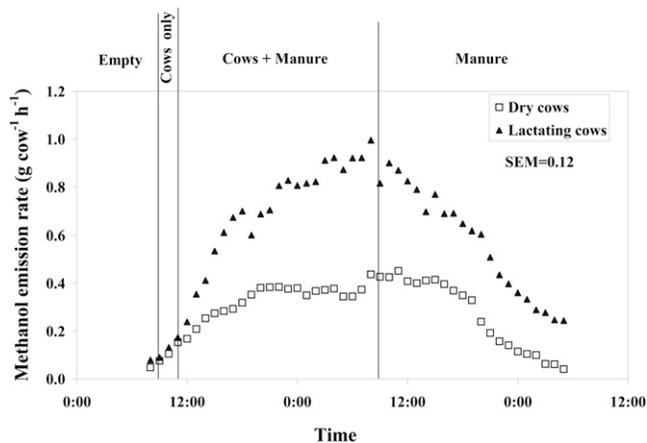
Fig. 1. Methanol emission rates from three groups of dry and lactating cows (*n* = 3). SEM = pooled standard error.

The emission flux rate was calculated using the following equation:

$$E = \frac{\sum_n Q \times (C_{out} - C_{in})}{n \times N}$$

[1]

where $E$ = gas emission rate from the chamber (mg cow$^{-1}$ h$^{-1}$), $C_{out}$ = mass concentration in the outlet air (mg m$^{-3}$), $C_{in}$ = mass concentration in the inlet air (mg m$^{-3}$), $Q$ = ventilation rate at 20°C and 1 atm (m$^3$ h$^{-1}$), $n$ = total effective measurement numbers, and $N$ = cow numbers.

## Validation Experiment

Validation experiments were conducted to evaluate the performance of the environmental chamber and gas monitoring system. Pure CH$_4$ (Airgas Inc., Radnor, PA) was continuously and evenly distributed into the chamber through Teflon tubes at a flow rate of 1.3 L min$^{-1}$. Pure methanol (99.9%) (Fisher Scientific Inc., Fair Lawn, NJ) and ethanol (≥99.5%) (Sigma-Aldrich) filled into glass plates were placed on a microbalance (Mettler-Toledo, Columbus, OH) that was situated on a table (40 cm height) in the chamber center. The amount of alcohol evaporated was continuously measured using a microbalance, and the data were visually recorded with a PC-based web camera. The gas concentrations at the chamber inlet and outlet were continuously monitored using the IN-NOVA field gas analyzer that was used during the animal studies. Air ventilation rate was measured before and after the validation experiment. Background concentrations in the chamber were also measured for 24 h before and after the validation experiment.

Mass balance calculation was conducted to evaluate the total recovery efficiency of the system. The recovery efficiency (*RE*) was calculated using the following equation:

$$RE = \frac{E'}{M_c} \times 100\%$$

where $E'$ = gas emission rate from the chamber during certain period (mg), and $M_c$ = total gas mass input into the chamber during same period (mg).

## Statistical Analysis

The Proc Mixed procedure (SAS Inst. Inc, Cary, NC) was used for statistical analysis. The model comparing air emissions from dry and lactating cows included animal type (dry vs. lactating cows), time, and an animal type × time interaction with the groups (hosting different animals for each group) as the random factor. The model investigating the effects of animal and manure on air emissions included animal type (dry vs. lactating cows), phases (three periods of "animal only," "animal and manure," and "manure only"), and animal type by phase interaction. Groups were treated as a random factor. Time was a continuous variable; all others were categorical variables. For all measures, the predicted difference test in Proc Mixed procedure in SAS was used to separate means when the overall F-value was significant ($P < 0.05$).

## Results and Discussion

The validation results indicated that the environmental chamber is well suited to accurately measure GHG and VOC emissions from animals and waste. The mass balance calculation showed approximately 90% of the total CH$_4$ input, 90% of the total methanol input, and 98% of the total ethanol input into the chamber were recovered at the outlet. The background concentrations of CH$_4$, N$_2$O, methanol, and ethanol before and after the validation experiment were approximately 1.40, 0.67, 0.08, and 0.13 μg L$^{-1}$, respectively

Methanol and ethanol were emitted at average fluxes and ranged from 0.25 to 0.70 g cow$^{-1}$ h$^{-1}$ during all periods in which fresh manure was present in the chamber (Fig. 1, 2). Enteric fermentation contributed to alcohol emissions, but fresh slurry seemed to be the main emission source. Upon entry of cows into the chamber, methanol and ethanol fluxes increased moderately (possibly enteric fermentation contribution). Major alcohol increases occurred over time coinciding with increasing accumulation of fresh manure (Fig. 1, 2). In the "manure only" phase without cows present, both alcohols remained at high, albeit decreasing, levels for several hours, confirming that manure was the main alcohol source. The decrease over time within the "manure only" phase might be related to a decrease in fermentable sugars and cellulose in the feces and a decrease in microbial activity (Williams, 1983) as well as the decrease of moisture on the manure surface that affects the mass transfer of alcohols from manure to air. The estimated average emission rates of methanol were 0.33 and 0.70 g cow$^{-1}$ h$^{-1}$ from dry and lactating cows, respectively, as well as their fresh manure (Table 2). The dry and lactating cows' manure emitted 0.27 and 0.53 g cow$^{-1}$ h$^{-1}$ methanol, respectively, during the second experimental day ("manure only" phase after cows were removed from the chamber). The estimated average emission rates of ethanol were 0.51 and 1.27 g cow$^{-1}$ h$^{-1}$ from dry and lactating cows as well as their fresh manure, respectively. The "manure only" phase resulting from dry and lactating cows emitted on average 0.33 and 0.70 g cow$^{-1}$ h$^{-1}$ ethanol, respectively. Lactating cows and their fresh manure produced considerably more methanol and ethanol than dry cows and their fresh manure ($P < 0.001$) most likely because of the larger amount of fermentable substrate in their feed (Table 1) (Wilkerson et al., 1995).
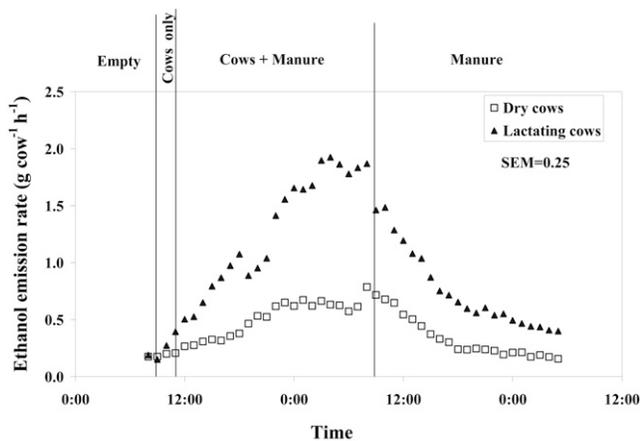
Fig. 2. Ethanol emission rates from three groups of dry and lactating cows (*n* = 3). SEM = pooled standard error.

| | Dry cows | Lactating cows |
|---|---|---|
| Average methane emission rate (g cow$^{-1}$ h$^{-1}$) | | |
| Empty chamber | 0.21 ± 0.11† | 0.26 ± 0.11 |
| Cows and manure (24 h) | 12.35 ± 1.61 | 18.23 ± 1.82 |
| Day time (1000 h to 2000 h) | 14.49 ± 0.56 | 20.59 ± 1.43 |
| Night time (2200 h to 0800 h) | 9.51 ± 1.38 | 15.88 ± 1.15 |
| Manure only | 0.27 ± 0.09 | 0.34 ± 0.11 |
| Average methanol emission rate (g cow$^{-1}$ h$^{-1}$) | | |
| Empty chamber | 0.03 ± 0.02 | 0.08 ± 0.02 |
| Cows and manure | 0.33 ± 0.21 | 0.70 ± 0.11 |
| Manure only | 0.27 ± 0.08 | 0.53 ± 0.12 |
| Average ethanol emission rate (g cow$^{-1}$ h$^{-1}$) | | |
| Empty chamber | 0.17 ± 0.03 | 0.15 ± 0.06 |
| Cows and manure | 0.51 ± 0.08 | 1.27 ± 0.26 |
| Manure only | 0.33 ± 0.09 | 0.70 ± 0.16 |

† Standard error; *n* = 3.

Filipy et al. (2006) predicted ethanol emission rates from fresh and aged dairy manure based on data by Miller and Varel (2001), who predicted that ethanol emission factor was 0.63 and 4.41 g cow$^{-1}$ h$^{-1}$ for fresh and aged beef cattle manure, respectively. Furthermore, Filipy et al. (2006) measured ethanol emissions under lactating cow freestall conditions on a commercial dairy. Their measured emission rate of ethanol was 3.69 ± 1.85 g cow$^{-1}$ h$^{-1}$ using an atmospheric tracer method and analysis on a gas chromatograph and mass spectrometer. The measured ethanol values in the present study were 0.51 for dry cows and 1.27 g cow$^{-1}$ h$^{-1}$ for lactating cows, which is close to the fresh manure values calculated by Filipy et al. (2006). Most modern dairies in the San Joaquin Valley use water to flush manure into a liquid storage pond (a.k.a. "lagoon") three times per day. Because the present study left the manure accumulating on the concrete floor (without flushing), we conducted a mitigation pilot study in which manure was flushed out of the chamber at 1100 h, 1500 h, and 1900 h, which led to a tenfold reduction of ethanol and methanol emissions (data not shown). Because alcohols are water soluble, a manure flush system might be effective in keeping these compounds in the liquid phase, thus preventing volatilization to the atmosphere.

Volatile fatty acids and phenols were apparently emitted from cows and fresh manure (Fig. 3, 4). However, VFA and phenol concentrations were measured close to the lower detection limit of the assay and instrumentation. The only VFA consistently above its LOQ was acetic acid (Fig. 3). On an emission mass basis, acetic acid contributed from 32 to 100% of total VFA emissions. The higher level of acetic acid emission compared with other VFAs is consistent with what has been reported for dairy farms and cattle feedlots (Martensson et al., 1999; McGinn et al., 2003; Moller et al., 2004, Spinhirne et al., 2004). Martensson et al. (1999) monitored VFAs in dairy barns and determined that acetic acid concentrations in air ranged from 31 to 78 μg m$^{-3}$, whereas butyric acid concentration ranged from 4 to11 μg m$^{-3}$. If data from the present study were scaled to reflect a similar population size (ignoring factors like diet, ventilation, etc.) as in the study by Martensson et al. (1999), the acetic acid concentration would range from 36 to 247 μg m$^{-3}$ and the butyric acid concentrations from 0 to 64 μg m$^{-3}$. Butyric acid was typically above the method LOQ during at least

one sampling event per replicate (Fig. 3). High variability across the three cow groups and concentrations near the lower detection limit of the assay make further interpretation of trends difficult.

On an emission mass basis in the present experiment, 3/4-methylphenol was the most significant phenolic compound, amounting to 50% of these compound group emissions (Fig. 4). All phenolic compounds were typically above method LOQ for outlet air samples, whereas inlet air samples were typically below method LOQ. Besides 3/4-methylphenol, the most significant phenolic compounds were phenol, 2-methylphenol, and 2-ethylphenol. Sonesson et al. (2001) reported detection of phenol (3–50 μg m$^{-3}$), 4-methylphenol (0.6–100 μg m$^{-3}$), and 4-ethylphenol (0.4–10 μg m$^{-3}$) on eight dairy farms in northern Sweden (farm size ranged from 10 to 82 milking cows). If data from the present study were scaled to reflect the Sonesson et al. (2001) dairy population size (ignoring potential differing conditions between studies like diet, etc.), our phenol concentration would have ranged from 9.6 to 50.7 μg m$^{-3}$, and our 4-methylphenol concentrations would have ranged from 21.9 to 200 μg m$^{-3}$. In summary, studies by Martensson et al. (1999) and Sonesson et al. (2001) agree with the present findings that emissions of VFAs and phenol compounds from dairy cows and fresh manure are generally low and, in our case, are close to the method LOQ.

Upon entry of dry and lactating cows into the chamber, CH$_4$ fluxes immediately increased, indicating that enteric fermentation is the main process responsible for production of this gas ("empty chamber" vs. "cows only" phases; *P* < 0.01) (Fig. 5). After removal of cows from chambers ("manure only" phase), CH$_4$ flux went back to background levels ("empty chamber") (Table 2), indicating that fresh manure did not produce noticeable CH$_4$ fluxes ("empty chamber" vs. "manure only"; *P* > 0.05). The emissions of CH$_4$ from dairy cows also showed a clear diurnal pattern, maintaining higher rates during the day than at night. Decreasing emission rates were found from 2000 h (when the light was turned off) to 0800 h the next morning. Kinsman et al. (1995) reported a similar pattern, with fluxes increasing at 0700 h and decreasing at 2100 h. Differences in CH$_4$ emissions between dry and lactating cows were anticipated and observed (Fig. 5; Table 2). Lactating cows produced approximately 1.3 times more CH$_4$ than nonlactating dry

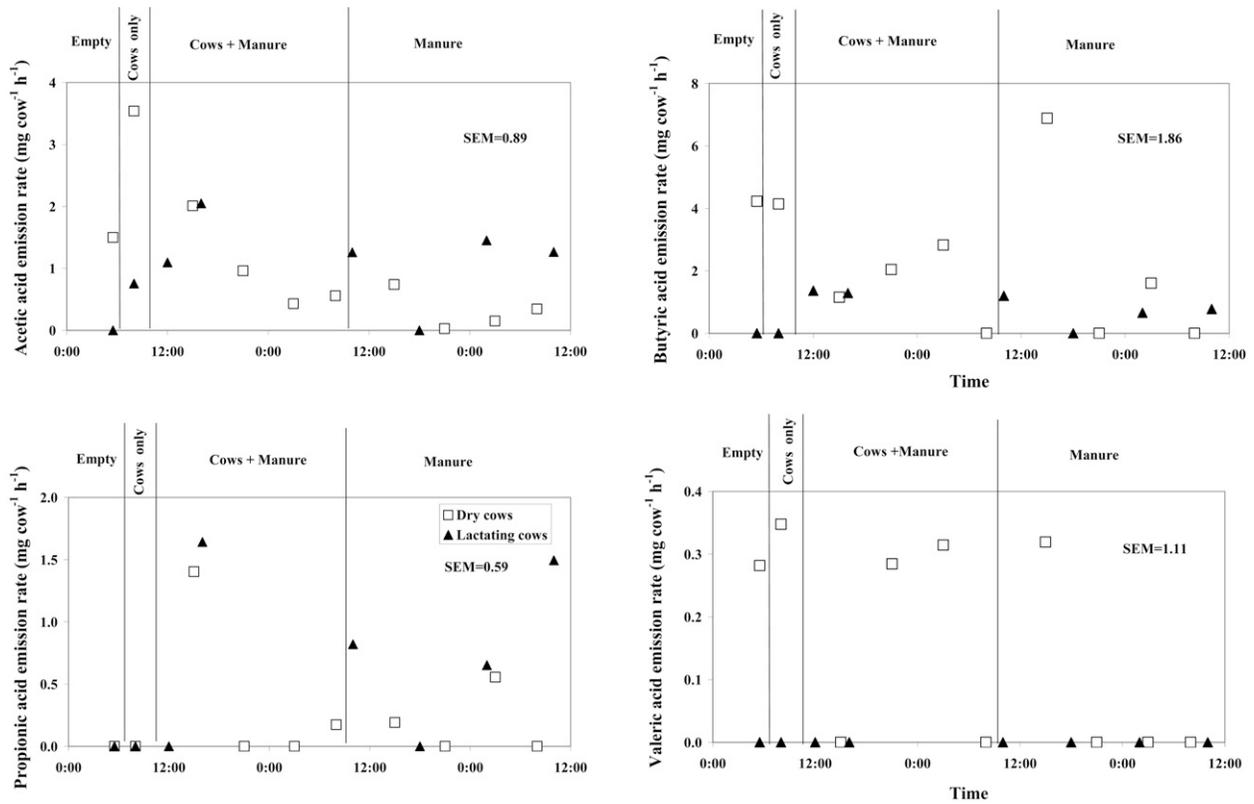Fig. 3. Acetic, propionic, butyric, and valeric acid emission rates from three groups of dry and lactating cows (*n* = 3). SEM = pooled standard error.
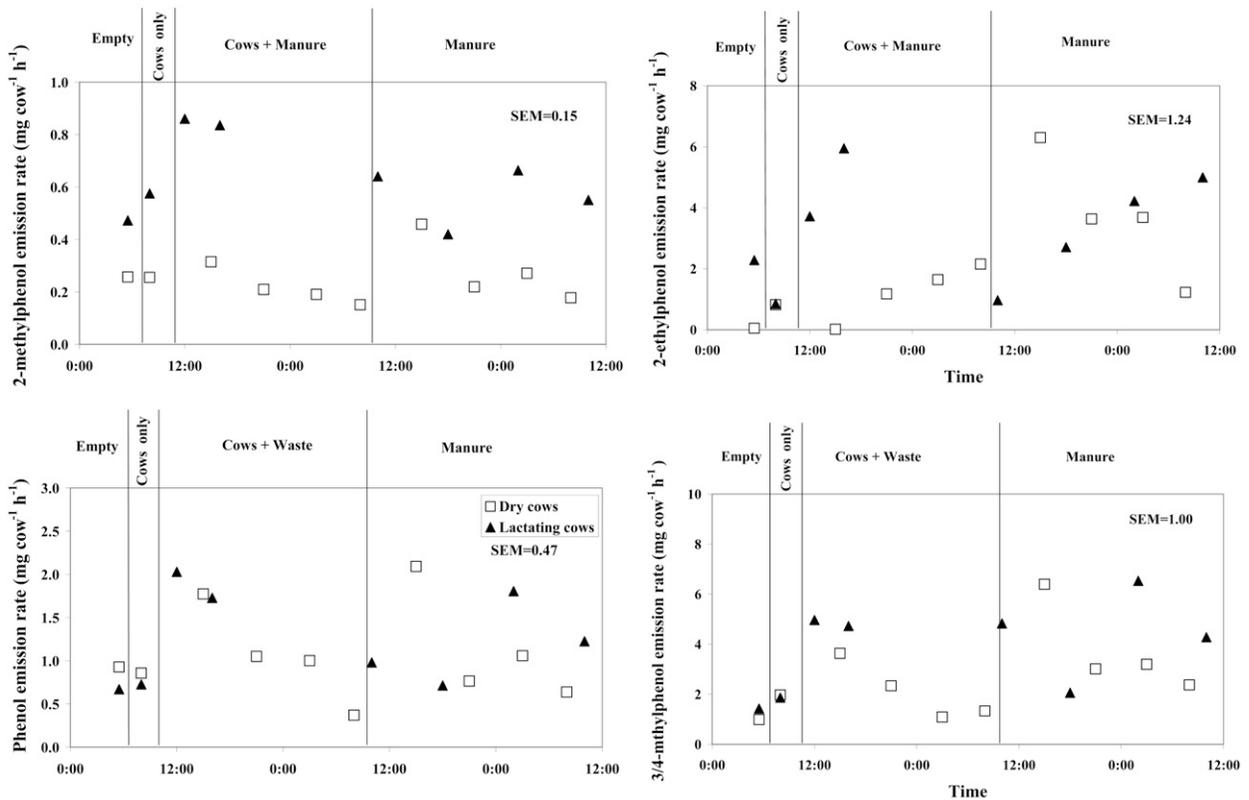


Fig. 4. 2-methylphenol, phenol, 2-ethylphenol, and 3/4 methylphenol emission rates from three groups of dry and lactating cows (*n* = 3). SEM = pooled standard error.

cows per animal ($P < 0.01$). This difference can be largely explained by the larger amount of readily fermentable substrate (i.e., corn) in the lactating vs. dry cows' diet, which was necessary to meet the nutritional requirements for cows at this stage of milk production (Table 1) (Wilkerson et al., 1995). In the present study, the estimated emission rate of $CH_4$ averaged 12.35 g cow$^{-1}$ h$^{-1}$ from dry cows and manure and 18.23 g cow$^{-1}$ h$^{-1}$ from lactating cows and manure, respectively. The average weights of dry and lactating cows were 770 and 656 kg, respectively. Therefore, per 500 kg livestock unit, the lactating cow produced approximately 1.7 times more $CH_4$ than dry cows, which is close to the ratio reported by Holter and Young (1992). The $CH_4$ fluxes observed in the present study for lactating cows were greater than the 13.03 g cow$^{-1}$ h$^{-1}$ determined for adult Holstein and Jersey cows (USEPA, 1998) that is being used by some air regulatory agencies. Because fresh manure did not produce noticeable $CH_4$ fluxes and under commercial conditions is usually flushed out of the animal housing area on average three times per day, the $CH_4$ emissions from animal housing components of a dairy can be estimated largely on animal emissions. Several recent reports showed a $CH_4$ flux of 17.47 g cow$^{-1}$ h$^{-1}$ from lactating cows' facilities (Kinsman et al., 1995; Sneath et al., 1997), which is in a good agreement with findings obtained in the present study.

Kaspar and Tiedje (1981) reported that a small quantity of $N_2O$ can be emitted by the cow most likely produced during nitrate reduction reactions occurring in the gut. The present study found elevated $N_2O$ emissions (vs. the background) when the cows stayed in the chamber. However, the $N_2O$ emissions could not be accurately quantified due to an error during calibration procedures. Although $N_2O$ emissions from cow enteric fermentation seem to be minor, additional research is needed due to its considerable heat forcing potential.

## Conclusions

Dairy farms may produce high fluxes of alcohol (>0.25 g cow$^{-1}$ h$^{-1}$), including methanol and ethanol, and $CH_4$ (>12 g cow$^{-1}$ h$^{-1}$) from animals and their fresh manure. Ethanol and methanol were emitted at average flux rates ranging from 0.25 to 0.70 g cow$^{-1}$ h$^{-1}$ from cows' fresh manure. However, flushing of animal housing has a high potential to reduce alcohol emissions due to their high water solubility.

Enteric fermentation was the main process responsible for production of $CH_4$, although fresh manure did not produce noticeable fluxes. Lactating cows and their manure produced more $CH_4$, methanol, and ethanol than dry cows and manure, most likely due to the larger amount of fermentable substrate in feed and feces. Compared with alcohol and $CH_4$ emissions, the emissions of VFAs and phenol compounds from dairy cows and their manure were very low and close to the lower detection limit of the assay and instrumentation. Variation in VFA and phenol concentrations across the three cow groups and low concentrations near the lower detection limit of the assay make further interpretation of trends difficult. Current emission inventories in the San Joaquin Valley in California underestimate alcohol emissions and may overestimate VFA emissions from dairy cow hous-
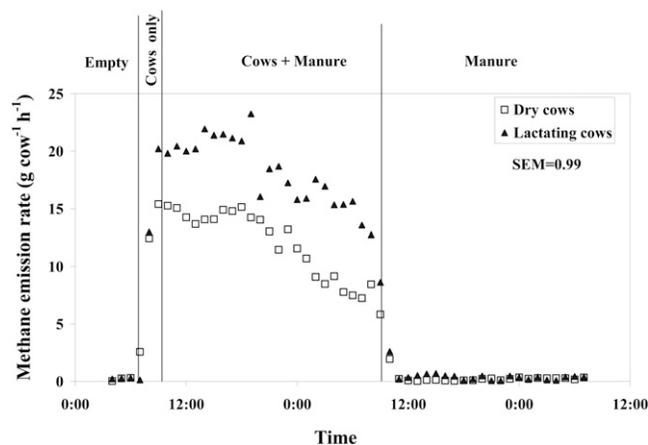


Fig. 5. Methane emission rates from three groups of dry and lactating cows ($n$ = 3). SEM = pooled standard error.

ing considerably. Future research needs to address the mitigation of VOC emissions that occur during fermentation of feedstuff and fresh manure as well as $CH_4$ from cow digestive processes.

## References

Agricultural Statistics Board. 2005. Agricultural Statistics, 2005. National Agricultural Statistics Service. Available at http://www.usda.gov/nass/pubs/agr05/agstats2005.pdf (verified 27 Dec. 2007).

American Conference of Governmental Industrial Hygienists. 1999. Threshold limit values for chemical substances and physical agents, biological exposure indices, TLVs, and BEIs. ACGIH, Cincinnati, OH.

Amon, B., T. Amon, J. Boxberger, and C.H. Alt. 2001. Emissions of $NH_3$, $N_2O$, and $CH_4$ from dairy cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading). Nutr. Cycling Agroecosyst. 60:103–113.

Association of Official Analytical Chemists. 1997a. Method 990.03. Official methods of analysis of AOAC International. 16th ed. AOAC Int., Gaithersburg, MD.

Association of Official Analytical Chemists. 1997b. Method 973.18. Official methods of analysis of AOAC International. 16th ed. AOAC Int., Gaithersburg, MD.

California Air Resources Board. 2005. Almanac emission projection data inventory. Sacramento, CA. Available at http://www.arb.ca.gov/ei/emissiondata.htm (verified 27 Dec. 2007).

Crutzen, P.J., I. Aselmann, and W. Seiler. 1986. Methane production by domestic animals, wild ruminants, other herbivorous fauna, and humans. Tellus 38B:271–284.

Filipy, J., B. Rumburg, G. Mount, H. Westberg, and B. Lamb. 2006. Identification and quantification of volatile organic compounds from a dairy. Atmos. Environ. 40:1480–1497.

Holter, J.B., and A.J. Young. 1992. Methane prediction in dry and lactating Holstein cows. J. Dairy Sci. 75:2165–2175.

IPCC. 2001. Good practice guidance and uncertainty management in national greenhouse gas inventories. IPCC National Greenhouse Gas Inventories Program Technical Support Unit, Kanagawa, Japan. Available at http://www.ipcc-nggip.iges.or.jp/public/gp/english (verified 27 Dec. 2007).

Jarvis, S.C., and B.F. Pain. 1994. Greenhouse gas emissions from intensive livestock systems: Their estimation and technologies for reduction.

Clim. Change 27:27–38.

Jungbluth, T., E. Hartung, and G. Brose. 2001. Greenhouse gas emissions from animal house and manure stores. Nutr. Cycling Agroecosyst. 60:133–145.

Kaspar, H.F., and J.M. Tiedje. 1981. Dissimilatory reduction of nitrate and nitrite in the bovine rumen: Nitrous oxide production and effect of acetylene. Appl. Environ. Microbiol. 41:705–709.

Kinsman, R., F.D. Sauer, H.A. Jackson, and M.S. Wolynetz. 1995. Methane and carbon dioxide emissions from dairy cows in full lactation monitored over a six-month period. J. Dairy Sci. 78:2760–2766.

Kirchgessner, M., W. Windisch, H.L. Muller, and M. Kreuzer. 1991. Release of methane and of carbon dioxide by dairy cattle. Agribiol. Res. 44:91–102.

Kuczynski, T., U. Dammgen, J. Webb, and A. Myczko. 2005. Emissions from European agriculture. Wageningen Academic Publ., Wageningen, The Netherlands.

Martensson, L.M., M.Y. Magnusson, Y.J. Shen, and J. Jonsson. 1999. Air concentration of volatile organic acids in confined animal buildings-determination with ion chromatography. Agric. Ecosyst. Environ. 75:101–108.

McGinn, S.J., J. Janzen, and T. Coates. 2003. Atmospheric ammonia volatile fatty acids and other odorants near beef feedlots. J. Environ. Qual. 32:1173–1182.

Miller, D.N., and V.H. Varel. 2001. In vitro study of the biochemical origin and production limits of odorous compounds in cattle feedlots. J. Anim. Sci. 79:2949–2956.

Moller, H., S. Sommer, and B. Ahring. 2004. Biological degradation and greenhouse gas emission during pre-storage of liquid animal manure. J. Environ. Qual. 33:27–36.

Phetteplace, H.W., D.E. Johnson, and A.F. Seidl. 2001. Greenhouse gas emissions from simulated beef and dairy livestock systems in the United States. Nutr. Cycling Agroecosyst. 60:99–102.

Rabaud, N.E., E. Ebeler, L.L. Ashbaugh, and R.G. Flocchini. 2003. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. Atmos. Environ. 37:933–940.

Sah, R.N., and R.O. Miller. 1992. Spontaneous reaction for acid dissolution of biological tissues in closed vessels. Anal. Chem. 64:230–233.

Sneath, R.W., V.R. Phillips, T.G.M. Demmers, L.R. Burgess, J.L. Short, and S.K. Welch. 1997. Long-term measurement of greenhouse gas emissions from UK livestock buildings. Proceedings of the Fifth International Livestock Environment Symp., Minneapolis-St. Paul, Minnesota, 29–31 May, ASAE, p. 146–153.

Sonesson, A.-L., J. Gullberg, and G. Blomquist. 2001. Airborne chemical compounds on dairy farms. J. Environ. Monit. 3:210–216.

Spinhirne, J.P., J.A. Koziel, B.H. Baek, and D.B. Parker. 2004. Determination of volatile fatty acid fluxes from cattle pens. Paper #04-A-646. *In* Proceedings of the 2004 Air and Waste Management Association Annual Meeting and Exhibition, Indianapolis, IN, June 2004.

USEPA. 1998. Greenhouse gas biogenic sources. AP 42. USEPA, Washington, DC. Available at http://www.epa.gov/ttn/chief/ap42/ch14/final/c14s04.pdf (verified 27 Dec. 2007).

Van Soest, P.J., J.B. Robertson, and B.A. Lewis. 1991. Methods for dietary fiber, neutral detergent fiber, and non-starch polysaccharides in relation to animal nutrition. J. Dairy Sci. 74:3583–3597.

Wilkerson, V.A., D.P. Casper, and D.R. Mertens. 1995. The prediction of methane production of Holstein cows by several equations. J. Dairy Sci. 78:2402–2414.

Williams, L.A. 1983. Theory and modeling of ethanol evaporative losses during batch alcoholic fermentation. Biotechnol. Bioeng. 25:1597–1612.

Woolfenden, E.A., and W.A. McClenny. 1997. Method TO-17, determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes. EPA/625/R-96/010b. USEPA, Research Triangle Park, NC.