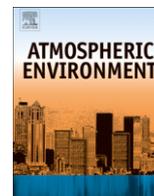


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## Temperature and air velocity effects on ethanol emission from corn silage with the characteristics of an exposed silo face

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### ABSTRACT

Volatile organic compounds (VOCs) from agricultural sources are believed to be an important contributor to tropospheric ozone in some locations. Recent research suggests that silage is a major source of VOCs emitted from agriculture, but only limited data exist on silage emissions. Ethanol is the most abundant VOC emitted from corn silage; therefore, ethanol was used as a representative compound to characterize the pattern of emission over time and to quantify the effect of air velocity and temperature on emission rate. Ethanol emission was measured from corn silage samples removed intact from a bunker silo. Emission rate was monitored over 12 h for a range in air velocity (0.05, 0.5, and 5 m s<sup>-1</sup>) and temperature (5, 20, and 35 °C) using a wind tunnel system. Ethanol flux ranged from 0.47 to 210 g m<sup>-2</sup> h<sup>-1</sup> and 12 h cumulative emission ranged from 8.5 to 260 g m<sup>-2</sup>. Ethanol flux was highly dependent on exposure time, declining rapidly over the first hour and then continuing to decline more slowly over the duration of the 12 h trials. The 12 h cumulative emission increased by a factor of three with a 30 °C increase in temperature and by a factor of nine with a 100-fold increase in air velocity. Effects of air velocity, temperature, and air-filled porosity were generally consistent with a conceptual model of VOC emission from silage. Exposure duration, temperature, and air velocity should be taken into consideration when measuring emission rates of VOCs from silage, so emission rate data obtained from studies that utilize low air flow methods are not likely representative of field conditions.

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### 1. Introduction

Troposphere ozone is a widespread air pollution problem and cause of premature death in the USA ((US Environmental Protection Agency) EPA, 2008; National Research Council, 2008; Jerrett et al., 2009). Decreases in emissions of volatile organic compounds (VOCs) and oxides of nitrogen, both reactants for tropospheric ozone formation, have been effective in reducing ozone concentrations over the past 40 years (EPA, 2003). In the US, VOC emissions from on-road vehicles and industrial sources (which account for approximately 75% of anthropogenic VOC emissions) have been significantly reduced, resulting in a 50% decline in total anthropogenic emissions since 1970 (EPA, 2003, 2009a,b). These sources may not be the most important sources in all regions, however.

Recently, agriculture has been implicated as a source of VOCs in California. Most of California's San Joaquin Valley—an area with high concentration of large dairy farms—is classified as an ozone

nonattainment area by the EPA (EPA, 2009c) and the San Joaquin Air Pollution Control Board reports that agriculture is the largest single emitter of VOCs (San Joaquin Valley Air Pollution Control District, 2008).

Many VOCs have been detected on dairy farms, including alcohols, acids, aldehydes, ketones, and esters (Alanis et al., 2008; Shaw et al., 2007; Filipy et al., 2006; Hobbs et al., 2004; Ngwabie et al., 2008; Rabaud et al., 2003; Sunesson et al., 2001). Few studies have measured VOC emission rates from isolated sources on dairy farms, but those that have demonstrate that silage and silage-containing total mixed rations (TMR) are together the largest source of VOC emissions (Card and Schmidt, 2006; Alanis et al., 2008; Chung et al., 2009). Card and Schmidt (Card and Schmidt, 2006; Schmidt, 2006) used an emission isolation flux chamber to measure VOC flux from six different sources on two California dairy farms. Measured fluxes from silage and TMR were more than an order of magnitude greater than fluxes from manure sources. Although the exposed area of silage and TMR is much smaller than that of other sources, the estimated contribution of silage was close to 50% of total farm VOC emissions for one farm and greater than 80% for the other. Chung et al. (2009) used a similar flux chamber

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method to measure VOC flux from isolated sources on six California dairies, and found that fluxes from silage and TMR were at least two orders of magnitude greater than fluxes from manure sources. Based on the fluxes and surface areas reported by Chung et al. (2009), silage and TMR contributed more than 90% of total dairy farm VOC emissions.

Previous studies indicate that silage VOC emissions are dominated by oxygenated VOCs, in particular ethanol (Chung et al., 2009; Mitloehner et al., 2009; Schmidt, 2006). Ethanol emission made up about 70% of the average total VOC emission reported by Schmidt (2006). In an environmental chamber study, alcohols contributed more than 80% of the total VOC emissions from TMR, corn, alfalfa, and cereal silages, with ethanol being the most abundant of six alcohols detected contributing 70–90% of alcohol emissions (Mitloehner et al., 2009). Chung et al. (2009) also reported that VOC emissions from feed were dominated by ethanol, contributing 60% of total VOC emissions from silage and about 90% of total VOC emissions from TMR.

Ethanol is produced during ensiling by yeasts and bacteria (Pahlow et al., 2003), and makes up about 1% of the dry matter mass in corn silage (McDonald et al., 1991). Emission of ethanol and other VOCs occur when silage is exposed to the atmosphere in the silo, during feed mixing operations, and from feed piles being fed to the animals. On large dairy farms silage is typically stored in bunker or stack silos (Fig. 1) and removal of silage for feeding occurs once or twice per day, exposing a fresh “face” of silage to the atmosphere. Opening the silo and exposing fermented material to oxygen rich air also triggers aerobic degradation of organic acids, alcohols and sugars at the exposed silo face, which increases the pH and produces microbial products toxic to ruminants. With good silo management, 100–300 mm of silage is removed from the silo face each day to reduce the risk of intoxication in animals and the respiration losses that occur during feed-out (Savoie and Jofriet, 2003).

Ethanol is clearly one of the dominant VOCs emitted from dairy farms. Fortunately, this compound is not highly reactive with regard to ozone formation. The maximum incremental reactivity (MIR)—an indicator of the potential of a VOC to form ozone—is  $1.45 \text{ g g}^{-1}$  for ethanol, much lower than that of highly reactive isoprene which is emitted by living plants ( $\text{MIR} = 10.28 \text{ g g}^{-1}$ ), but substantially higher than ethane ( $\text{MIR} = 0.26 \text{ g g}^{-1}$ ), which is generally assumed to be non-reactive (Avery, 2006; Carter, 2009).

Despite recent attention given to the problem of VOC emissions from silage, few measurements represent silage emission rates as they occur on farms. Field measurements such as Schmidt (2006), Alan et al. (2008), and Chung et al. (2009) utilized emission isolation flux chambers designed for diffusion-limited conditions

where air velocity has no influence on emissions. The isolation flux chamber methodology prescribes an air flow rate of  $0.005 \text{ m}^3 \text{ min}^{-1}$  for a  $0.030 \text{ m}^3$  chamber which translates into an air speed of about  $0.05 \text{ m s}^{-1}$  inside the chamber (Eklund, 1992). Measurements made in environmental chambers by Mitloehner et al. (2009) were at very low air velocities (approximately  $0.03 \text{ m s}^{-1}$ ), which again were not representative of farm conditions. Furthermore, previous studies do not report emission rates over time, even though VOC emission rate is expected to decrease as molecules near the exposed surface are depleted. Lastly, there has been no attempt to quantify the effect of environmental parameters such as air velocity and silage temperature on emissions.

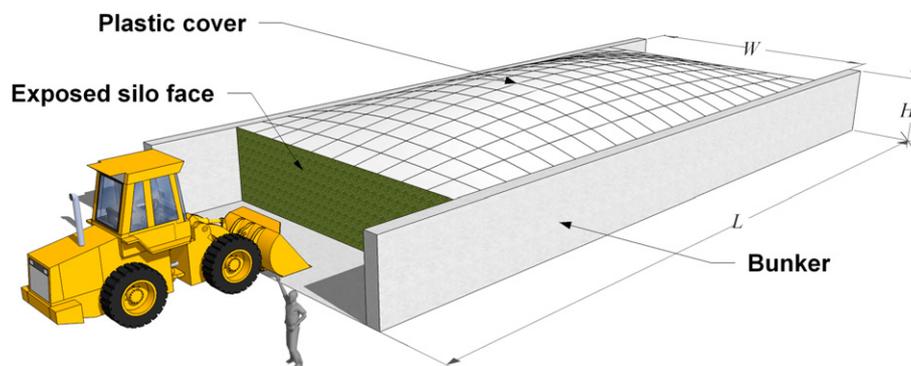
Our objectives were to measure ethanol emission rates from silage under conditions representative of an exposed silo face on dairy farms, and to quantify the effects of exposure duration, air velocity, and silage temperature on emission. Corn silage was selected as a representative material, given its importance as cattle feed in the USA (Wilkinson and Toivonen, 2003) with about 100 million Mg of corn used annually to produce silage (USDA-National Agricultural Statistics Service, 2009). Ethanol was chosen as a representative compound because of its abundance in silage, and it serves as a model for other VOC emissions.

## 2. Methods

### 2.1. Silage sample collection and analysis

Corn silage was collected from a bunker silo at the Pennsylvania State University dairy farm. Minimally disturbed samples of fresh silage were collected by removing and discarding about 10 cm from the silage surface and driving a steel box (11 cm wide by 26 cm long by 15 cm high, wall thickness of 4 mm) into the freshly exposed silage. The sampling box was then excavated, resulting in a minimally disturbed silage sample with in situ density and particle orientation. The sampling box with the sample was placed on a flat plastic board and immediately covered with plastic film, carried to the laboratory, and stored for short periods of time at  $2 \text{ }^\circ\text{C}$  until emission measurement trials began.

For measurement of silage chemical properties, approximately 1 kg of silage was collected from the walls of the cavity left by the excavated sample, vacuum sealed, and frozen at  $-30 \text{ }^\circ\text{C}$  for long-term storage until it was shipped to a commercial laboratory for analysis (Analab, Fulton IL, USA). Dry matter, ethanol, and lactic, acetic, and butyric acid concentrations were measured. Dry matter was determined by mass difference between a fresh sample and the sample dried in a convection oven for 8 h at  $105 \text{ }^\circ\text{C}$ . Dry matter



**Fig. 1.** Diagram of a bunker silo used for storing silage. The height, length and width of the silo ( $H$ ,  $L$  and  $W$ ) vary from small experimental silos (2, 5 and 15 m) to large silos with 2.5 m high walls and exceeding 50 m long and wide. A stack silo is formed by stacking chopped forage up to 5 m high without any lateral retaining structure (adapted from Savoie and Jofriet, 2003).

content determined in this manner excluded the mass of volatile compounds and therefore is a slight ( $\sim 3\%$ ) underestimate (Porter and Murray, 2001). Volatile fatty acid concentrations were measured in  $0.05 \text{ mol L}^{-1}$  sulfuric acid extracts by capillary zone electrophoresis using a P/ACE MDQ system (Beckman Coulter Inc., Fullerton CA, USA). Ethanol content was determined in water extracts with an Agilent 7890 gas chromatograph equipped with a flame ionization detector (Agilent Technologies, Inc., Santa Clara CA, USA). A 30 m capillary column (J & W Scientific, 19091F-433 HP-FFAP, 0.25 mm inner diameter, 0.25  $\mu\text{m}$  film thickness) was used for the gas chromatography analysis with  $\text{H}_2$  as the carrier at a flow rate of  $40 \text{ mL min}^{-1}$ . Column temperature was initially  $50 \text{ }^\circ\text{C}$  and was increased to  $80 \text{ }^\circ\text{C}$  over 1.5 min.

Silage density was calculated for each sample based on sample mass and sampling box volume ( $0.0038 \text{ m}^3$ ). Total porosity was estimated based on sample density, dry matter content, and a particle density of  $1600 \text{ kg m}^{-3}$  (Rees et al., 1983). Gas-filled porosity was calculated from total porosity using silage water content and the density of pure water as influenced by temperature (Dean, 1999). Silage pH was measured directly in samples using a spear tip electrode designed for use in semisolid food materials (Orion ROSS 81-63, Thermo Scientific, Waltham MA, USA).

## 2.2. Wind tunnel system

The wind tunnel system used to measure ethanol emission was formed by attaching a metal chamber to the top of the sampling box. This chamber was connected by a flexible aluminum duct to a calibrated orifice, an air stream sampling port, and flow control valves (Fig. 2). All contact areas between the chamber, the steel box, and the plastic support were sealed with rubber “weatherseal”. The wind tunnel system was placed inside a controlled environment growth chamber (Conviron PGR15 plant growth chamber, Controlled environments Ltd, Winnipeg, Canada) that maintained a set air temperature and humidity. Fresh air was drawn from the interior of the growth chamber, through the wind tunnel, and over the silage sample using a 12 V DC blower ( $0.23 \text{ m}^3/\text{min}$  BFB0712H, Delta Products Corporation, Fremont, CA) or a 100 V AC 2.5 HP shop vacuum (Shop-Vac Corporation, Williamsport, PA), depending on the air flow rate needed. Air flow rate was determined by measuring the pressure drop across a calibrated orifice (Oripac 5300, Lamda Square, Babylon, NY) using a micromanometer (TSI 8705, reported

**Table 1**

Summary of weather data for the U.S (NOAA, 2009). Percentiles were calculated from normal daily values for each month of the year, and therefore capture geographic variability and variability from month to month, but not daily or annual variability.

Variable	Percentile							
	$n^a$	0.1	1	10	50	90	99	99.9
Average wind ( $\text{m s}^{-1}$ ) <sup>b</sup>	275	1.43	1.88	2.73	3.98	5.45	7.38	18.3
Maximum wind ( $\text{m s}^{-1}$ ) <sup>b</sup>	276	4.47	4.47	10.3	19.7	27.3	35.3	77.6
Relative humidity (%) <sup>b</sup>	548	13	22	50	70	85	91	94
Mean daily temperature ( $^\circ\text{C}$ ) <sup>c</sup>	283	-23.9	-14.6	-2.03	13.6	26.1	28.9	33.5
Maximum daily temperature ( $^\circ\text{C}$ ) <sup>c</sup>	283	-20.0	-10.2	2.67	19.8	30.9	35.0	40.3

<sup>a</sup> Number of stations included in the analysis.

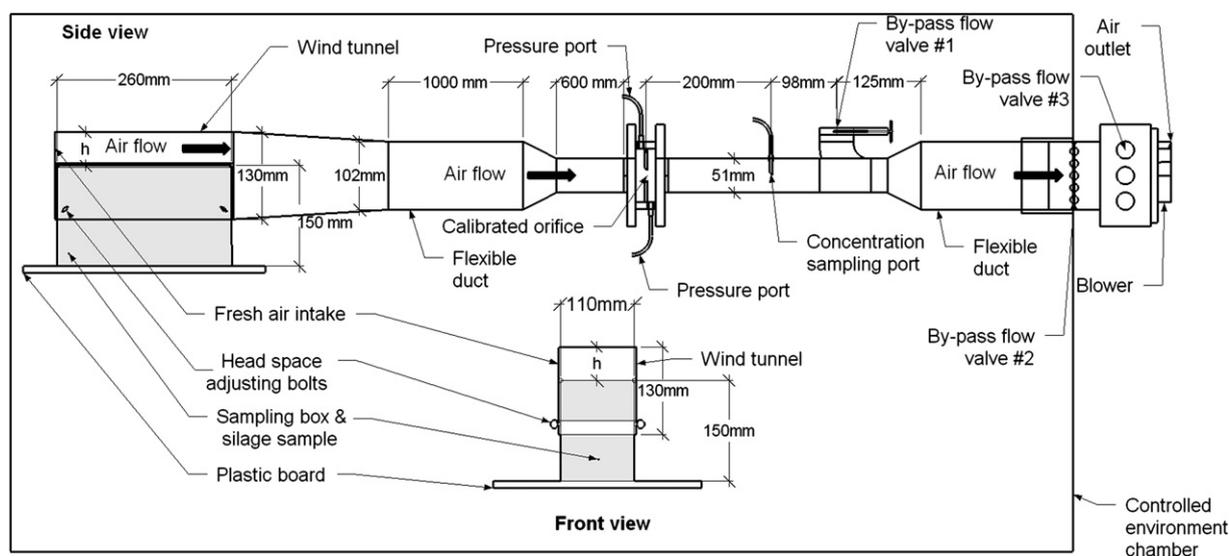
<sup>b</sup> Averages are based on 3–124 years depending upon the station.

<sup>c</sup> Climatological normals (1971–2000).

accuracy 1 Pa, TSI Incorporated, Shoreview, MN). Pressure drop was converted to flow rate based on Equation 9.121 in Miller (1996). The air flow inside the wind tunnel was fine-tuned by adjusting valves that allowed air to bypass the sampling box. Air velocity over the silage was calculated from the air flow rate and the cross-sectional area of the wind tunnel above the sample.

Ethanol concentration in the wind tunnel air stream was measured using an Innova 1412 photoacoustic gas monitor (LummaSense Technologies, Ballerup, Denmark) with optical filters to measure ethanol, methanol, acetic acid, ammonia, non-methane hydrocarbons, and water vapor, with the cross interference correction option activated. The gas monitor drew air samples from the air stream inside the wind tunnel 0.2 m downstream of the calibrated orifice. Gas samples were taken every minute for the first 10 min, every five the following 20 min, every ten the following hour, and every 30 min thereafter until 12 h of measurement were completed.

The monitor’s accuracy was tested by measuring ethanol concentration in defined gas mixtures containing ethanol, methanol, and acetic acid. Error in ethanol measurement was less than 10% for mixtures where concentrations of acetic acid and methanol were comparable to or less than ethanol. Since ethanol dominates emissions of VOCs from corn silage, acetic acid and methanol were unlikely to cause significant interferences in ethanol measurement. However, other gases that were not measured may interfere.



**Fig. 2.** Main components of the wind tunnel system used to measure ethanol emissions from silage (not drawn to scale).

**Table 2**  
Properties of the corn silage used in this study and of typical corn silage.

This study	Dry matter (%)	pH	Lactic acid (%) <sup>a</sup>	Acetic acid (%) <sup>a</sup>	Ethanol (%) <sup>a</sup>	Wet density (kg/m <sup>3</sup> )	Dry density (kg/m <sup>3</sup> )	Total porosity	Gas-filled porosity
Min.	28.9	3.32	3.35	0.82	0.75	528	184	0.806	0.214
Mean	33.5	3.39	6.93	1.12	1.13	798	267	0.833	0.301
Median	33.5	3.39	7.06	1.1	1.12	832	273	0.829	0.272
Max.	35.8	3.46	8.28	1.49	1.45	897	310	0.885	0.541
SD <sup>b</sup>	1.49	0.039	0.919	0.146	0.18	91.4	31	0.0194	0.0812
Typical <sup>c</sup>									
Min.	30	3.7	4	1	1	370	125		
Max.	40	4.2	7	3	3	960	378		

<sup>a</sup> Expressed as percent of dry matter content.<sup>b</sup> SD = standard deviation.<sup>c</sup> Typical values were taken from the following references: dry matter, pH, lactic acid, acetic acid and ethanol: Kung and Shaver (2001); density: Darby and Jofriet (1993) and Muck and Holmes (2000).

To assess this possibility, and to verify the accuracy of ethanol determination in silage emission samples, a subset of wind tunnel air stream samples were analyzed for ethanol using a gas chromatograph equipped with a flame ionization detector (Varian CP-3800, Varian Inc., Palo Alto, CA, USA). The column was a 0.53 mm (inner diameter) capillary column with a 0.5  $\mu\text{m}$  SPB-1000 coating (Supelco Analytical, Bellefonte, PA, USA). The carrier gas was helium at a flow rate of 10 mL min<sup>-1</sup>. Injector and detector temperatures were both 250 °C. The column oven temperature was programmed to maintain 60 °C for 1.9 min, followed by an increase to 180 °C over 3 min to remove acetic acid and other compounds. Results from the photoacoustic monitor were close to results from the gas chromatograph; the difference ranged from -26% to +36%, with a mean difference of 9%, over a concentration range of 5.0–230 mg m<sup>-3</sup>.

The adjustable space above the sampling box in our system (distance  $h$  in Fig. 2) allowed us to decouple air velocity from air flow rate. This allowed a wide range of air velocities (velocity varied by a factor of 100 in this work) and quantification of ethanol concentration at low fluxes, even at high air velocities. One drawback of this approach was that the air flow conditions inside the wind tunnel, and thus the relationship between the mass transfer coefficient and air velocity, may have changed as the chamber dimensions changed. Additionally, when placed at the small chamber volume settings (short distance  $h$ , in Fig. 2), the influence of the top and sides of the chamber on air flow conditions changed.

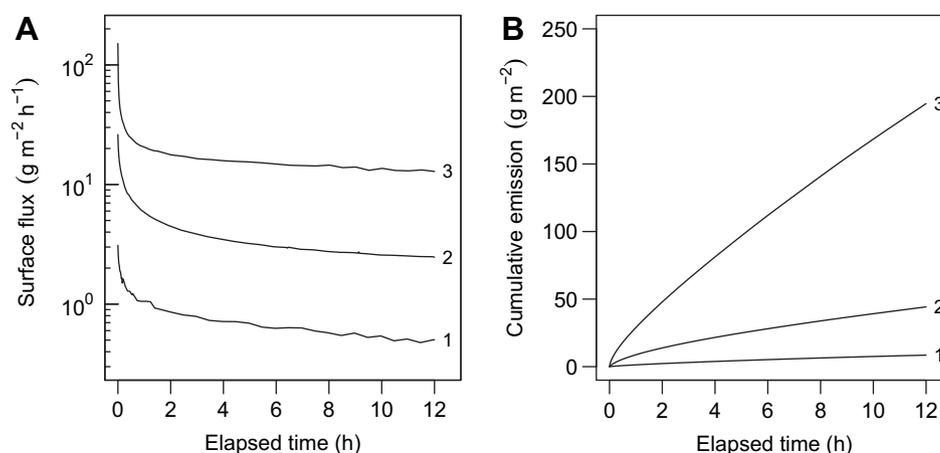
The accuracy of the wind tunnel system was tested by performing mass balance tests with ethanol solutions. Between 2 and 20 g of solution were used for these tests. Tests were stopped when

the ethanol concentration in the wind tunnel air stream declined to <1% of the initial value, indicating that approximately 99% of the ethanol was lost from solution. Calculated mean ethanol recovery was 96%, with a standard deviation of 11%.

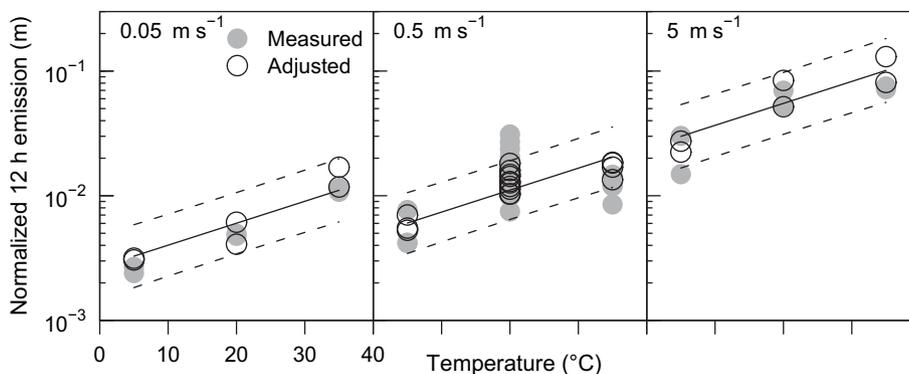
### 2.3. Experimental design and data analysis

A series of trials were conducted to quantify the effects of temperature and air velocity on ethanol emission from corn silage. A duplicate 3 × 3 factorial design was used, with eight additional center point replicates. Temperature levels were 5, 20 and 35 °C and air velocity levels were 0.05, 0.5 and 5 m s<sup>-1</sup>. Air velocities were selected so that the values of the mass transfer coefficient in the wind tunnel system were similar to those expected for a bunker or stack silo on a farm. Relative humidity was 70% for all trials. These levels were selected to encompass a large fraction of weather conditions expected in the U.S. (Table 1).

Ethanol concentration recorded with the photoacoustic monitor and air flow measurements obtained with the calibrated orifice were used to calculate ethanol flux and cumulative emission. Ethanol emission rate (g h<sup>-1</sup>) at each sampling time was calculated as the product of air stream concentration (g m<sup>-3</sup>) and air flow rate (m<sup>3</sup> h<sup>-1</sup>). The air flow rate was taken as the mean flow rate for each individual measurement trial. Ethanol flux (g m<sup>-2</sup> h<sup>-1</sup>) was calculated by dividing the emission rate by the area of the open top of the sampling box (0.025 m<sup>2</sup>), and cumulative emission (g m<sup>-2</sup>) was determined by numerically integrating flux. To eliminate variability due to different initial concentrations of ethanol in the samples, both flux and cumulative emission were normalized by dividing



**Fig. 3.** Flux (A) and cumulative emission (B) of ethanol from intact silage samples for conditions of (1) 5 °C, 0.05 m s<sup>-1</sup>, (2) 20 °C, 0.5 m s<sup>-1</sup> and (3) 35 °C, 5.0 m s<sup>-1</sup>.



**Fig. 4.** Normalized cumulative 12 h ethanol emission from intact silage samples versus temperature at three air velocities. Measured data points represent values as measured, while adjusted data points were standardized to mean gas-filled porosity (0.29) using the gas-filled porosity coefficient given in Table 3. Solid lines represent predictions from the complete model given in Table 3, adjusted to the mean gas-filled porosity. Dashed lines represent 95% prediction intervals for the same conditions.

them by the initial volumetric ethanol concentration ( $\text{g m}^{-3}$ ) in each sample. Therefore, normalized ethanol flux is reported in units of  $\text{m h}^{-1}$  (or  $\text{mm h}^{-1}$ ) (i.e.,  $\text{g m}^{-2} \text{h}^{-1}$  divided by  $\text{g m}^{-3}$ ) and cumulative ethanol emission is in units of m (or mm) (i.e.,  $\text{g m}^{-2}$  divided by  $\text{g m}^{-3}$ ). These units facilitate comparisons between samples with different ethanol concentrations. Intuitively, these units reflect the thickness of a silage layer that contains the mass of ethanol emitted. Maximum normalized cumulative emission equaled the silage depth, which was 0.15 m in these trials.

Regression analysis of normalized ethanol flux and cumulative emissions was done using log-transformed data. This transformation converted the expected multiplicative effects of temperature and air speed to additive effects facilitating the use of additive linear models in the analysis (Steel et al., 1997). For each response variable, we fit the following general model:

$$\log_{10}(y) = \beta_0 + \beta_1 T + \beta_2 \log_{10}(v) + \beta_4 \log_{10}(\phi) \quad (1)$$

where  $y$  = the response variable,  $T$  = temperature,  $v$  = air velocity, and  $\phi$  = air-filled porosity. Second-order (squared) terms and second-order interactions were also considered.

### 3. Results

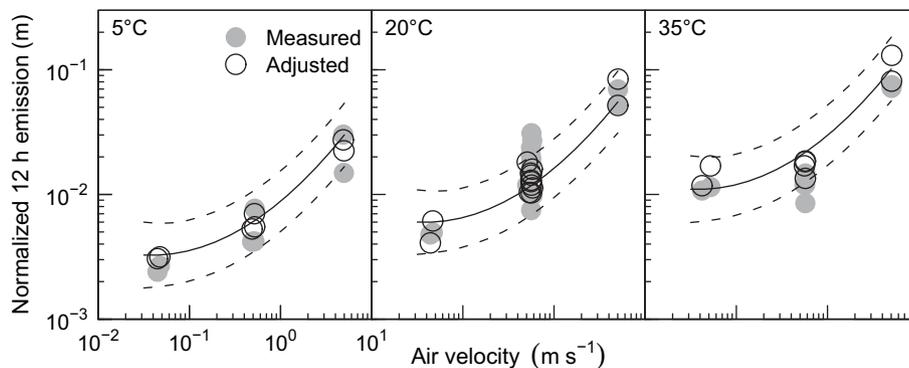
Corn silage sample characteristics were generally within the range expected for typical silage (Table 2). An exception was pH, which appeared lower than typical values. Measurements were made directly on the silage material and not in deionized water extracts as is commonly done, which may have led to lower pH

values. Ethanol concentration varied significantly, with the maximum value approaching 2-fold the minimum value.

Ethanol emission from silage followed a distinct pattern over time (Fig. 3). Ethanol flux was highest immediately after exposing silage to moving air, declined rapidly within the first hour and then continued to decline much more slowly for the duration of the trial. This pattern translated into a brief early period of rapid increase in cumulative emission, followed by a long period of slower increase that accounted for most of the 12 h cumulative emission (Fig. 3). Initial flux ranged from 2.7 to  $210 \text{ g m}^{-2} \text{ h}^{-1}$  and was 3.3–28 times the final flux. Twelve hour cumulative emission ranged from 8.5 to  $260 \text{ g m}^{-2}$ .

#### 3.1. Effect of temperature and air velocity on ethanol emission

Cumulative 12 h emission, normalized by the initial volumetric ethanol concentration in the sample, showed an exponential response to temperature (Fig. 4), increasing by a factor of three with a temperature increase from 5 to 35 °C. Cumulative emission increased by a factor of 9 as air velocity changed from 0.05 to  $5.0 \text{ m s}^{-1}$  (Fig. 5). Regression analysis showed that cumulative emission was positively related to temperature, velocity, and air-filled porosity (Table 3). The response of log-transformed cumulative emission to temperature appeared linear (Fig. 4) and a second-order term was not significant in a regression model ( $P = 0.057$ ). Interaction terms were not significant for either response variable ( $P > 0.25$ ). The relative change in cumulative emission was smaller as air velocity increased from 0.05 to  $0.5 \text{ m s}^{-1}$  than it was from 0.5 to  $5.0 \text{ m s}^{-1}$



**Fig. 5.** Normalized cumulative 12 h ethanol emission from intact silage samples versus air velocity at three temperatures. Measured data points represent values as measured, while adjusted data points were standardized to mean gas-filled porosity (0.29) using the gas-filled porosity coefficient given in Table 3. Solid lines represent predictions from the complete model given in Table 3, adjusted to the mean gas-filled porosity. Dashed lines represent 95% prediction intervals for the same conditions.

**Table 3**  
Multiple regression results for normalized cumulative 12 h emissions. The response variable is  $\log_{10}(\text{cumulative emission [m]})$ .

Variable	Coefficient	Standard error	<i>t</i>	<i>P</i>
Intercept	-1.29	0.110	-11.7	<0.0001
Temperature (°C)	0.0176	0.00195	9.05	<0.0001
$\log_{10}(\text{air velocity})$ ( $\text{m s}^{-1}$ )	0.610	0.0424	14.4	<0.0001
$\log_{10}(\text{porosity})$ ( $\text{m}^3 \text{m}^{-3}$ )	1.64	0.207	7.90	<0.0001
$\log_{10}(\text{air velocity})^2$ ( $\text{m s}^{-1}$ )	0.215	0.042	5.11	<0.0001

Degrees of freedom = 24, residual standard error = 0.111,  $R^2 = 0.936$ , Adjusted  $R^2 = 0.925$ .

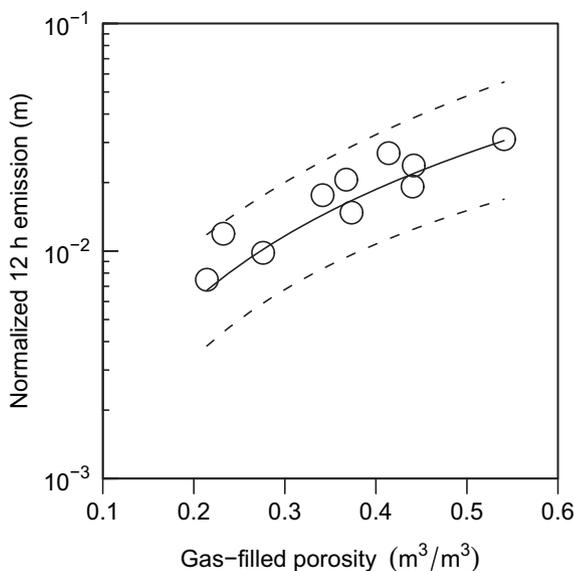
(Fig. 5), as implied by a significant second-order term (Table 3). Porosity, which was not controlled in this work, appeared to have a substantial positive effect on ethanol emission. Normalized cumulative 12 h emission increased by a factor of four with an increase in porosity from 0.20 to 0.53 (Fig. 6). The regression model presented in Table 3 captured the response of measured emission over the entire 30-fold range in 12 h emission (Fig. 7). The 95% prediction intervals spanned approximately 0.5  $\log_{10}$  units, representing a factor of three. Regression analysis for the normalized initial flux showed that the response to change in temperature and porosity were similar to the response obtained for cumulative emission (Table 4). However, normalized initial flux showed a larger response to air velocity, i.e., a 30-fold increase from the lowest to the highest air velocity.

### 3.2. Flux and emission patterns over time

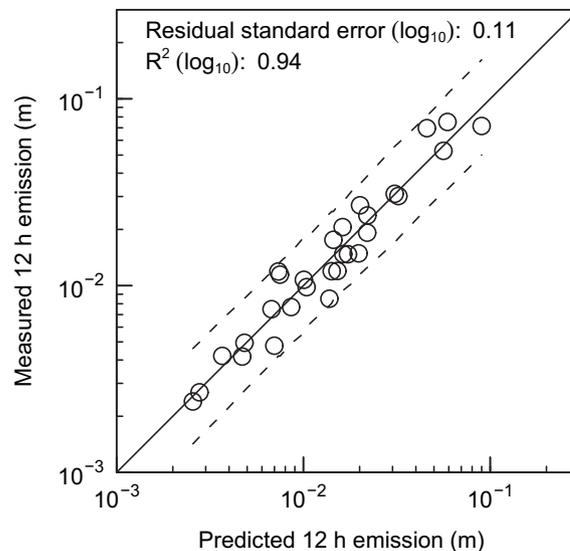
To explore the possibility of predicting ethanol emission over time, a simplified form of the Richards equation (Demeyer et al., 1995) was fit to cumulative emission data:

$$M = a(1 - e^{-ct})^i \quad (2)$$

where  $M$  = normalized cumulative emission at any time ( $t$ ),  $a$  = maximum normalized emission (equal to the sample depth of 0.15 m in this study), and  $c$  and  $i$  are empirical constants. Parameter  $c$  is a time constant that determines how rapidly the cumulative



**Fig. 6.** Normalized cumulative 12 h ethanol emission from intact silage samples versus gas-filled porosity at 20 °C and a nominal air velocity of 0.5  $\text{m s}^{-1}$ . The line represents predictions from the model given in Table 3.



**Fig. 7.** Measured normalized 12 h cumulative ethanol emission from intact silage samples versus predictions from the response surface model given in Table 3. The solid line shows the 1:1 response, while dashed lines show the 95% prediction interval.

emission approaches the maximum; therefore, the time to reach a given value of cumulative emission is inversely proportional to  $c$ . Ethanol flux can be determined from the fitted data by calculating the derivative of Eq. (2). This model has been previously applied to ammonia emission (Demeyer et al., 1995).

Best-fit values of  $c$  and  $i$  were determined using 12 h cumulative emission data for each individual trial and the nls function in R (R Development Core Team, 2009; Ritz and Streibig, 2008). Resulting estimates of  $c$  ranged from 0.00026 to 0.048  $\text{h}^{-1}$ , while estimates of  $i$  ranged from 0.58 to 0.92. Predictions from Eq. (2) showed a very good fit to measured cumulative emission and flux (Fig. 8). Equation (2) was able to capture the evolution of ethanol emission rate during the 12 h following exposure of the silage surface to air. Regression analysis showed that the value of parameter  $c$  was strongly related to the same predictors that influenced initial flux and 12 h emissions, i.e., temperature, air velocity and porosity (data not shown).

## 4. Discussion

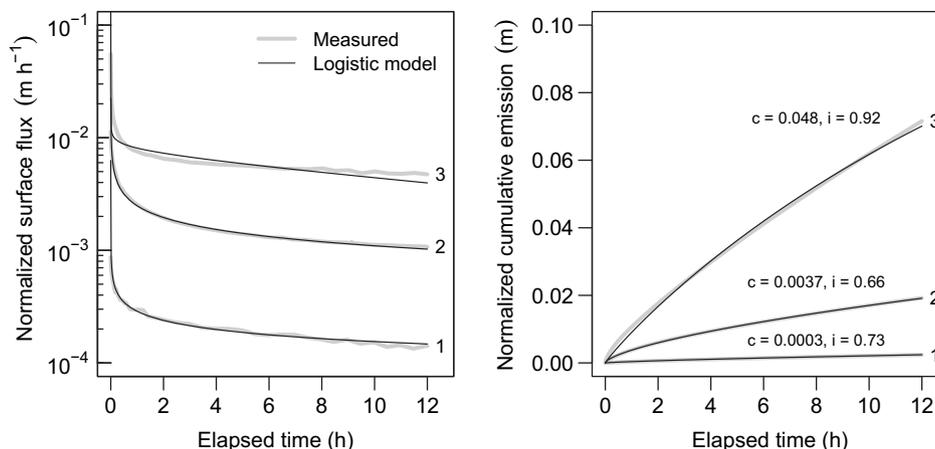
### 4.1. Factors affecting ethanol emission rate

The observed patterns of ethanol emission from silage are best understood when related to a conceptual model of VOC emission. Following the model of Jury et al. (1984)—developed for emission of organic contaminants from soils—ethanol may exist in silage in three phases: aqueous, gas, and sorbed to particulate material. Partitioning of ethanol among these three phases influences the

**Table 4**  
Multiple regression results for normalized initial flux. The response variable is  $\log_{10}(\text{initial flux [m h}^{-1}])$ .

Variable	Coefficient	Standard error	<i>t</i>	<i>P</i>
Intercept	-1.49	0.105	-14.1	<0.0001
Temperature (°C)	0.0172	0.00186	9.25	<0.0001
$\log_{10}(\text{air velocity})$ ( $\text{m s}^{-1}$ )	0.794	0.0404	19.6	<0.0001
$\log_{10}(\text{porosity})$ ( $\text{m}^3 \text{m}^{-3}$ )	1.51	0.198	7.66	<0.0001
$\log_{10}(\text{air velocity})^2$ ( $\text{m s}^{-1}$ )	0.127	0.0401	3.18	0.0041

Degrees of freedom = 24, residual standard error = 0.109,  $R^2 = 0.964$ , Adjusted  $R^2 = 0.958$ .



**Fig. 8.** Measured normalized flux and cumulative emission of ethanol from intact corn silage samples and model predictions from Eq. (2) for three emission trials (1) 5 °C, 0.05 m s<sup>-1</sup>, (2) 20 °C, 0.5 m s<sup>-1</sup> and (3) 35 °C, 5.0 m s<sup>-1</sup>. For the logistic model [Eq. (2)], parameters  $c$  and  $i$  were determined separately for each individual trial.

magnitude of aqueous and gas-phase transport of ethanol in silage. At an exposed silage surface, ethanol emission takes place through convective mass transfer, which is dependent on air velocity and gas-phase ethanol concentration.

This simple conceptual model explains the observed pattern of ethanol flux over time. As ethanol is depleted near the exposed surface, aqueous and gas-phase concentrations decline, which decreases the emission rate. The decline in surface concentrations also creates a concentration gradient within the silage, causing net transport of ethanol toward the surface. The shape of the flux versus time curve is expected to depend on the magnitudes of the mass transfer coefficient at the exposed surface and the effective diffusion coefficient within the bulk silage.

This conceptual model also provides insight into the effects of air velocity, temperature, and porosity on 12 h cumulative ethanol emission. Disregarding sorption, ethanol partitioning between aqueous and gas phases can be described by Henry's law. Near 20 °C, the Henry's law constant for ethanol decreases by approximately 50% with a 10 °C increase in temperature (Warneck, 2006), representing a two-fold increase in gas-phase ethanol concentration for a constant aqueous concentration. The observed five-fold increase over a 30 °C range strongly suggests that gas-phase transport of ethanol in silage is more important than aqueous-phase transport, at least at 20 °C and above.

The positive relationship between cumulative emission and porosity is consistent with increased gas-phase transport, as the cross-sectional area available for transport increases with porosity. However, the observed response to porosity is surprisingly large, suggesting that diffusion may not be the only process responsible for mass transport through silage. Regardless, these results support the hypothesis that gas-phase transport is much more important than aqueous-phase transport. The observed effects of air velocity are also consistent with our conceptual model. Higher air velocities increased both cumulative emission and initial flux, but increased initial flux to a larger degree.

In the above discussion, we assume that ethanol is not produced nor destroyed during emission trials. Although some species of yeast may produce ethanol from carbohydrates under aerobic conditions (Pahlow et al., 2003), the low energy recovery of this process suggests that it is not significant in silage. Conversely, it is known that acetic acid bacteria oxidize silage ethanol to acetic acid upon exposure to air. However, previous measurements have shown that this process occurs over a period of days (Spoelstra et al., 1988), and therefore should not be significant during the emission trials reported in the current work.

#### 4.2. VOC emission from silage on farms

One objective of this work was to measure ethanol emission under conditions representative of an exposed silo face on farms. While our wind tunnel more closely replicates field conditions than other methods, there remain differences between our system and a field setting. Based on the conceptual model described in Section 4.1, normalized ethanol emission is dependent on the magnitudes of the mass transfer coefficient, effective diffusion coefficient, and partitioning of ethanol among phases. Partitioning is dependent upon temperature, and is not expected to differ between the laboratory and field. The value of the mass transfer coefficient is dependent on the type of air flow over a surface and its velocity, as well as the characteristics of the exposed surface. However, air flowing over the surface of a porous medium may also influence mass transport through gas pores within the medium (Neeper, 1991). Without a better understanding of this effect, it is not possible to predict emission at higher air velocities than those used in this work. Understanding the effect of surface air velocity on the mass transport of ethanol through gas pores within the silage will improve the accuracy of field measurement of ethanol emission rates and the development of models to predict ethanol emissions.

Our results have important implications for estimating VOC emission from silage and TMR in the field. It is clear that ethanol emission rate is dependent on time of exposure, temperature, and air velocity, and a similar response is expected to exist for other VOCs as well. In order to compare emission measurements from different materials, locations, or storage conditions, similar exposure time, temperature, and air velocity need to be incorporated into measurement protocols. Additionally, our work has demonstrated a strong positive effect of air-filled porosity on VOC emission; therefore, sample porosity should also be considered when measuring VOC emission. It is expected that loose silage in mixed feed rations will have higher VOC emission rates since porosity and exposed surface area are increased under these conditions.

Our measurements indicate greater VOC emissions from silage than those from previous studies. Schmidt (2006) reported an ethanol flux from corn silage in a bunker silo that varied from 0.8 to 1 g m<sup>-2</sup> h<sup>-1</sup>. Chung et al. (2009) reported an average VOC flux of 0.5 g m<sup>-2</sup> h<sup>-1</sup> from silage. Average rates that we measured for intact silage over 12 h ranged from 0.5 g m<sup>-2</sup> h<sup>-1</sup> at 5 °C and 0.05 m s<sup>-1</sup> to 19 g m<sup>-2</sup> h<sup>-1</sup> at 35 °C and 5 m/s. Average rates calculated for shorter exposure durations would be higher. The difference between our

measured emission rates and those of other studies is probably due to the much higher air flow rates used in our work.

Although ethanol has been shown to dominate VOC emissions from silage and TMR, other silage VOCs may have a larger contribution to ozone formation, depending on their reactivity and emission rates. Based on the conceptual model discussed in Section 4.1, compounds with higher volatility will show greater emission rates when compared to ethanol under similar conditions. For example, at 20 °C the Henry's law constant for acetaldehyde is 18 mol kg<sup>-1</sup> atm<sup>-1</sup>. Therefore, this compound is expected to be emitted at much higher (normalized) rates than ethanol, which has a Henry's law constant of 280 mol kg<sup>-1</sup> atm<sup>-1</sup> (Staudinger and Roberts, 2001; Warneck, 2006).

To predict silage VOC emissions under specific farm conditions, a generic emission factor approach is inappropriate. Instead, a flexible mechanistic model is needed that represents important emission processes and their interactions. Development of such a model requires a better understanding of VOC transport within silage. Verification of model predictions requires measurement of emission rates of multiple VOCs under farm conditions from exposed silo faces and loose silage in mixed feed rations. Application of such a model requires data for VOC concentrations within silage, which are largely unknown, apart from alcohols and volatile fatty acids.

## 5. Conclusions

Ethanol emission from silage is a transient process sensitive to silage characteristics and environmental conditions. Emission rates measured from corn silage samples retaining the characteristics of an exposed silo face were highest immediately after exposure to moving air, declined rapidly within the first hour, and then declined more slowly over 12 h. Emission rates ranged from 0.47 to 210 g m<sup>-2</sup> h<sup>-1</sup> depending on the time after exposure, temperature, air velocity near the exposed surface, and air-filled porosity of the silage. Twelve hour cumulative emission varied with temperature, air velocity and air-filled porosity of the silage ranging from 8.5 to 260 g m<sup>-2</sup>. A conceptual model based on flow through porous media, Henry's law constant, and convective mass transfer explained the changes in ethanol emission as silage characteristics and environmental conditions varied.

Accurate estimates of VOC emission rates from silage and mixed feed requires recognition that emissions are influenced by measurement method, environmental conditions, and characteristics of the silage. Data obtained using methods designed for diffusion-limited mass transport are probably not representative of VOC emission rates from silage under farm conditions. Thus, emission rate data generated using methods such as the emission isolation flux chamber should be interpreted with caution.

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## References

Alanis, P., Sorenson, M., Beene, M., Krauter, C., Shamp, B., Hasson, A., 2008. Measurement of non-enteric emission fluxes of volatile fatty acids from

- a California dairy by solid phase micro-extraction with gas chromatography/mass spectrometry. *Atmospheric Environment* 42 (26), 6417–6424.
- Avery, R., 2006. Reactivity-based VOC control for solvent products: more efficient ozone reduction strategies. *Environmental Science and Technology* 40 (16), 4845–4850.
- Card, T., Schmidt, C., 2006. Dairy air emissions: summary of dairy emission estimation procedures. Report prepared to the California Air Resources Board. Retrieved April, 2009 from: <http://www.arb.ca.gov/ag/caf/SchmidtDairyEmissions2005.pdf>.
- Carter, W., 2009. Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales. Center for Environmental Research and Technology, College of Engineering, University of California. Retrieved April, 2009 from: <http://www.engr.ucr.edu/~carter/SAPRC/>.
- Chung, M., Beene, M., Ashkan, S., Krauter, C., Hasson, A., 2009. Evaluation of non-enteric sources of non-methane volatile organic compound (NMVOC) emissions from dairies. *Atmospheric Environment*. doi:10.1016/j.atmosenv.2009.11.033.
- Darby, D., Jofriet, J., 1993. Density of silage in horizontal silos. *Canadian Agricultural Engineering* 34, 275–280.
- Dean, J., 1999. *Lange's Handbook of Chemistry*, 15th ed. McGraw-Hill, New York, p. 5.87.
- Demeyer, P., Hofman, G., Vancleemput, O., 1995. Fitting ammonia volatilization dynamics with a logistic equation. *Soil Science Society of America Journal* 59 (1), 261–265.
- Eklund, B., 1992. Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. *Journal of the Air Waste Management Association* 42 (12), 1583–1591.
- EPA, 2003. National Air Quality and Emissions Trends Report. EPA 454/R-03–005. U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Emissions Monitoring and Analysis Division Air Quality Trends Analysis Group, Research Triangle Park, North Carolina 27711. Retrieved April, 2009, from: <http://www.epa.gov/air/airtrends/aqtrnd03/>.
- EPA, 2008. Ground-level Ozone: Basic Information. U.S. Environmental Protection Agency. Retrieved April, 2009, from: <http://www.epa.gov/air/ozonpollution/basic.html>.
- EPA, 2009a. Air Emissions Summary through 2005. U.S. Environmental Protection Agency. Retrieved November, 2009, from: [http://www.epa.gov/airtrends/2006/emissions\\_summary\\_2005.html](http://www.epa.gov/airtrends/2006/emissions_summary_2005.html).
- EPA, 2009b. Volatile Organic Compounds Emissions. U.S. Environmental Protection Agency. Retrieved November, 2009, from: <http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewWind&lv=list.listByAlpha&r=188211&subtop=341>.
- EPA, 2009c. 8-Hour Ozone Nonattainment Area State Map. U.S. Office of Air, Environmental Protection Agency. Retrieved April, 2009, from: <http://www.epa.gov/air/oaqps/greenbk/map8hrnm.html>.
- Filipy, J., Rumburg, B., Mount, G., Westberg, H., Lamb, B., 2006. Identification and quantification of volatile organic compounds from a dairy. *Atmospheric Environment* 40 (8), 1480–1494.
- Hobbs, P., Webb, J., Mottram, T., Grant, B., Misselbrook, T., 2004. Emissions of volatile organic compounds originating from UK livestock agriculture. *Journal of the Science of Food and Agriculture* 84 (11), 1414–1420.
- Jerrett, M., Burnett, R., Pope, C., Ito, K., Thurston, G., Krewski, D., Shi, Y., Calle, E., Thun, M., 2009. Long-term ozone exposure and mortality. *New England Journal of Medicine* 360 (11), 1085–1095.
- Jury, W., Russo, D., Streile, G., El Abd, H., 1984. Evaluation of volatilization by organic chemicals residing below the soil surface. *Water Resources Research* 26 (1), 13–20.
- Kung, L., Shaver, R., 2001. Interpretation and Use of Silage Fermentation Analysis Reports. In: *Focus on Forage*, vol. 3. University of Wisconsin –Extension (13), 1–5. Retrieved June, 2009, from: <http://www.uwex.edu/ces/crops/ufwforage/Fermentation.pdf>.
- McDonald, P., Henderson, N., Heron, S., 1991. *The Biochemistry of Silage*, second ed. Chalcombe Publications, Shedfield, UK.
- Miller, R., 1996. *Flow Measurement Engineering Handbook*, third ed. McGraw-Hill, New York, NY, pp. 9.110–9.111.
- Mitloehner, F., Malkina, I., Kumar, A., Green, P., 2009. Volatile organic compounds emitted from dairy silages and other feeds. In: *Proceedings of the XVth International Silage Conference*. July 27–29. Madison WI, USA. U.S. Dairy Forage Research Center, USDA-Agricultural Research Service, 1925 Linden Drive West, Madison WI 53706.
- Muck, R., Holmes, B., 2000. Factors affecting bunker silo densities. *Applied Engineering in Agriculture* 16 (6), 613–620.
- National Research Council, 2008. *Estimating Mortality Risk Reduction and Economic Benefits from Controlling Ozone Air Pollution*. National Academies Press, Washington, D.C.
- Neeper, D., 1991. Soil vapor extraction enhanced by oscillatory flow. Presented at the Fifth National Outdoor Action Conference, Las Vegas, NV. Retrieved April, 2009, from: [http://www.osti.gov/energycitations/product.biblio.jsp?osti\\_id=6002439](http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=6002439).
- Ngwabie, N., Schade, G., Custer, T., Linke, S., Hinz, T., 2008. Abundances and flux estimates of volatile organic compounds from a dairy cowshed in Germany. *Journal of Environmental Quality* 37 (2), 565–573.
- NOAA, 2009. Comparative climatic data for the United States through 2008. Retrieved June, 2009, from: <http://ols.nndc.noaa.gov/plolstore/plsql/olstore.prodspcific?prodnum=C00095-PUB-A0001>.
- Pahlow, G., Muck, R., Driehuis, F., Oude Elferink, S., Spoelstra, S., 2003. Microbiology of ensiling. In: *Silage Science and Technology*. Agronomy Monograph No 42. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, pp. 31–93.

- Porter, M., Murray, R., 2001. The volatility of components of grass silage on oven drying and the inter-relationship between dry-matter content estimated by different analytical methods. *Grass and Forage Science* 56 (4), 405–411.
- R Development Core Team, 2009. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. Retrieved April, 2009 from: <http://www.R-project.org>.
- Rabaud, N., Ebeler, S., Ashbaugh, L., Flocchini, R., 2003. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. *Atmospheric Environment* 37 (7), 933–940.
- Rees, D., Audsley, E., Neale, M., 1983. Some physical-properties that affect the rate of diffusion of oxygen into silage. *Journal of Agricultural Science* 100, 601–605.
- Ritz, C., Streibig, J., 2008. *Nonlinear Regression with R*. Springer, New York, NY.
- San Joaquin Valley Air Pollution Control District, 2008. Annual report to the community. San Joaquin Valley Air Pollution Control District, 1990 E. Gettsburg Avenue Fresno, CA 93726. USA. <http://www.valleyair.org>
- Savoie, P., Jofriet, J., 2003. Silage storage. In: *Silage Science and Technology*. Agronomy Monograph No 42. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, pp. 448–449.
- Schmidt, C., 2006. Results of the dairy emissions evaluation using flux chambers, phase III Merced and Kings County Dairies. Technical memorandum prepared for the California Air Resources Board. Retrieved April, 2009, from: <http://www.arb.ca.gov/ag/caf/SchmidtDairyTestData2005.pdf>.
- Shaw, S., Mitloehner, F., Jackson, W., DePeters, E., Holzinger, R., Fadel, J., Robinson, P., Goldstein, A., 2007. Volatile organic compound emissions from dairy cows and their waste as measured by proton-transfer-reaction mass spectrometry. *Environmental Science and Technology* 41 (4), 1310–1316.
- Spoelstra, S., Courtin, M., van Beers, J., 1988. Acetic acid bacteria can initiate aerobic deterioration of whole crop maize silage. *Journal of Agricultural Science* 111, 127–132.
- Staudinger, J., Roberts, P., 2001. A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. *Chemosphere* 44 (4), 561–576.
- Steel, R., Torrie, J., Dickey, D., 1997. *Principles and Procedures of Statistics. A Biometrical Approach*. McGraw-Hill Series in Probability and Statistics, third ed. McGraw-Hill New York, NY, pp. 242–243.
- Sunesson, A., Gullberg, J., Blomquist, G., 2001. Airborne chemical compounds on dairy farms. *Journal of Environmental Monitoring* 3 (2), 210–216.
- USDA-National Agricultural Statistics Service, 2009. National agricultural Statistics Service Quick Stats Retrieved April, 2009, from: <http://www.nass.usda.gov/#top>.
- Warneck, P., 2006. A note on the temperature dependence of Henry's Law coefficients for methanol and ethanol. *Atmospheric Environment* 40 (37), 7146–7151.
- Wilkinson, J., Toivonen, M., 2003. *World Silage: a Survey of Forage Conservation Around the World*. Chalcombe Publications, Lincoln, United Kingdom, p. 201.