Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Ethanol emission from loose corn silage and exposed silage particles

Sasha D. Hafner [a,*], Felipe Montes [a], C. Alan Rotz [a], Frank Mitloehner [b]

[a] USDA Agricultural Research Service, Pasture Systems and Watershed Management Research Unit, 3702 Curtin Rd., University Park, PA 16802, USA
[b] Department of Animal Science, University of California at Davis, Davis, CA, USA

ARTICLE INFO

ABSTRACT

Silage on dairy farms has been identified as a major source of volatile organic compound (VOC) emissions. However, rates of VOC emission from silage are not accurately known. In this work, we measured ethanol (a dominant silage VOC) emission from loose corn silage and exposed corn silage particles using wind tunnel systems. Flux of ethanol was highest immediately after exposing loose silage samples to moving air (as high as $220 \, \mathrm{g \, m^{-2} \, h^{-1}}$) and declined by as much as 76-fold over 12 h as ethanol was depleted from samples. Emission rate and cumulative 12 h emission increased with temperature, silage permeability, exposed surface area, and air velocity over silage samples. These responses suggest that VOC emission from silage on farms is sensitive to climate and management practices. Ethanol emission rates from loose silage were generally higher than previous estimates of total VOC emission rates from silage and mixed feed. For 15 cm deep loose samples, mean cumulative emission was as high as $170 \, \mathrm{g \, m^{-2}}$ (80% of initial ethanol mass) after 12 h of exposure to an air velocity of $5 \, \mathrm{m \, s^{-1}}$. Emission rates measured with an emission isolation flux chamber were lower than rates measured in a wind tunnel and in an open setting. Results show that the US EPA emission isolation flux chamber method is not appropriate for estimating VOC emission rates from silage in the field.

Published by Elsevier Ltd.

1. Introduction

Anthropogenic emissions of volatile organic compounds (VOCs) contribute to the formation of tropospheric ozone, which is a cause of premature death (National Research Council, 2008) and is regulated as an air pollutant by the United States Environmental Protection Agency (US EPA) (US EPA, 2009a). Dairy farms have recently been identified as a significant source of VOCs in California (Shaw et al., 2007; San Joaquin Valley Air Pollution Control District, 2008; Howard et al., 2008; Alanis et al., 2008; Chung et al., 2009; Howard et al., 2010). The San Joaquin Air Pollution Control District (2008) estimates that agriculture is the largest single emitter of VOCs in the San Joaquin Valley, but there is substantial uncertainty associated with quantifying this estimate (Crow, 2005). The San Joaquin Valley Air Pollution Control District is currently developing new estimates of dairy VOC emission rates (Gill and Norman, 2010), largely based on measurements made using the emission isolation flux chamber method (Kienbusch, 1986).

Studies that have measured VOC emission rates from individual sources on dairy farms have concluded that silage and silage-containing mixed feed together contribute at least 50% of total farm VOC emissions (Card and Schmidt, 2006; Alanis et al., 2008; Chung et al., 2009). (These studies used the emission isolation flux chamber method to measure emission rates. Although measurements of VOC emission rates from agricultural surfaces made with this method are probably not accurate, as discussed below, it is reasonable to expect that comparisons between individual sources provide some indication of relative importance.)

Silage emission of VOCs is dominated by oxygenated compounds, especially ethanol (Schmidt, 2006; Chung et al., 2009; Mitloehner et al., 2009; Howard et al., 2010). The importance of ethanol is not surprising, considering that it is a major fermentation end product in corn silage (McDonald et al., 1991; Rooke and Hatfield, 2003), which is the most common type of silage in the US (Wilkinson and Toivonen, 2003). Ethanol commonly makes up about 1% of the dry mass of corn silage (McDonald et al., 1991), but can exceed 3% (e.g., Kleinschmit et al., 2005). The total quantity of whole corn used to produce silage annually in the US is about 98 million Mg (USDA National Agricultural Statistics Service, 2009). Based on typical conditions (whole-plant dry matter content of 30–40% [Kung and Shaver, 2001], total dry matter loss of 15% [Muck and Holmes, 2006], and ethanol concentration of 1.5% [Kleinschmit et al., 2006]) we estimate that total annual ethanol production in corn silage in the US is about 0.4–0.5 million Mg. If a large fraction of this total is emitted to the atmosphere, it makes a small but important contribution to national anthropogenic

* Corresponding author. Tel.: +1 301 504 8904; fax: +1 301 504 5048.
E-mail address: sasha.hafner@ars.usda.gov (S.D. Hafner).

VOC emissions, which are estimated to be about 14 million Mg (US EPA, 2009b).

Previous estimates of the emission rate of ethanol and other VOCs from silage and mixed feed were made using the emission isolation flux chamber method (commonly known as the US EPA flux chamber method). This method was designed for conditions where emission is limited by resistance within the emitting medium, and therefore is not sensitive to air movement at the surface (Kienbusch, 1986). Air movement within the chamber is low compared to air movement due to wind or mechanical ventilation outside or inside a dairy barn (Eklund, 1992). [For their measurements, Card and Schmidt (2006) (see Schmidt, 2006), Alanis et al. (2008), Chung et al. (2009) all used a 30 L chamber with a sweep gas flow rate of 5.0 L min^{-1}, which is the recommended procedure (Kienbusch, 1986).] As has been observed for numerous systems, air velocity often does have a significant effect on emission rate (Hudson and Ayoko, 2008; Parker et al., 2010). The effect of air flow rate or air velocity on ammonia emission rate from soils as measured in chambers was noted as early as the 1970s (Watkins et al., 1972; Kissel et al., 1977). More recently, Parker et al. (2010) demonstrated that air velocity has a substantial effect on VOC emission from cattle manure and wastewater.

Using a simple convection–diffusion model, Hafner et al. (2009) predicted that emission of two VOCs (ethanol and acetic acid) from silage is dependent on air velocity. Based on wind tunnel measurements, Montes et al. (2010) showed that 12 h cumulative ethanol emission from intact packed silage from a bunker silo increased by a factor of nine with an air velocity increase from 0.05 m s^{-1} to 5 m s^{-1}. These results suggest that the US EPA flux chamber method is not an appropriate method for estimating VOC emission rates from silage in the field. A recent review of devices used for sampling odor emission rates concluded that wind tunnels best represent the emission process found in the field (Hudson and Ayoko, 2008).

Montes et al. (2010) utilized a wind tunnel for measuring ethanol emission from intact corn silage from a bunker silo, and estimates were much higher than previously reported values (Schmidt, 2006; Chung et al., 2009). However, VOC emissions from silage storage structures may be less than emissions from silage that has been removed from storage structures for mixing and feeding, due to a larger exposed area of feed in feed lanes or bunks (Card and Schmidt, 2006; Chung et al., 2009), and higher emission rates that may result from higher porosity of "loose" silage. The current study extends the work of Montes et al. (2010) by measuring emission from loose silage. We use the term loose to mean that the original silage density and structure present while in storage was disrupted, resulting in a lower density and higher porosity, as typically happens after removal of silage from a storage structure.

The overall goal of this work was to develop a more complete understanding of VOC emission from loose silage. We focused on corn silage, because it is the most widely used type of silage in the US, and ethanol, because it dominates the VOC emission profile from silage. Specific objectives were to: 1) provide estimates of the rate of ethanol emission from loose corn silage in a farm setting, 2) quantify the effects of temperature, air velocity, and exposed surface area on ethanol emission rates, and 3) assess the accuracy of the US EPA emission isolation flux chamber method for measuring VOC emission from loose silage.

2. Methods

2.1. Silage sample collection and analysis

Corn silage was collected from a tower silo (silage A) and a bunker silo (silage B) at The Pennsylvania State University dairy farm in State College, Pennsylvania, US, and from a bunker silo at a central Pennsylvania dairy farm (silage C). These sources provided a range of particle size distributions (Table 1). Before collecting bunker samples, we removed at least 10 cm of silage to provide a fresh sample. Tower silo samples were collected from a top-unloaded silo using an electric unloader. All samples were transported to our laboratory in plastic bags, and stored at <5 °C. Subsamples were analyzed for dry matter, pH, and ethanol concentration within one week of collection (ethanol concentration was found to be stable for more than one week) or else were vacuum sealed and frozen.

Silage dry matter content was determined by drying samples at 105 °C. Silage pH was measured directly using a spear tip electrode designed for use with semisolids (Orion ROSS 81-63, Thermo Scientific, Waltham MA, US). Ethanol concentration was measured by gas chromatography using a headspace method. Specifically, about 10 g of silage and 75 g of distilled water were added to a 125 mL jar, which was sealed with a cover that contained a septum (I-Chem Septa Jars, Fisher Scientific, Hampton, NH, US). The jars were intermittently shaken until headspace ethanol concentration stabilized (2–3 h). Headspace ethanol concentration was quantified via direct injection into a gas chromatograph equipped with a flame ionization detector (Varian CP-3800, Varian Inc., Palo Alto, CA, US). A 0.53 mm (inner diameter) capillary column with a 0.5 μm SPB-1000 coating (Supelco Analytical, Bellefonte, PA, US) was used for separation, with 10 mL min^{-1} of He as a carrier gas. Injector and detector temperatures were both 250 °C.

Table 1
Properties of the corn silage samples used for ethanol emission measurements.

Silage[a]	Dry matter (%)	pH	Fermentation end products (% of DM)			Particle size (mm)		Permeability (mm^2)[c]
			Lactic acid	Acetic acid	Ethanol	Mean	Distribution, s [b]	
A	41 (2.7)[d]	4.0 (0.20)	5.1	3.7	1.2 (0.13)	6.6 (0.75)	2.1 (0.09)	0.0053 (0.000082)
B	34 (1.5)	3.4 (0.07)	6.9 (0.88)	1.1 (0.16)	1.1 (0.18)	10.0 (0.69)	1.8 (0.02)	0.015 (0.00027)
C	31 (2.4)	3.8 (0.03)	4.6 (0.26)	2.8 (1.7)	1.4 (0.61)	11.2 (0.37)	1.7 (0.06)	0.014 (0.0011)
Typical[e]								
Min.	30	3.7	4	1	1			
Max.	40	4.2	7	3	3			

[a] Silage A was from a tower silo, and B and C were from bunker silos.
[b] Standard deviation of the particle distribution, calculated following Heinrichs and Kononoff's (2002) spreadsheet (http://www.das.psu.edu/research-extension/dairy/nutrition/forages/resolveuid/3f85b0f4ef052d442f76d1fed68c7f3d).
[c] Interpolated permeability at a gas-filled porosity of 0.70 m^3 m^{-3}.
[d] Values given in each cell are means of the results from individual batches, while values in parentheses are the standard deviation among batches. Values for each batch were single measurements (lactic acid, acetic acid, particle size, and dry matter and ethanol for most samples of silage B) or were calculated as the mean of three replicates (dry matter, pH, and ethanol).
[e] Typical values from Kung and Shaver (2001).

The column temperature was held at 60 °C for 1.9 min, followed by an increase to 180 °C over 3 min. For calibration, we injected headspace samples from solution standards of ethanol. This approach relies on the assumption that the Henry's law constant for ethanol was the same in the standards and samples, but does not require an estimate of the constant itself. Concentrations of lactic and acetic acid were determined by a forage analysis laboratory (Analab, Fulton IL, US) in $0.05 \, mol \, L^{-1}$ sulfuric acid extracts by capillary zone electrophoresis using a P/ACE MDQ system (Beckman Coulter Inc., Fullerton CA, US). Silage particle distribution was estimated using the Penn State Forage Particle Separator, following the recommended procedure (Heinrichs and Kononoff, 2002).

Silage permeability was measured using a steady-state permeameter (0.6 m long, 0.10 m inner diameter) (Bear, 1972; Tidwell, 2006). Compressed air entered the permeameter through a screen at the bottom, where inlet pressure was measured using a micromanometer (TSI 8705 micro-manometer, reported accuracy 1 Pa, TSI Incorporated, Shoreview, MN). Gas flow rate was measured using a rotameter (Dwyer RMB-51D or RMA-3, Dwyer Instruments, Michigan City, IN, US). Silage density was adjusted by manual compaction, and permeability was measured at 10 or more densities from about $300 \, kg \, m^{-3}$ to $650 \, kg \, m^{-3}$. Paired flow and pressure values (at pressures between 10 and 30 Pa) were used to calculate permeability based on the equation for one-dimensional flow of an ideal gas (Tidwell, 2006).

2.2. Ethanol emission from loose silage

Silage A was used to quantify the effects of temperature and air velocity on ethanol emission from loose silage. Three temperatures (5, 20, and 35 °C) and three air velocities were used $(0.05, 0.5, \text{ and } 5 \, m \, s^{-1})$ in a fractional factorial design, where the four extreme combinations were excluded. Three trials were completed at the center point (20 °C and $0.5 \, m \, s^{-1}$), while two trials were completed for other conditions. To quantify differences among the three sources of silage, three additional trials each were completed with silages B and C at 20 °C and $0.5 \, m \, s^{-1}$. For all of these trials ethanol emission was measured from a 15 cm deep 1.2 kg silage sample for 12 h. To quantify the effect of exposed surface area (surface area to sample mass ratio), three 4 h trials were completed with a 3 cm deep sample of silage A. The wind tunnel system described by Montes et al. (2010) was used to measure ethanol emission from loose samples. A brief description of the system follows. Silage was contained in an open-top steel box 26 cm long and 11 cm wide. Air was drawn over the top of the sample, and vapor phase ethanol concentration was measured downstream of the sample using a photoacoustic gas monitor (Innova 1412, LummaSense Technologies, Ballerup, Denmark). The frequency of measurements varied from $1 \, min^{-1}$ at the start of each trial to $2 \, h^{-1}$ after 1.5 h. For all trials, silage wet density was $317 \, kg \, m^{-3}$ (dry matter density varied). Samples were warmed from a storage temperature <5 °C to the trial temperature for 4–6 h prior to starting each trial.

Although the wind tunnel used in this work was designed to simulate field conditions, it was not a perfect representation. Perhaps most importantly, the pressure gradient required to create a given air velocity within the wind tunnel was greater than the pressure gradient present for the same velocity in an open setting. A maximum pressure gradient of $460 \, Pa \, m^{-1}$ (over 26 cm) was observed during the $5 \, m \, s^{-1}$ trials, where the space between the silage surface and the top of the wind tunnel was 1.0 cm. The expected average pressure gradient in the field is negligible relative to this value, although fluctuations in pressure due to turbulent flow have been observed to create transient gradients as large as $20 \, Pa \, m^{-1}$ over 15 cm with $5–7 \, m \, s^{-1}$ air velocity (Farrell et al.,

1966). To determine if the wind tunnel pressure gradient or other characteristics of the wind tunnel system significantly influenced emission, cumulative ethanol emission from silage samples in an open setting was measured. Samples (15 cm deep, 1.2 kg, wet density $317 \, kg \, m^{-3}$) were placed in the same steel sample boxes used in the wind tunnel trials, and were exposed to moving air from a fan. The fan and the boxes were oriented so that air flow was parallel to the longest dimension of the boxes. Air velocity and temperature were measured about 2 cm from the silage surface using a hot wire anemometer (Testo 405-V1, Testo, Sparta, NJ, US). Trials were carried out at $0.5 \, m \, s^{-1}$ and $5 \, m \, s^{-1}$ at room temperature for silages A and C. Silage ethanol content was measured before and after 12 h of exposure, using the GC procedure described above, and cumulative ethanol emission was calculated by difference. We assumed that generation and destruction of ethanol by microbial activity during the incubations was insignificant. Although some yeasts produce ethanol under aerobic conditions, this process has not been reported for silage. Upon exposure to air, ethanol in silage is oxidized, but at room temperature this process is slow, occurring over a period of several days (Woolford, 1983; Spoelstra et al., 1988).

2.3. Ethanol emission from exposed silage particles

Ethanol emission was measured from exposed silage particles, a scenario which represents the maximum exposed surface area to mass ratio for a silage sample (excluding alteration of particle size). The emission measurement procedure was similar to that described in section 2.2, i.e., silage samples were exposed to moving air and ethanol emission was measured by measuring the flow and ethanol concentration in exhaust. However, for exposed particles, we used much smaller samples that were exposed to air flow on all sides within a smaller wind tunnel system. The system consisted of a 28 cm length × 0.95 cm inner diameter transparent polyvinyl chloride (PVC) tube, connected to a controlled flow of compressed purified air ("ultra zero": $H_2O < 2 \, ppm$, total hydrocarbons < 0.05 ppm, GTS-Welco, State College, PA, US). Small silage samples were placed near the downstream end of the tube. Samples contained several individual particles with a total mass of 170–730 mg, resulting in an initial mass of ethanol of 0.71–3.1 mg. The projected area of each sample was determined by analyzing scanned images of complete samples, and surface area was estimated as twice the projected area. Air flow rate was measured using a rotameter (Dwyer Rate-Master, stated accuracy $0.3 \, L \, min^{-1}$, Dwyer Instruments, Michigan City, IN, US). Measurements were made at an air velocity of $0.5 \, m \, s^{-1}$ only. Vapor phase ethanol concentration was measured downstream of the silage sample using the photoacoustic gas monitor.

Some volatilization of ethanol presumably occurred during the process of weighing silage samples and loading them into the wind tunnel. To minimize volatilization, silage was kept at <5 °C until the start of each trial. Emission measurements continued until the vapor phase ethanol concentration dropped below 0.1 ppm ($0.2 \, mg \, m^{-3}$), which occurred within 2.7 h for all trials.

2.4. Analysis of wind tunnel data

Emission rate (mass time^{-1}) was calculated at each time step as the product of the vapor phase ethanol concentration and mean air flow rate. Cumulative emission (mass) was determined by numerically integrating emission rate. Ethanol flux (mass length^{-2} time^{-1}) and area-based cumulative emission (mass length^{-2}) were calculated by dividing emission rate and cumulative emission by the area of the open top of the sampling box ($0.025 \, m^2$) for loose samples and by the particle surface area for exposed particles. To

eliminate the effect of initial ethanol content on emission, both emission rate and cumulative emission were normalized. For exposed particles, emission rate (mass time^{-1}) and cumulative emission (mass) were normalized by dividing by the final cumulative emission, which was taken as an estimate of the initial mass of ethanol present. Final cumulative emission ranged from 62% to 94% of the initial ethanol mass, as calculated based on measured ethanol content of the silage samples—the difference was most likely due to volatilization before starting emission measurements. Normalized emission rate therefore had the dimension time^{-1}, and normalized cumulative emission was dimensionless (i.e., proportion of initial ethanol lost). For loose samples, flux (mass length^{-2} time^{-1}) and cumulative emission (mass length^{-2}) were normalized by dividing by the initial volumetric ethanol concentration of the bulk silage sample (mass length^{-3}). Normalized flux therefore had the dimension length time^{-1}, and normalized cumulative emission had the dimension length. Normalized flux and cumulative emission reflect the thickness of an initial silage sample containing the mass of ethanol emitted. This relationship follows from the observation that the product of the initial ethanol concentration of a sample (mass length^{-3}) and the sample thickness (length) is maximum cumulative emission (mass length^{-2}). Therefore, maximum normalized cumulative emission was equal to the sample thickness.

To characterize the pattern of ethanol emission over time, a logistic model (Demeyer et al., 1995) was fit to cumulative emission data from each individual trial:

$$M = a\left(1 - e^{-ct}\right)^{i} \qquad (1)$$

where M = cumulative emission at any time (dimension varies), a = maximum cumulative emission (same dimension as M), t = time, and c (time^{-1}) and i (dimensionless) are empirical constants. Equation (1) can be used to predict cumulative emission in various dimensions, depending on the dimension for parameter a, e.g. mass length^{-2}, length, or proportion of initial ethanol (dimensionless). Values of parameters c and i are independent of the dimension of a and M. For normalized cumulative emission in cm, a is equal to silage sample depth. For predicting the proportion of initial ethanol lost, a is equal to unity. Best-fit values of c and i were determined for each individual trial by weighted-least squares nonlinear regression using the nls function in R v. 2.10.1 (Ritz and Streibig, 2008; R Development Core Team, 2009). Residuals were weighted based on the inverse of sampling frequency. Best-fit values of i did not vary greatly, and i was fixed at 0.6 for the results discussed below (although adjusting both c and i resulted in a significantly better fit for some trials).

2.5. Emission isolation flux chamber measurements

A stainless steel emission isolation flux chamber (St. Croix Sensory Ac'scent, 0.41 m diameter, 0.13 m^2 cross-sectional area, 25 L volume, Stillwater, MN, US) was used to provide measurements of ethanol emission rate for comparison to wind tunnel and open setting measurements, following the procedure described in Kienbusch (1986). Initially, the flux chamber was simply inserted 1–2 cm into a 15 cm deep silage sample. However, virtually all of the sweep gas leaked through the silage sample instead of exiting through the outlet line. We used an alternative approach to address this problem. Silage was added to an 18 cm deep round rubber bin that was lined with a plastic bag. The flux chamber fit inside the bin, and the top of the plastic bag was sealed against the side of the flux chamber with duct tape. This setup reduced leakage to about 50% of the sweep gas flow rate.

Compressed purified air (as described above) was used as the sweep gas at a flow rate of either 2.5 L min^{-1} or 5.0 L min^{-1}. Vapor phase ethanol concentration in the outlet line was measured as described above. After four volume exchanges, vapor phase ethanol concentration was measured every 2 min. Ethanol flux was calculated based on the vapor phase concentration in the outlet line, the sweep gas flow rate (measured before gas entered the flux chamber—no correction was made for leakage), and the cross-sectional area of the flux chamber. Silage wet density was 317 kg m^{-3}.

3. Results and discussion

3.1. Overview of wind tunnel results

Ethanol emission from loose corn silage samples was initially high, but declined rapidly, and then declined more slowly for an extended period (Fig. 1). The period of slow decline contributed most to cumulative emission over the 12 h trials. Over 12 h, this decline in flux ranged from a factor of 4.7 to 76 (for individual samples), and did not follow a first-order response (which would result in a constant slope for log[flux] vs. time). The initial ethanol flux ranged from 4.6 to 220 g m^{-2} h^{-1}, while 12 h cumulative emission ranged from 15 to 200 g m^{-2}. Normalized 12 h cumulative emission ranged from 0.98 to 13 cm, representing 6.6% to 85% of the initial mass of ethanol present. Temperature, air velocity, and differences among silages all had significant effects on ethanol emission.

Results from the open setting trials did not suggest that the wind tunnel overestimated emission in an open setting. For silage A, loss of ethanol in the open setting trials (Table 2) was greater than cumulative emission measured in the wind tunnel under similar conditions (Table 3), but results were similar for silage C. For all conditions, 95% confidence intervals overlapped (although statistical power was low for some trials).

Ethanol flux from exposed silage particles was initially similar to the flux of ethanol from loose samples at the same temperature and similar air velocity (Fig. 2). However, flux from exposed particles declined faster, dropping by more than three orders of magnitude to below the detection limit within 2.7 h. Initial ethanol emission rate ranged from 0.15 to 0.63 mg min^{-1} and final cumulative emission ranged from 0.59 to 2.3 mg. Normalized initial emission rate ranged from 0.19 to 0.38 min^{-1}. Trajectories of ethanol emission over time were similar for silages A and B, although we observed substantial variability among samples (Fig. 2).

The logistic model (Eq. (1)) was able to describe ethanol emission over time for both loose silage (Fig. 3) and exposed particles (Fig. 4). For all trials, pseudo-R^2 (Schabenberger and Pierce, 2002) ranged from 0.97 to >0.99. Least-squares values of c varied substantially with temperature, air velocity, silage type, and exposed surface area (Table 4).

3.2. Factors affecting ethanol emission

Temperature and air velocity had large effects on ethanol emission from silage A (Figs. 1 and 5, Table 5). Cumulative 12 h emission increased by a factor of 4.0 in response to a 30 °C increase in temperature, and by a factor of 10 in response to a 90-fold increase in air velocity. Log-transformed 12 h cumulative emission showed a linear response to log-transformed air velocity (Fig. 5, Table 5). We observed an exponential response of emission to temperature (Fig. 5, Table 5). These responses to air velocity and temperature were similar to previously reported results for intact packed samples of silage B (Montes et al., 2010). However, packed corn silage showed upward curvature in the response of log-
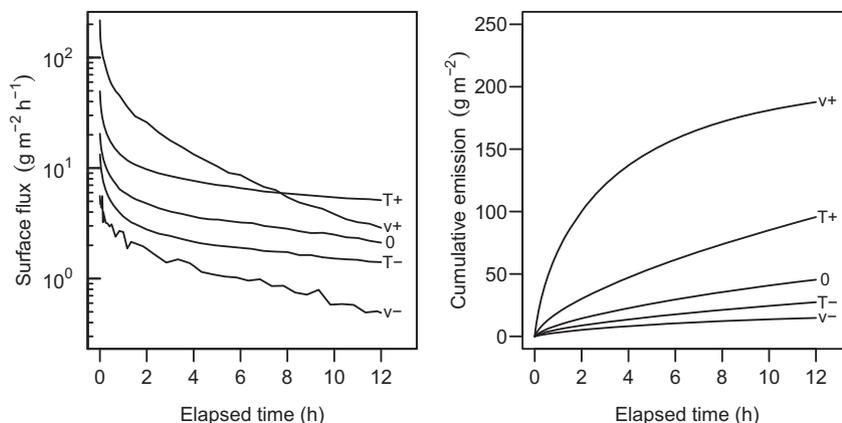
Fig. 1. Ethanol emission from 15 cm deep loose corn silage samples (silage A). Results are shown from a single trial for each of five conditions: 0, 20 °C and 0.5 m s^{-1}; v+, 20 °C and 5 m s^{-1}; v−, 20 °C and 0.05 m s^{-1}; T+, 35 °C and 0.5 m s^{-1}; T−, 5 °C and 0.5 m s^{-1}.

transformed emission to log-transformed velocity (Montes et al., 2010).

Weighted least-squares values of parameter c (Eq. (1)) were strongly related to air velocity and temperature (Table 6). In Eq. (1), the time required for a fixed loss (e.g. 50%) is inversely proportional to c. For example, a 50% loss of ethanol at 5 m s^{-1} would require about 1% of the time required for a 50% loss at 0.05 m s^{-1} (Table 4). The observed responses of ethanol emission to temperature and air velocity are consistent with a simple conceptual model of VOC emission from porous media, as described in previous work (Montes et al., 2010). Briefly, a positive response to temperature is consistent with an increase in volatility, and a positive response to air velocity is consistent with an increase in convective mass transport at the silage surface (increased transport through gas pores may also have an effect [Neeper, 1991]).

Normalized ethanol emission increased from silage A to silages B and C (Fig. 6A), with mean normalized 12 h cumulative emission of 3.3, 11, and 9.1 cm, respectively (at 20 °C and 0.5 m s^{-1}). Gas-phase porosity was about 0.70 m^3 m^{-3} for all three silages, but gas permeability was much higher for silages B and C (Table 1). The positive correlation observed between particle size and permeability (Table 1) is consistent with empirical and theoretical relationships for predicting permeability (Bear, 1972). These results suggest that the higher emission rates observed for silages B and C were due to lower internal resistance to gas-phase transport of ethanol.

Comparison of ethanol emission from loose samples of silage B to that measured from intact packed silage (Montes et al., 2010) shows that normalized emission is much greater from loose silage

(Fig. 6A). This response is probably due to a reduction in resistance to gas-phase transport with an increase in gas-phase porosity. Mean gas-phase porosity for the intact samples used in Montes et al. (2010) was 0.3 m^3 m^{-3}. Although permeability measurements are not available for packed samples of silage B, reported values for grass silage at a similar wet density (800 kg m^{-3}) are less than 1% the value measured for silage B at a porosity of 0.70 m^3 m^{-3} (Table 1).

Over short periods of time, silage depth did not affect normalized ethanol emission; mean normalized 4 h cumulative emission was 1.9 cm and 1.6 cm from samples of silage A that were 3 cm and 15 cm deep, respectively (standard deviation = 0.11 cm and 0.10 cm). However, expressed as a fraction of the initial mass of ethanol present, losses were 63% and 11% from 3 cm and 15 cm samples, respectively (Fig. 6B). The same response is apparent in the rapid loss of ethanol from exposed silage particles. Comparison of emission from exposed particles to results from the loose sample trials demonstrates the substantial effect of exposed surface area (Fig. 6B). The displayed responses are captured in the value of c in Eq. (1) (Table 4). Compared to a 15 cm thick loose sample of silage A ($c \approx 0.007$ h^{-1}), exposed particles ($c \approx 5$ h^{-1}) lose a given fraction of total ethanol (e.g., 50%) in about 1/700th as much time.

The air velocities and temperatures used in these experiments encompass a majority of the conditions that silage is exposed to both inside and outside dairy barns in the US. Based on data from 275 weather stations throughout the US (NOAA, 2009), an air velocity of 5.0 m s^{-1} is equivalent to the 80th percentile of monthly average wind speed. Both 0.05 and 0.5 m s^{-1} are below the 1st percentile, but may reflect outdoor conditions close to the silage surface or in a protected area. Air velocity in naturally and mechanically ventilated dairy barns has been reported to range

Table 2
Cumulative ethanol loss from silage exposed to moving air in an open setting for 12 h.[a]

Silage	Air T (°C)[b]	Air velocity (m s^{-1})	Moisture loss (%)	Ethanol loss (%)[c]	(g m^{-2})	(cm)
A	24.4 (0.39)[d]	0.54 (0.23)	9.3	36 [24, 48][e]	93	5.4
A	18.6 (1.61)	5.0 (0.50)	27	98 [97, 99]	220	15
C	24.4 (0.39)	0.49 (0.22)	13	61 [55, 67]	110	9.1
C	23.3 (1.05)	4.8 (1.01)	24	85 [82, 88]	160	13

[a] Additional trials with silage A near 5 m s^{-1} gave similar results.
[b] Air temperature in °C.
[c] Percentage of the mass of ethanol present initially.
[d] Values in parentheses are standard deviation.
[e] 95% confidence interval, based on error in determination of initial and final ethanol ($n = 3$ for each).

Table 3
Cumulative ethanol loss as measured from 15 cm deep loose silage samples in a wind tunnel over 12 h.

Silage	Air T (°C)[a]	Air velocity (m s^{-1})	Ethanol loss (%)[b]	(g m^{-2})	(cm)
A	20	0.56 (0.017)[c]	22 [19, 24][d]	49	3.3
A	20	5.0 (0.01)	78 [38, 100]	170	12
C	20	0.58 (0.012)	61 [51,70]	180	9.1

[a] Target air temperature in °C (actual value was within 0.5 °C of target).
[b] Percentage of the mass of ethanol present initially.
[c] Standard deviation among trials.
[d] 95% confidence interval, based on error among trials ($n = 3$ for 1st row, $n = 2$ for others). The arcsine transformation (Zar, 1999: 278) was used for this calculation.
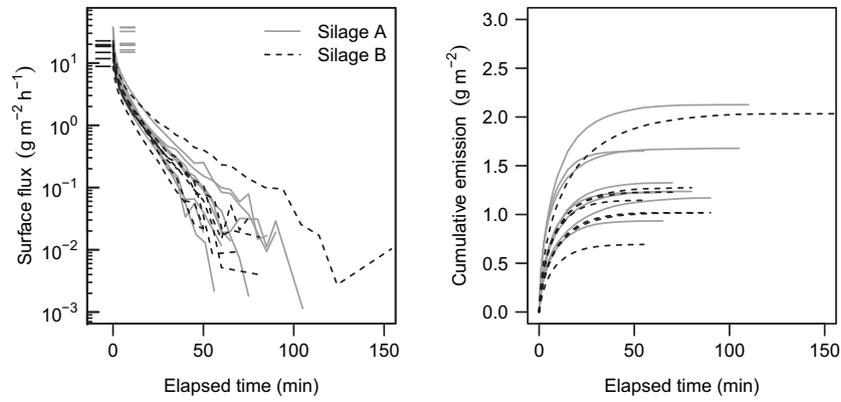
Fig. 2. Ethanol emission from exposed silage particles ($0.5 \, \mathrm{m\,s^{-1}}$ air velocity, $20\,^\circ\mathrm{C}$). Each line represents an individual trial with 0.17 to 0.73 g of silage particles. The short horizontal lines in the left panel show the value of the initial flux for individual trials.
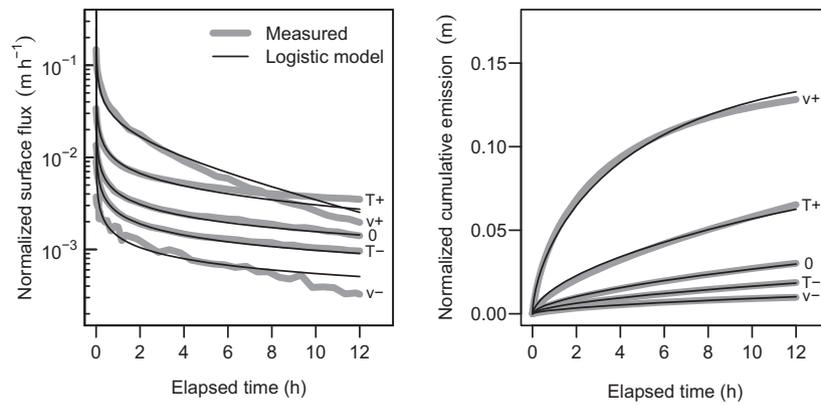

Fig. 3. Measured and predicted normalized ethanol emission from 15 cm deep loose corn silage samples. Predicted values were calculated from the logistic model, using weighted least-squares estimates of c and a value of 0.6 for i.
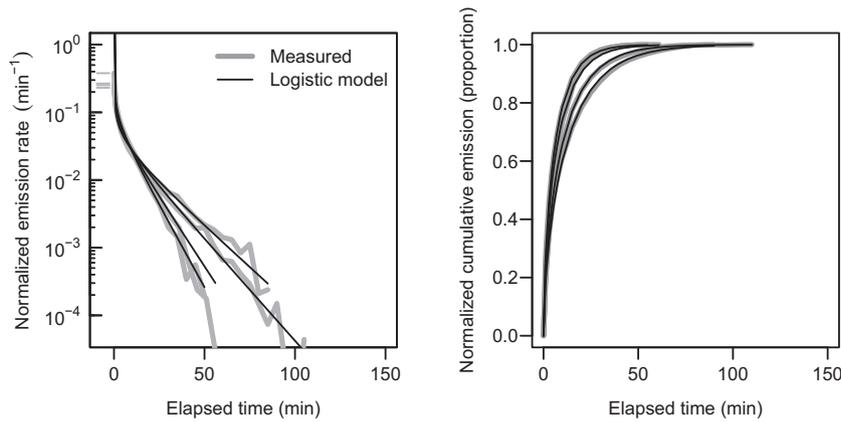

Fig. 4. Measured and predicted normalized ethanol emission from four of the trials shown in Fig. 2 (exposed particles of silage A, $20\,^\circ\mathrm{C}$, air velocity $0.5 \, \mathrm{m\,s^{-1}}$). Predicted values were calculated from the logistic model, using weighted least-squares estimates of c and a value of 0.6 for i.

from $< 0.1 \, \mathrm{m\,s^{-1}}$ to $\sim 4 \, \mathrm{m\,s^{-1}}$ (Sheffield et al., 2007; Matkovic et al., 2009). Air velocity close to the ground will be less than values measured at typical heights (often 2 m). The 99th percentile of NOAA climatological maximum daily temperature for 283 stations throughout the US is $35\,^\circ\mathrm{C}$ (NOAA, 2009). Silage may be exposed to air temperatures below $5\,^\circ\mathrm{C}$, and in this case ethanol emission rate will be lower than what we measured at $5\,^\circ\mathrm{C}$ due to a reduction in volatility.

3.3. Emission isolation flux chamber measurements

The US EPA emission isolation flux chamber method provides point estimates of emission rates, which are not useful for determining cumulative emission over several hours, because ethanol emission rate from silage exposed to moving air declines rapidly over time (e.g., Fig. 1). Point estimates from a flux chamber may be higher or lower than average rates measured in a wind tunnel

Table 4
Weighted least-squares estimates for parameter c in the logistic model (Eq. (1)) for predicting ethanol emission for each of the conditions studied.[a]

Silage	Thickness (cm)	T (°C)	Air velocity (m s^{-1})	Parameter c (h^{-1})
A	15	5	0.54 (0.014)[b]	0.0027 (0.00020)
A	15	20	0.055 (0.00051)	0.0011 (0.00026)
A	15	20	0.56 (0.017)	0.0066 (0.00067)
A	15	20	5.0 (0.0087)	0.12 (0.032)
A	15	35	0.56 (0.0044)	0.030 (0.011)
B	15	20	0.54 (0.014)	0.060 (0.0095)
C	15	20	0.56 (0.0054)	0.043 (0.0067)
A	3	20	0.55 (0.0047)	0.14 (0.018)
A[c]	Particles	20	0.47 (–[d])	4.9 (1.0)
B[c]	Particles	20	0.47 (–)	4.5 (0.96)

[a] For all trials, parameter i was fixed at 0.6.
[b] Standard deviation among trials is given in parentheses ($n = 2$ or 3 trials).
[c] Results in these rows are from exposed silage particles. Preceding rows are for loose silage samples.
[d] Standard deviation not determined.

Table 5
Multiple regression results for normalized cumulative 12 h ethanol emission from 15 cm deep loose corn silage (silage A).[a]

Variable	Coefficient	Standard error	t	P
Intercept	−1.70	0.0457	−37.2	<0.0001
Temperature (°C)	0.0196	0.00205	9.57	<0.0001
$\log_{10}$(air velocity [m s^{-1}])	0.518	0.0314	16.5	<0.0001

[a] Response variable is $\log_{10}$(normalized cumulative emission [m]). Degrees of freedom = 8, residual standard error = 0.0614, $R^2 = 0.979$, Adjusted $R^2 = 0.973$, $F = 183$, $P = 2 \times 10^{-7}$.

Table 6
Multiple regression results for parameter c in Eq. (1), based on weighted least-squares values of c fit to cumulative ethanol emission data from 15 cm deep loose corn silage (silage A).[a]

Variable	Coefficient	Standard error	t	P
Intercept	−2.51	0.0857	−29.2	<0.0001
Temperature (°C)	0.0338	0.00373	9.05	<0.0001
$\log_{10}$(air velocity [m s^{-1}])	1.14	0.0709	16.1	<0.0001
$\log_{10}$(air velocity [m s^{-1}])^2	0.199	0.0734	2.71	0.030

[a] Response variable is $\log_{10}$(c [h^{-1}]). Degrees of freedom = 7, residual standard error = 0.112, $R^2 = 0.983$, Adjusted $R^2 = 0.976$, $F = 139$, $P = 1 \times 10^{-6}$.

depending on the length of the averaging period. We compared flux chamber measurements to wind tunnel measurements of initial flux and average flux over 0.5 h and 12 h (calculated from cumulative emission data). Emission rates measured with the flux chamber were much lower than average rates measured at 0.5 m s^{-1} and above (Table 7). However, results from the flux chamber were close to wind tunnel results for silage A at 0.05 m s^{-1}, for which the mean initial flux was 5.0 g m^{-2} h^{-1}, and mean 0.5 h and 12 h average fluxes were 3.6 and 1.4 g m^{-2} h^{-1}, respectively.

As described above, the US EPA emission isolation flux chamber method was designed for conditions where emission is not sensitive to air movement at the surface. Our wind tunnel and open setting measurements show that air velocity has a major effect on ethanol emission rate from silage (Figs. 1 and 5, Table 2). Even at the low sweep gas flow rates used with the flux chamber, emission rate was dependent on air flow rate; ethanol flux at 5.0 L min^{-1} was about twice the flux measured at 2.5 L min^{-1} (Table 7). This effect has been observed for soils as well (Eklund, 1992). The US EPA emission isolation flux chamber may provide an estimate of emission rate from silage in the field at some low air velocity, but this velocity is likely lower than typical air velocities experienced in and around dairy barns.

Suppression of VOC emission due to vapor phase accumulation is an additional problem with the flux chamber method. Kienbusch (1986, pp. 3–4) noted that vapor phase VOC concentration should not exceed 10% of the equilibrium concentration to avoid suppression. During the measurements we made using the flux chamber, ethanol concentrations in the outlet line ranged from 0.89 to 0.96 g m^{-3}. These concentrations were well above 10% of the expected equilibrium vapor phase concentrations, which ranged from 0.87 to 1.7 g m^{-3} for silage B at 20 °C (unpublished data).

A final problem with the application of the US EPA emission isolation flux chamber method to VOC emission from silage is leakage of sweep gas through silage, as described in the methods section. Calculated emission rates from "unsealed" trials where a plastic bag was not used were <1/2 of the values given in Table 7 (data not shown).

Ethanol emission rates measured in our wind tunnel (at air velocities higher than 0.05 m s^{-1}) and in the open setting trials were higher than total VOC fluxes measured in previous studies using the flux chamber method. Chung et al. (2009) reported average total VOC fluxes from silage and mixed feed on six dairies that ranged from about 0.1 to 0.7 g m^{-2} h^{-1}. Emissions were dominated by ethanol. Average total VOC flux from intact packed corn silage was reported as 1.3 and 3.0 g m^{-2} h^{-1} for the two farms studied by Card and Schmidt (2006) (units are normalized to moles of carbon and expressed as the equivalent flux of methane—reported fluxes would be about 40% higher if expressed as the equivalent flux of ethanol).
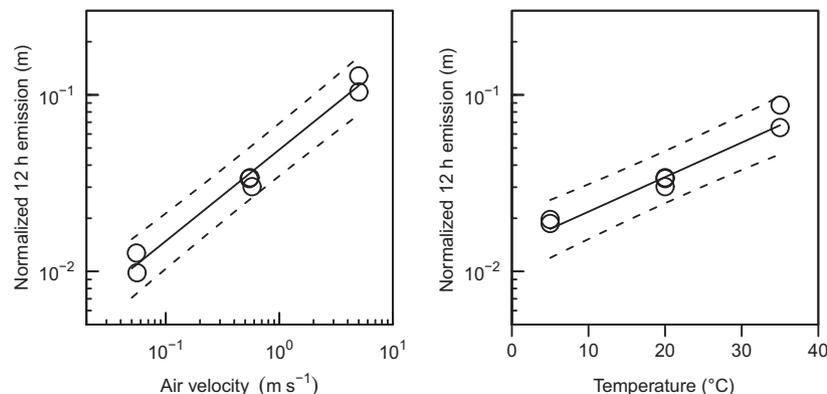

Fig. 5. Normalized 12 h cumulative ethanol emission from 15 cm deep loose corn silage (silage A) as a function of air velocity and temperature. Solid lines show predictions from the regression model given in Table 5, while dashed lines show 95% prediction intervals.
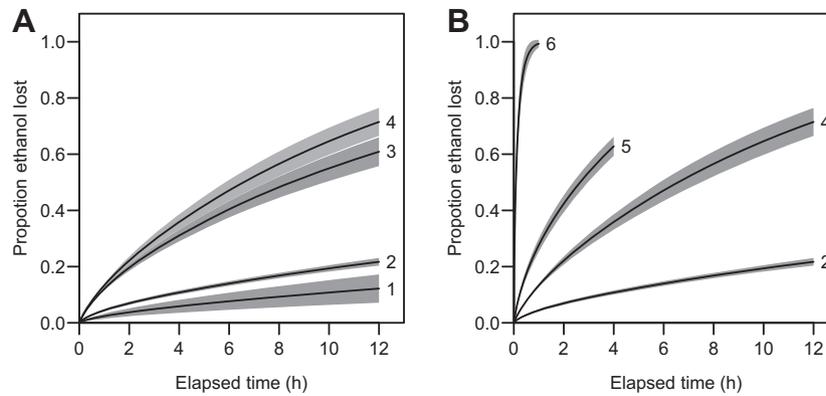
Fig. 6. Normalized ethanol emission for select trials demonstrating the apparent effects of internal resistance to transport (A) and exposed surface area (B) on ethanol emission (all trials at 20 °C and 0.5 m s^{-1}). Lines show mean normalized ethanol emission for specific conditions, while the gray areas represent one standard deviation above and below the mean response. Conditions are as follows, 1, 15 cm intact silage B (Montes et al., 2010); 2, 15 cm bulk loose silage A; 3, 15 cm bulk loose silage C; 4, 15 cm bulk loose silage B; 5, 3 cm loose silage A; 6, exposed particles of silages A and B.

Table 7
Measured ethanol emission rates from two types of corn silage using an emission isolation flux chamber compared to results from the wind tunnel.[a]

Silage	Emission isolation flux chamber flux (g m^{-2} h^{-1})	
	5.0 L min^{-1}[b]	2.5 L min^{-1}
A	2.0 (0.011)[c]	1.1 (0.0028)
C	1.6 (0.033)	0.87 (0.0088)
	Wind tunnel flux at 0.5 m s^{-1} and 20 °C (g m^{-2} h^{-1})		

	Initial	30 min average	12 h average
A	26 (4.6)	13 (1.6)	4.1 (0.27)
C[d]	65 (2.3)	43 (1.4)	15 (1.36)

[a] Average wind tunnel fluxes were calculated by dividing cumulative emission by elapsed time.

[b] The emission isolation flux chamber was tested at two sweep air flow rates (5.0 L min^{-1} and 2.5 L min^{-1}).

[c] Standard deviation is given in parentheses ($n = 3$ consecutive measurements from the same silage sample for the emission isolation flux chamber and, 3 12 h trials with 3 separate silage samples for the wind tunnel).

[d] Volumetric ethanol concentration for the silage samples used in these trials (1960 g m^{-3}) was higher than for the samples used with the emission isolation flux chamber (1220 g m^{-3}) and in the open setting trials (1250 g m^{-3}). Reported average fluxes can be divided by these values to correct for these differences.

4. Conclusions

Ethanol emission rate from loose silage exposed to moving air declines over time, similar to packed silage. Therefore, a single point estimate of flux is not sufficient to determine cumulative emission. The US EPA emission isolation flux chamber method is not suitable for measuring VOC emission rates from silage, because it does not adequately capture changes in emission rate over time and generally underestimates the rate of ethanol emission from silage. These shortcomings explain why our (wind tunnel) estimates of VOC emission rates from loose silage are generally higher than previous estimates.

Because ethanol is lost much more rapidly from loose silage than from packed silage under identical conditions, loose silage present in feed lanes and feed bunks has the potential to be a major source of VOC emissions on dairy farms. However, development of accurate estimates of VOC emissions from individual farm processes (e.g., silage storage or feeding) will require consideration of the conditions that silage is exposed to for each process, as well as cumulative loss from previous processes. Substantial positive effects of air velocity, temperature, silage permeability, and exposed surface area on ethanol emission rate indicate that emission from silage on farms is probably sensitive to climate and management practices. Relationships described in this work can ultimately contribute to better estimates of the magnitude of VOC emissions from dairy farms, and to the development of practices for reducing emissions.

References

Alanis, P., Sorenson, M., Beene, M., Krauter, C., Shamp, B., Hasson, A.S., 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, 6417–6424.

Bear, J., 1972. Dynamics of Fluids in Porous Media. Elsevier, New York.

Card, T., Schmidt, C., 2006. Dairy Air Emissions: Summary of Dairy Emission Estimation Procedures. California Air Resources Board, Sacramento, CA. http://www.arb.ca.gov/ag/caf/SchmidtDairyEmissions2005.pdf.

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 44, 786–794.

Crow, D., 2005. Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies. San Joaquin Valley Air Pollution Control District, Fresno, CA, USA. http://www.valleyair.org/busind/pto/dpag/APCO%20Determination%20of%20EF_August%201_.pdf.

Demeyer, P., Hofman, G., Vancleemput, O., 1995. Fitting ammonia volatilization dynamics with a logistic equation. Soil Science Society of America Journal 59, 261–265.

Eklund, B., 1992. Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. Journal of the Air and Waste Management Association 42, 1583–1591.

Farrell, D., Greacen, E., Gurr, C., 1966. Vapor transfer in soil due to air turbulence. Soil Science 102, 305–313.

Gill, S., Norman, R., 2010. Air Pollution Control Officer's Revision of the Dairy VOC Emissions Factor. San Joaquin Valley Air Pollution Control District, Fresno, CA, USA. http://www.valleyair.org/busind/pto/dpag/2010_VOC_Jan/Draft%20Dairy%20EF%20Report%20%281-14-10%29.pdf.

Hafner, S., Montes, F., Rotz, C.A., 2009. Modeling emission of volatile organic compounds from silage. Presented at the 2009 ASABE Annual International Meeting, Reno, NV. American Society of Agricultural and Biological Engineers, 2950 Niles Road, St. Joseph, MI, 49085, US. http://asae.frymulti.com/abstract.asp?aid=27008andt=1.

Heinrichs, J., Kononoff, P., 2002. Evaluating Particle Size of Forages and TMRs Using the New Penn State Forage Particle Separator. Pennsylvania State University,

College of Agricultural Sciences, Cooperative Extension, University Park, PA, US. http://www.das.psu.edu/research-extension/dairy/nutrition/pdf/evaluating-particle-size-of-forages.pdf.

Howard, C., Yang, W., Green, P., Mitloehner, F., Malkina, I., Flocchini, R., Kleeman, M., 2008. Direct measurements of the ozone formation potential from dairy cattle emissions using a transportable smog chamber. Atmospheric Environment 42, 5267–5277.

Howard, C., Kumar, A., Malkina, I., Mitloehner, F., Green, P., Flocchini, R., Kleeman, M., 2010. Reactive organic gas emissions from livestock feed contribute significantly to ozone production in central California. Environmental Science and Technology 44, 2309–2314.

Hudson, N., Ayoko, G., 2008. Odour sampling. 2. Comparison of physical and aerodynamic characteristics of sampling devices: a review. Bioresource Technology 99, 3993–4007.

Kienbusch M.R. 1986. Measurement of gaseous emission rates from land surfaces using an emission-isolation flux chamber. Report number PB-86-223161/XAB. Radian Corp., Austin, TX. http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=5043609.

Kissel, D., Brewer, H., Arkin, G., 1977. Design and test of a field sampler for ammonia volatilization. Soil Science Society of America Journal 41, 1133–1138.

Kleinschmit, D., Schmidt, R., Kung, L., 2005. The effects of various antifungal additives on the fermentation and aerobic stability of corn silage. Journal of Dairy Science 88, 2130–2139.

Kleinschmit, D., Schmidt, R., Kung, L., 2006. A meta-analysis of the effects of *Lactobacillus buchneri* on the fermentation and aerobic stability of corn and grass and small-grain silages. Journal of Dairy Science 89, 4005–4013.

Kung, L., Shaver, R., 2001. Interpretation and use of silage fermentation analysis reports. In: Focus on Forage, vol. 3. University of Wisconsin Extension, Madison, WI, US. http://www.uwex.edu/CES/crops/uwforage/Fermentation.pdf.

Matkovic, K., Vucemilo, M., Vinkovic, B., Pavicic, Z., Matkovic, S., Benic, S., 2009. Airborne fungi in a dairy barn with emphasis on microclimate and emissions. Veterinarsky Arhiv 79, 207–218.

McDonald, P., Henderson, N., Heron, S., 1991. The Biochemistry of Silage, second ed. Chalcombe Publications, Shedfield, UK.

Mitloehner, F., Malkina, I., Kumar, A., Green, P., 2009. Volatile organic compounds emitted from dairy silages and other feeds. Presented at the 2009 International Silage Conference, Madison, WI. US Dairy Forage Research Center, 1925 Linden Dr. W., Madison, WI, 53706-1108, USA.

Montes, F., Hafner, S., Rotz, C.A., 2010. Temperature and air velocity effects on ethanol emission from corn silage with the characteristics of the exposed face of a bunker silo. Atmospheric Environment 44, 1987–1995.

Muck, R., Holmes, B., 2006. Bag silo densities and losses. Transactions of the ASABE 49, 1277–1284.

National Research Council, 2008. Estimating Mortality Risk Reduction and Economic Benefits from Controlling Ozone Air Pollution. National Academies Press, Washington, D.C., USA. http://books.nap.edu/catalog.php?record_id=12198.

Neeper, D.A., 1991. Soil vapor extraction enhanced by oscillatory flow. Presented at the Fifth National Outdoor Action Conference, Las Vegas, NV. http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=6002439.

NOAA, 2009. Comparative Climatic Data for the United States through 2008. National Oceanic and Atmospheric Administration, Washington, DC, US. http://ols.nndc.noaa.gov/plolstore/plsql/olstore.prodspecific?prodnum=C00095-PUB-A0001.

Parker, D.B., Caraway, E., Rhoades, M., Cole, N., Todd, R., Casey, K., 2010. Effect of wind tunnel air velocity on VOC flux from standard solutions and CAFO manure/wastewater. Transactions of the ASABE 53, 831–845.

R Development Core Team, 2009. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org.

Ritz, C., Streibig, J., 2008. Nonlinear Regression with R. Springer, New York.

Rooke, J., Hatfield, R., 2003. Biochemistry of Ensiling. In: Buxton, M., Muck, R., Harrison, J. (Eds.), Silage Science and Technology. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Madison, WI, USA, pp. 95–139.

San Joaquin Valley Air Pollution Control District, 2008. Annual Report to the Community. San Joaquin Valley Air Pollution Control District, Fresno, CA, USA. http://www.valleyair.org/General_info/pubdocs/2008AnnualReportfinal-web.pdf.

Schabenberger, O., Pierce, F., 2002. Contemporary Statistical Models for the Plant and Soil Sciences. CRC Press, Boca Raton, FL, USA.

Schmidt, C.E., 2006. Results of the Dairy Emissions Evaluation Using Flux Chambers: Phase III Merced and Kings County Dairies. California Air Resources Board, Sacramento, CA. http://www.arb.ca.gov/ag/caf/SchmidtDairyTestData2005.pdf.

Shaw, S., Mitloehner, F., Jackson, W., Depeters, E., Fadel, J., Robinson, P., Holzinger, R., 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, 1310–1316.

Sheffield, R., de Haro Marti, M., Smith, J., Harner, J., 2007. Air emissions from a low-profile cross-ventilated dairy barn. Presented at the 2007 ASABE International Symposium on Air Quality and Waste Management for Agriculture, Broomfield, Colorado. American Society of Agricultural and Biological Engineers, 2950 Niles Road, St. Joseph, MI, 49085, USA. http://asae.frymulti.com/azdez.asp?JID=1andAID=23878andCID=aqwm2007andT=2.

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.

Tidwell, V., 2006. Air permeability measurements in porous media. In: Ho, K., Webb, S. (Eds.), Gas Transport in Porous Media. Springer, Dordrecht, The Netherlands.

US EPA, 2009a. Six Common Air Pollutants. United States Environmental Protection Agency, Washington, DC, USA. http://www.epa.gov/air/urbanair/.

US EPA, 2009b. Volatile Organic Compounds Emissions. United State Environmental Protection Agency, Washington, DC, USA. http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewIndandlv=list.listByAlphaandr=188211andsubtop=341#datashow.

USDA National Agricultural Statistics Service, 2009. Quick Stats. National Agricultural Statistics Service, Washington, DC, USA. http://quickstats.nass.usda.gov/.

Watkins, S., Strand, R., Debell, D., Esch, J., 1972. Factors influencing ammonia losses from urea applied to northwestern forest soils. Soil Science Society of America Proceedings 36, 354–357.

Wilkinson, J.M., Toivonen, M.I., 2003. World Silage. Chalcombe Publications, Southampton, UK.

Woolford, M., 1983. Gamma radiation in the preparation of maize silage for studies on the aerobic deterioration process. Journal of Agricultural Science 101, 711–716.

Zar, J., 1999. Biostatistical Analysis. Prentice Hall, Upper Saddle River, NJ.