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A mass transfer model for VOC emission from silage

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ABSTRACT

Silage has been shown to be an important source of emissions of volatile organic compounds (VOCs), which contribute to the formation of ground-level ozone. Measurements have shown that environmental conditions and silage properties strongly influence emission rates, making it difficult to assess the contribution of silage in VOC emission inventories. In this work, we present an analytical convection-diffusion-dispersion model for predicting emission of VOCs from silage. It was necessary to incorporate empirical relationships from wind tunnel trials for the response of mass transfer parameters to surface air velocity and silage porosity. The resulting model was able to accurately predict the effect of temperature on ethanol emission in wind tunnel trials, but it over-predicted alcohol and aldehyde emission measured using a mass balance approach from corn silage samples outdoors and within barns. Mass balance results confirmed that emission is related to gas-phase porosity, but the response to air speed was not clear, which was contrary to wind tunnel results. Mass balance results indicate that alcohol emission from loose silage on farms may approach 50% of the initial mass over six hours, while relative losses of acetaldehyde will be greater.

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1. Introduction

Silage on dairy farms has recently been identified as an important source of volatile organic compound emissions in the San Joaquin Valley of California, USA (Shaw et al., 2007; Chung et al., 2009; Howard et al., 2010; Malkina et al., 2011). Alcohols appear to be the most important compounds emitted from silage with respect to potential ozone formation (Howard et al., 2010). For corn silage, which dominates silage production in the US (Wilkinson and Toivonen, 2003), ethanol is generally the most concentrated alcohol (typically about 10 g kg^{-1} in corn silage, i.e., 1% of dry matter (Kleinschmit and Kung, 2006)), followed by 1-propanol and other alcohols. Understanding the impact of VOC emissions from silage on air quality will require accurate methods for estimating emissions.

Measurements of VOC emission rates from silage have been made using the emission isolation flux chamber method (Alanis et al., 2008; Chung et al., 2009); large (room-sized) environmental chamber methods (Howard et al., 2010); and wind tunnel systems (Hafner et al., 2010; Montes et al., 2010). Wind tunnel measurements have demonstrated that ethanol emission is

sensitive to surface air velocity and temperature, as well as to silage properties, including porosity and particle size (Hafner et al., 2010; Montes et al., 2010). Accurate prediction of emission of ethanol or other VOCs from silage will therefore require a model that incorporates these relationships. Our objectives were to develop a model for predicting VOC emission from silage, and to evaluate the model by comparing predicted emission to emission measurements made in barns and outdoors.

2. Methods

2.1. Model description

We developed a one-dimensional transport and emission model that is similar to other models that have been developed for VOC transport in porous media (Jury et al., 1990). Our model was developed to predict VOC emission from a silage surface (such as the front of a bunker silo or from the upper surface of feed in a feed bunk or feed lane) that is exposed to moving air (Fig. S-1). VOC creation and destruction are not included, but rather our model captures processes that occur after fermentation is complete. Oxidation of alcohols in silage does occur when silage is exposed to air, but this process typically takes place over a period of days (Woolford, 1983; Spoelstra et al., 1988), while the emission processes of interest takes place over a period of hours. Oxidation of aldehydes and other VOCs may be more rapid, but measurements

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of these processes are not available. In our model, we assume local equilibrium between a gas and aqueous phase, and that sorption to particles is negligible. VOCs may be transported to an exposed surface through either the gas or aqueous phase, and are lost by convection from the exposed surface.

Advective transport was not included in our model. The gas phase in stored silage is a denser-than-air mixture of CO₂ and N₂, which can lead to gravity-driven advective flow through silage in storage structures (Parsons, 1991; Williams et al., 1997). However, predictions from a two-dimensional advection model suggest that the contribution of this mechanism to ethanol emission from stored silage is minor compared to diffusive transport (Hafner et al., 2009) and to emission rates measured in a wind tunnel (Montes et al., 2010). Additionally, net gas production (as CO₂) during fermentation of ensiled forage contributes to pressure-driven advective gas flow out of silage storage structures (Williams et al., 1997). A simple calculation (see Supplementary data) shows that the loss of alcohols through this route will typically be <1% of that present during fermentation. (Since alcohols are primarily produced during silage fermentation, the concentration of alcohols during this stage are probably lower than the concentration measured after fermentation is complete). Although these losses could be significant under some conditions, it appears that they are generally much lower than losses from the pathways included in our model.

2.1.1. Model equations

Partitioning between aqueous and gas phases is described using Henry's law:

$$K_H = \frac{m}{P} \quad (1)$$

where K_H = Henry's law constant (mol kg⁻¹ atm⁻¹), m = molal concentration of a particular compound, and P = partial pressure of the compound in equilibrium with m (atm). We assumed that activity coefficients for all VOCs in solution are unity, and that sorption to particles is insignificant. Following the van't Hoff equation, $\log K_H$ was assumed to be inversely proportional to absolute temperature:

$$\log K_H = a + \frac{b}{T} \quad (2)$$

where a and b are empirical parameters (b is related to enthalpy of solvation), and T = temperature (K). Parameter values for the three alcohols and one aldehyde that we focused on in this study are given in Table 1. Conversion of Henry's law constant to one based on concentrations is done with

$$H = K_H RT \quad (3)$$

where H = concentration-based Henry's law constant (m³ kg⁻¹) and R = universal gas constant (8.2057 · 10⁻⁵ m³ atm K⁻¹ mol⁻¹).

Table 1
Coefficients used to calculate Henry's law constants (mol kg⁻¹ atm⁻¹) (Eq. (2)).

Compound	a	b	K_H at 20 °C (mol kg ⁻¹ atm ⁻¹)	H at 20 °C (m ³ kg ⁻¹)	Temperature range (K)
Acetaldehyde	-7.524	2573	17.9	0.432	273–313
Methanol	-5.358	2292	289	6.94	273–353
Ethanol	-6.852	2713	253	6.10	273–333
1-Propanol	-8.808	3260	205	4.94	273–298

Notes: Data are from Snider and Dawson (1985), Betterton (1991), and Benkelberg et al. (1995) for acetaldehyde; Warneck (2006) for methanol and ethanol; and Snider and Dawson (1985) for 1-propanol. Original data were changed from volumetric concentration units to mass-based concentration units by assuming the density of water to be that of pure water.

Transport through aqueous and gas phases was modeled using Fick's law (Bird et al., 2002):

$$j = -k_{sg} \frac{dc_g}{dx} - D_{ss} \frac{dc_{aq}}{dx} \quad (4)$$

where j = total flux (g m⁻² s⁻¹), k_{sg} = gas-phase diffusion-dispersion coefficient (m² s⁻¹), c = volumetric concentration of compound i in silage solution or gas (g m⁻³), x = distance from the emitting surface, and the subscripts sg and ss indicate silage gas and silage solution, respectively. The gas-phase diffusion-dispersion coefficient was based on an empirical relationship determined from wind tunnel measurements, as described below. The density of water in silage solution was taken as the density of pure water for calculation of volumetric concentrations. For silage solute diffusivity, the Penman–Millington–Quirk model (as described in Moldrup et al. (1997) with $m = 1$) can be used:

$$D_{ss} = D_{H_2O} \frac{\theta^{11/3}}{\Phi^{3.06}} \quad (5)$$

where D_{H_2O} = diffusivity in clear water (m² s⁻¹), which we took as 1.3 · 10⁻⁹, 1.8 · 10⁻⁹, 1.4 · 10⁻⁹, and 9.9 · 10⁻¹⁰ m² s⁻¹ for acetaldehyde, methanol, ethanol, and propanol, respectively (EPA, 2012); θ = volumetric water content (m³ m⁻³); and Φ = total porosity (m³ m⁻³).

In our model, equilibrium between aqueous and gas phases was assumed for all times and locations. To distribute a compound between the two phases, Eqs. (6) and (1) were used:

$$c_{aq} = \frac{c_b}{\rho_w w + \frac{\phi}{H}} \quad (6)$$

where c_b = bulk volumetric concentration of compound i (g m⁻³), ρ_w = wet silage density (kg m⁻³), w = gravimetric water content (kg kg⁻¹), and ϕ = gas-phase porosity (m³ m⁻³). A derivation of Eq. (6) is given in the Supplementary data.

Emission from the silage surface was modeled using a mass transfer coefficient approach (Bird et al., 2002):

$$j_{surface} = h_m c_{g,surface} \quad (7)$$

where h_m = mass transfer coefficient (m s⁻¹).

2.1.2. Model solution

We developed an analytical solution to our model, based on Crank's (1989) solution for surface evaporation from a plane sheet. The bulk volumetric concentration at the exposed surface of a semi-infinite plane of thickness l (m), with an exposed surface at $x = l$ and an impermeable boundary at $x = 0$ is given by

$$c_{b,surface} = c_{b,t=0} \sum_{n=1}^{\infty} \frac{2L \cos \beta_n e^{(-\beta_n^2 D_b t / l^2)}}{(\beta_n^2 + L^2 + L) \cos \beta_n} \quad (8)$$

where $c_{b,t=0}$ = bulk volumetric concentration before emission has started (g m⁻³) (initially invariant with depth) and β_n is the n th root of

$$\beta \tan \beta = L \quad (9)$$

In our model, we solve for the first 500 roots using a numerical algorithm. Eq. (8) is only valid when the background concentration of the VOC in air is negligible (see the Supplementary data for a general version). Constants are based on the effective transport parameters α and D_b , which are the effective mass transfer

coefficient at the surface (m s^{-1}) and diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) for bulk volumetric concentrations, respectively. The parameter L is

$$L = \frac{l\alpha}{D_b} \quad (10)$$

Expressions for effective transport parameters, given below, are derived in the [Supplementary data](#).

$$D_b = \frac{k_{sg}}{H\rho_w W + \phi} + \frac{D_{ss}\rho_{H_2O}}{\rho_w W + \frac{\phi}{H}} \quad (11)$$

$$\alpha = \frac{h_m}{H\rho_w W + \phi} \quad (12)$$

Given the bulk volumetric concentration of a VOC at the surface from Eq. (8), the surface flux is calculated from

$$j_{\text{surface}} = \alpha c_{b,\text{surface}} \quad (13)$$

Cumulative emission is given by

$$\frac{M}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 e^{-\beta_n^2 D_b t / L^2}}{\beta_n^2 (\beta_n^2 + L^2 + L)} \quad (14)$$

where M = cumulative emission (g m^{-2}), and the subscript ∞ indicates infinite exposure time. In our model, $M_\infty = l c_{b,t=0}$.

2.1.3. Parameter estimation

We used wind tunnel measurements of ethanol emission from packed and loose corn silage from [Montes et al. \(2010\)](#) and [Hafner et al. \(2010\)](#) to develop equations for k_{sg} and h_m . Briefly, emission measurements were made at mean air velocities of 0.05, 0.5, and 5.0 m s^{-1} and 5, 20, and $35 \text{ }^\circ\text{C}$ for three types of corn silage under loose and packed conditions. Data from each trial consisted of ethanol flux and cumulative emission over 12 h at a variable sampling frequency (1 min^{-1} near the start to 2 h^{-1} after 1.5 h). Additionally, dry matter content, density, mean particle length, and initial ethanol concentration were measured. We used density and dry matter content to estimate volumetric water content and gas-phase porosity by assuming a particle density of 1600 kg m^{-3} ([Rees et al., 1983](#)). We used only data from $20 \text{ }^\circ\text{C}$ for parameter estimation; other data were reserved for model evaluation. Two of the silages (B and C) had larger particle size than the other (A), and data from one of these (C) were reserved for model evaluation, leaving 24 wind tunnel trials for model calibration, and 25 for model evaluation.

We calculated h_m from measurements of initial flux for each trial. Despite limitations, this approach was the only independent method available for estimating h_m . Resulting estimates were related to wind velocity through linear regression, and estimates of h_m from this linear model were used in a nonlinear regression procedure (using the Levenberg–Marquardt algorithm via the function `nls.lm` from the package `minpack.lm` in R ([R Development Core Team, 2011](#))) to develop least-squares estimates of k_{sg} for ethanol. Sum of squares was based on cumulative emission, weighted by the inverse of the sampling frequency, so each trial had an equal weight. To avoid negative values for k_{sg} for three trials, we assumed that aqueous-phase diffusion was negligible for all trials. Resulting estimates of k_{sg} were related to gas-phase porosity, air velocity, and particle length through linear regression.

To provide a comparison to our convection-diffusion model, we also applied a fully empirical logistic model ([Demeyer et al., 1995](#)) following [Hafner et al. \(2010\)](#). Best-fit values for c and i were determined for each trial (all wind tunnel trials) as described

above. Because values for i did not vary much (mean of 0.69, standard deviation of 0.088) and were not related to trial properties, it was fixed at the mean value, and new best-fit estimates of c were made. These new values of c were related to sample thickness, gas-phase porosity, air velocity, and particle length through linear regression.

2.2. Model evaluation

Two types of data were used for model evaluation: wind tunnel and mass balance. Wind tunnel data were used by comparing predicted and measured cumulative ethanol emission from the reserved trials. We used the mass balance results previously reported in [Hafner et al. \(2010\)](#), and also carried out two sets of new trials. In the earlier trials ([Hafner et al., 2010](#)), ethanol emission was measured by mass balance from loose corn silage samples exposed to moving air from a fan. In the first set of new trials, we measured ethanol concentrations in loose corn silage before and after exposure to natural air movement within a barn. Samples were held in boxes 63 or 150 mm deep, and air speed was measured about 20 mm above the silage surface in two directions using two hot-wire anemometers. Values were recorded at a frequency of 1 min^{-1} and converted to a single speed. Corn silage for these and all previous trials was from the Pennsylvania State University dairy facility. In a second set of new trials, we measured acetaldehyde, methanol, ethanol, and 1-propanol in loose corn silage samples before and after exposure to moving air inside a barn or outdoors. Acetaldehyde was included along with the more concentrated alcohols because it is an important VOC in some types of silage ([Howard et al., 2010](#)), and to test the model for more volatile compounds. Corn silage for these trials was from the USDA-ARS Beltsville Area Research Center dairy facility (MD, USA). Samples were held in boxes 100 mm deep. Wind speed and direction was measured at 1 Hz using a two-dimensional sonic anemometer (Gill WindSonic, Lymington, Hampshire, UK), at a height of 1 m. Net VOC conversion (i.e., production minus destruction) was measured by incubating samples simultaneously in sealed 20 L buckets at the same locations. Oxygen concentration in the headspace of one bucket was monitored to confirm that it remained close to ambient. Emission of VOCs was calculated as the net change over time minus estimated net VOC conversion. Concentrations of VOCs within silage samples were measured using a headspace gas chromatography method ([Hafner et al., 2010](#)). Compounds were identified by retention time, and quantified with a flame ionization detector based on peak area. We hypothesized that our model could be accurately applied to the evaluation trials by using the parameter relationships developed from wind tunnel data but substituting mean air speed for mean air velocity.

3. Results and discussion

3.1. Model parameters

Calculated h_m values increased with air velocity and showed only small differences among silage types ([Fig. 1](#)). The following equation was calculated using results from all calibration trials ($P < 1 \cdot 10^{-10}$, $R^2 = 0.94$):

$$\log h_m = -1.885 + 0.793 \log v \quad (15)$$

where v = velocity (m s^{-1}). Best-fit k_{sg} values were higher than clear-air diffusivity for most trials, indicating that diffusion alone could not explain mass transfer rates. Values increased with air velocity, porosity, and particle length ([Fig. 1](#)). All of these

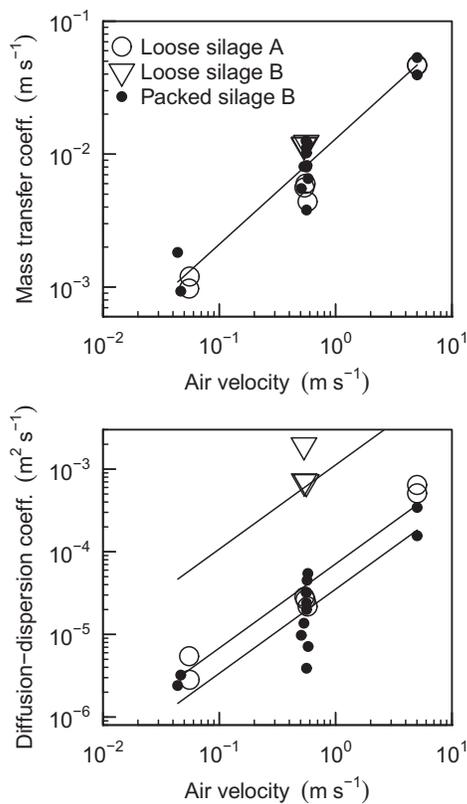


Fig. 1. Calculated values of mass transfer coefficient versus air velocity (top) and best-fit values of diffusion-dispersion coefficient versus air velocity (bottom) for ethanol emission from corn silage, measured in a wind tunnel. Data for all calibration trials are shown. Lines show predictions from Eqs. (15) and (16).

parameters were significant predictors in a regression model, resulting in the following equation ($P < 7 \cdot 10^{-5}$, $R^2 = 0.92$):

$$\log k_{sg} = -8.402 + 1.019 \log v + 0.3838 p - 3.461 \phi^2 \quad (16)$$

where p = mean particle length (mm).

At low air velocity, where Eq. (16) predicts a lower value than the Millington–Quirk model, Eq. (17), the latter was used:

$$D_{sg} = D_{air} \frac{\phi^{10/3}}{\phi^2} \quad (17)$$

where D_{air} is the clear-air diffusion coefficient, which we took as $1.3 \cdot 10^{-5}$, $1.6 \cdot 10^{-5}$, $1.2 \cdot 10^{-5}$, and $1.0 \cdot 10^{-5}$ m² s⁻¹ for acetaldehyde, methanol, ethanol, and propanol, respectively (EPA, 2012).

The response of k_{sg} to surface air velocity shows that air movement over a silage surface in our wind tunnel increases transport through silage pores. A possible explanation for this response is an increase in gas-phase dispersion due to the propagation of pressure oscillations (present in turbulent fluid flow) away from the surface. Although such oscillations will not cause significant net advective transport to the surface, they can contribute to hydrodynamic dispersion (Farrell et al., 1966; Scotter and Raats, 1969) or other transport processes (Nepper, 1991). This mechanism has been used to explain the effect of wind speed on water vapor transport through mulches (Hanks and Woodruff, 1958).

For the fully empirical logistic model, we used a fixed value of $i = 0.693$, and found that best-fit values of c were strongly related

to silage and environmental properties ($P < 7 \cdot 10^{-6}$, adjusted $R^2 = 0.92$):

$$\begin{aligned} \log c = & -16.086 + 0.755 \log v + 0.02660 T - 1.621 \log l \\ & + 2.651 \log p + 2.883 \phi \end{aligned} \quad (18)$$

where T = absolute temperature (K), l = silage layer thickness (m), and other variables are defined above. Eq. (18) was developed from results for all wind tunnel trials. It was not possible to use calibration trials only, since the response to both silage layer thickness and temperature had to be calibrated (unlike the convection-diffusion model).

3.2. Model evaluation

3.2.1. Wind tunnel evaluation

We made predictions with the complete convection-diffusion model for all ethanol emission trials using Eq. (15) to calculate h_m , and Eq. (16) or (17) for k_{sg} . For wind tunnel trials, the model generally captured the shape of ethanol flux and cumulative emission over time, as well as the magnitude of the response to temperature and air velocity (Fig. 2). Accuracy of the model in predicting emission for some individual trials was poor, due in part to high variability among trials for some conditions. The predicted response of cumulative emission to temperature was consistent with measurements (Fig. 3). This response was not calibrated, but

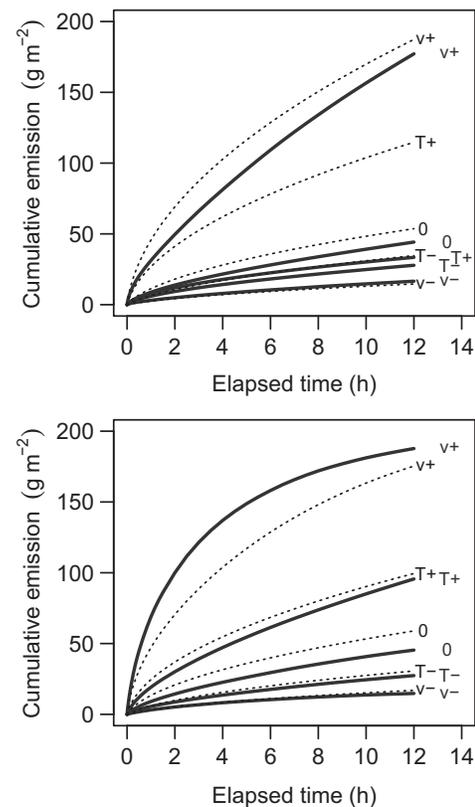


Fig. 2. Comparison of measured (solid lines, labels to right) and predicted (dashed lines) cumulative ethanol emission from packed corn silage B (top) and loose corn silage A (bottom), measured in a wind tunnel, for select trials. Results are shown from a single trial for each of five conditions: 0, 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. All trials at 20 °C were used in model calibration.

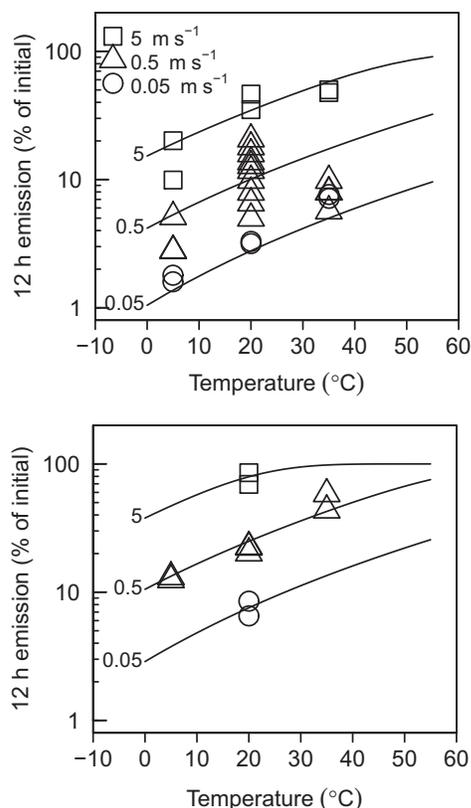


Fig. 3. Measured and predicted normalized cumulative 12 h ethanol emission (expressed as a percentage of the initial mass of ethanol present) for packed corn silage B (top) and loose corn silage A (bottom), measured in a wind tunnel. Trials at 20 °C were used for calibration; all others were reserved for evaluation. Lines show model predictions for mean conditions (air velocity, dry matter content, porosity). Variability in emission seen in the top panel at 20 °C and 0.5 m s⁻¹ is partially related to gas-phase porosity.

rather is based on an increase in volatility with temperature (Table 1).

The model also adequately captured the effects of both internal resistance to transport (related to porosity and particle size) and silage layer thickness (Fig. 4). For example, loose silage A had smaller particles than silages B and C, and this is reflected in both measured and predicted emission (compare line 2 to lines 3 and 4 in Fig. 4). Over all trials and times, the model showed a tendency to slightly over-predict emission (overall mean model error for evaluation trials was 40%, compared to 12% for calibration trials). The poorest fit between measured and predicted emission was seen for packed silage at 35 °C and 0.5 m s⁻¹. However, these trials were also inconsistent with the general trend of the data; cumulative emission was lower than for some 20 °C, 0.5 m s⁻¹ trials (Fig. 3). It is possible that aerobic deterioration occurred in some of these samples. Incubations for warming samples lasted more than 24 h for some samples, and the final temperature was elevated for one sample.

The fully empirical logistic model performed slightly better than the convection-diffusion model (Supplementary data). This was not surprising, since the empirical model has more parameters and was calibrated using all wind tunnel trials. Since the response of parameter *c* to silage layer thickness in the empirical model was calibrated to only one set of trials at a depth less than 15 cm, it was not appropriate to attempt to apply the model to the mass balance trials.

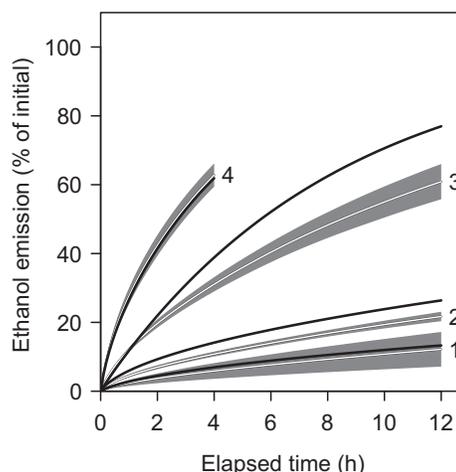


Fig. 4. Comparison between measured and predicted cumulative ethanol emission from corn silage, measured in a wind tunnel. White lines and gray areas show mean measured response \pm one standard deviation ($n = 3$ for lines 2, 3, and 4, and $n = 9$ for line 1). Black lines show model predictions. Conditions are: 1, 15 cm packed silage B; 2, 15 cm loose silage A; 3, 15 cm loose silage B; 4, 3 cm loose silage A. All trials were carried out at 20 °C. Data shown as lines 1 and 2 were used in model calibration.

3.3. Mass balance evaluation

Ethanol emission in the mass balance trials ranged from 15% to 99% of the initial mass present. In the trials where three alcohols and acetaldehyde was measured, relative emission of acetaldehyde (the most volatile of the four compounds) was always greater than emission of alcohols (45%–92% for acetaldehyde, 21%–59% for alcohols). Comparison between measured and predicted VOC emission in the mass balance trials showed two different responses. For trials where a fan blew directly over the samples, model predictions were generally close to measured losses, although the model over-predicted emission from samples with a larger mean particle size and lower density (Table 2). For almost all other trials, the model substantially overestimated emission losses (Tables 3 and 4). In general, mean air speed did not show a clear effect in these trials. Analysis of covariance using the data in Table 4 suggested that emission depended on porosity and temperature but not mean air speed (coefficient = -0.011 , $P = 0.61$) (Table 5). This lack of response is contrary to the wind tunnel results used to calibrate our emission model.

It is possible that differences in the setup of wind tunnel and mass balance trials contributed to the different responses

Table 2

Comparison between measured and predicted ethanol emission from corn silage samples in mass balance trials. Samples were held in 260 × 110 × 150 mm (length × width × depth) boxes indoors and air flow was from an electric fan. Air velocity was measured about 20 mm above the silage surface using a hot-wire anemometer. All trials lasted 12 h. Measurements are from Hafner et al. (2010).

Length (mm)	Density (kg m ⁻³)	Velocity (m s ⁻¹)	Temperature (°C)	Emission (%)	
				Meas.	Pred.
6.6	130	0.54	24	36	42
6.6	130	3.6	23	99	99
6.6	130	5.0	19	98	98
11	97	0.49	24	61	89
11	97	4.8	23	85	100

Notes: "Length" is the mean particle length. Air velocity and temperature are mean values. Density is dry density. Initial ethanol concentration was 11–13 g kg⁻¹ (1.1–1.3%). Standard deviation in measured ethanol concentrations was 5% of the initial concentration or less ($n = 3$).

Table 3

Comparison between measured and predicted ethanol emission from corn silage samples in mass balance trials. Samples were held in 350 × 250 (length × width) boxes within a barn with natural air flow. Air velocity was measured about 20 mm above the silage surface in two directions using two hot-wire anemometers, and data were combined to calculate a mean speed. The mean particle length for all samples was 9.5 mm.

Depth (mm)	Speed (m s ⁻¹)	Density (kg m ⁻³)	Temperature (°C)	Time (h)	Emission (%)	
					Meas.	Pred.
63	0.14	93	24	6.3	29	60
63	0.18	90	22	12	27	87
63	0.71	97	32	5	52	100
150	0.14	100	23	6.3	22	26
150	0.18	100	23	12	15	47
150	0.71	110	22	5	21	56

Notes: Air speed and temperature are means. Initial ethanol concentration was 18–20 g kg⁻¹. Standard deviation in measured ethanol concentration was 6.5% of the initial concentration or less ($n = 3$).

observed. Most wind tunnel trials (which were used for calibration) were carried out with 150 mm of silage, while depth varied for the mass balance trials. However, the model accurately predicted ethanol emission from both 150 and 30 mm thick samples in the wind tunnel (Fig. 4). Alternatively, different approaches for measuring air velocity may confound comparisons. For the wind tunnel trials air velocity was calculated from measured volumetric air flow rate and cross-sectional area of the wind tunnel headspace. Air velocity was measured directly for all mass balance trials, at either about 20 mm or 0.9 m above the silage surface. Although data are too limited to conclusively determine why wind tunnel and mass balance results were so different, differences in model fit between mass balance trials with directed air flow from a fan (Table 2) and natural plus forced ventilation within a barn (Table 3) (in both cases air speed was measured at 20 mm) suggest that height of air speed measurement alone does not explain differences.

It is not clear how wind tunnel transport parameters can be related to parameters in other settings. Clearly, air flow at a given mean air velocity within our wind tunnel does not produce the same emission as wind with a mean speed that is numerically equal. Further, the general lack of response of emission in the mass balance trials to air speed (Tables 3–5) and the over-prediction of emission from silages with large particle size in the mass balance trials which used a fan (Table 2) suggest a qualitatively different response. Parker (2012) has reviewed challenges in relating wind tunnel measurements of emission to emission in the field for solutions. Silage presents an additional challenge since air

movement at the surface may affect transport through pores in addition to surface convection.

Without more complete emission measurements from silage under air flow conditions similar to what silage in barns and outdoors is exposed to, it is difficult to rigorously modify our model to improve its accuracy for predicting emission on farms. The strong response to gas-phase porosity and the lack of response to air speed in the barn and outdoor trials suggest that mass transfer through silage limits emission. (This general response was also seen in the wind tunnel results, but there, air velocity appeared to influence transfer through silage.) Therefore, the magnitude of the mass transfer coefficient may be less important than the diffusion-dispersion coefficient. We determined best-fit values of ethanol k_{sg} for all the trials in Table 4 with h_m fixed at 0.01 m s⁻¹. Regression analysis indicated that values of k_{sg} determined in this manner were related to gas-phase porosity (m³ m⁻³) and temperature (°C) ($0.05 < P < 0.07$ for all terms, for overall model $P = 0.084$ and adjusted $R^2 = 0.61$):

$$\log k_{sg} = -92.277 + 113.430 \phi + 3.357 T - 4.337 \phi T \quad (19)$$

Our model with Eq. (19) for k_{sg} and h_m fixed at 0.01 m s⁻¹ provided predictions that appear unbiased overall for trials conducted in barns and outdoors (those trials shown in Tables 3 and 4), but with substantial error for some trials (Fig. S-2). It is not clear how accurate this approach would be in different settings, especially at porosities or temperatures outside of the calibration range. The interaction term does not clearly correspond to a physical response, and may be spurious. An alternative is to use fixed values for both mass transfer parameters. The median best-fit k_{sg} when h_m is fixed at 0.01 m s⁻¹ is $3.3 \cdot 10^{-5}$ m² s⁻¹. Use of these two values shows no strong overall bias, but less accuracy for individual trials (Fig. S-2).

The mass balance trials provide some indication of the magnitude of VOC emissions from loose silage or mixed feed on farms. Although emission losses depend on temperature, silage properties, air flow, and silage layer thickness, emission of acetaldehyde is likely to be >50% of the initial mass for ≥6 h of exposure under common conditions. A likely range for alcohol emission is 20%–60%. Assuming 75% loss for acetaldehyde and 40% for alcohols; a corn silage consumption rate of 10 kg cow⁻¹ d⁻¹ (dry matter basis); and VOC concentrations of 30, 600, 10,000, and 40 mg kg⁻¹ for acetaldehyde, methanol, ethanol, and 1-propanol (personal observation), typical VOC emission rates from corn silage can be estimated as 0.1 kg cow⁻¹ yr⁻¹ of acetaldehyde and 16 kg cow⁻¹ yr⁻¹ of alcohols. Actual rates may vary substantially among locations.

Table 4

Comparison between measured (Meas.) and predicted (Pred.) VOC emission from corn silage samples in mass balance trials. Samples were held in 380 × 320 × 100 mm (length × width × depth) boxes within a barn, exposed to natural air flow and air flow from fans (first four rows), or outdoors, exposed only to wind (remaining rows). Air speed was measured at a 1 m height using a two-dimensional sonic anemometer. All trials lasted six hours.

Speed (m s ⁻¹)	Density (kg m ⁻³)	Temp. (°C)	Emission loss (%)							
			Acetaldehyde		Methanol		Ethanol		1-Propanol	
			Meas.	Pred.	Meas.	Pred.	Meas.	Pred.	Meas.	Pred.
0.59	69	25	92	100	58	93	56	96	59	98
0.59	82	26	91	100	40	86	34	91	36	96
0.91	54	26	86	100	49	99	50	100	55	100
0.91	70	26	83	100	48	97	50	99	55	100
1.9	72	25	79	100	38	100	35	100	36	100
1.9	110	24	45	100	24	96	21	98	21	99
2.6	86	21	79	100	50	99	49	100	54	100
2.6	120	26	72	100	34	98	29	99	31	100

Notes: Air speed and temperature are means. Initial concentrations were 7–9, 430–610, 1400–4000, and 35–2000 mg kg⁻¹ (dry matter basis) for acetaldehyde, methanol, ethanol, and 1-propanol, respectively. Standard deviation in measured concentrations was generally less than 5% of the initial concentration ($n = 2$ or 3). Net conversion ranged from -4% to +2% of the initial concentrations, except for acetaldehyde (-11% to +5%). Emission estimates were corrected for net conversion.

Table 5

Analysis of covariance results for predicting the fraction of each compound lost in mass balance trials shown in Table 4.

Variable	Estimate	se	t-value	P-value
Intercept	−29.0	6.33	−4.59	$8.5 \cdot 10^{-5}$
Porosity ($\text{m}^3 \text{m}^{-3}$)	39.5	8.35	4.73	$5.9 \cdot 10^{-5}$
Temperature ($^{\circ}\text{C}$)	1.12	0.247	4.53	$1.0 \cdot 10^{-4}$
Porosity \times temperature	−1.48	0.326	−4.54	$9.6 \cdot 10^{-5}$
Methanol	−0.356	0.0334	−10.7	$2.2 \cdot 10^{-11}$
Ethanol	−0.372	0.0345	−10.8	$1.7 \cdot 10^{-11}$
1-Propanol	−0.345	0.0334	−10.3	$4.5 \cdot 10^{-11}$

Notes: Residual standard error: 0.0787, degrees of freedom: 28, adjusted R^2 : 0.850, $F = 33.1$, $P < 1 \cdot 10^{-10}$. Acetaldehyde was taken as the default compound; statistical tests for the other compounds are for a comparison to it.

Mass balance results do not provide much information on management practices for reducing emission. A possible exception is porosity, to which emission responded in both wind tunnel and mass balance trials. Based on the regression model from the mass balance trials (Table 5), an increase of $0.1 \text{ m}^3 \text{m}^{-3}$ in porosity will cause an additional loss of 25% of the initial compound mass (at 20°C). However, it is possible that VOC concentrations within silage will be the most important parameter for predicting and controlling emission. Relative ethanol emission in our trials conducted in barns and outdoors varied by less than a factor of 3, while ethanol concentration varied by a factor of 14 (for silage produced in two different states).

4. Conclusions

A convection-diffusion-dispersion model, with both the surface mass transfer coefficient and the diffusion-dispersion coefficient estimated from wind tunnel measurements, was generally accurate for predicting ethanol emission from silage measured under a range of air velocities and temperatures in a wind tunnel. However, emission of alcohols and acetaldehyde measured using a mass balance approach from silage samples outdoors and within barns was substantially lower than the model predicted, suggesting that the model will not provide accurate estimates of VOC emission from silage on farms. Mass balance trials confirmed that emission is related to gas-phase porosity. Results from mass balance trials indicated that alcohol emission may approach 50% of the initial mass, while relative emission of acetaldehyde will be higher. Additional research is needed to identify and quantify the variables that control VOC emission from silage under farm conditions.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2012.03.005.

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