



A mass transfer model for VOC emission from silage

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ARTICLE INFO

Article history:

Received 10 November 2011

Received in revised form

1 March 2012

Accepted 2 March 2012

Keywords:

Dairy farms

Silage

Volatile organic compounds

Emission

Model

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.

Published by Elsevier Ltd.

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):

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

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

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

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

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