Modeling Emissions of Volatile Organic Compounds from Silage

Sasha D. Hafner, Agricultural Engineer

Felipe Montes, Agricultural Engineer

C. Alan Rotz, Agricultural Engineer

USDA-ARS Pasture Systems and Watershed Management Research Unit, 3702 Curtin Road, University Park, PA 16802-3702

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Abstract*. Volatile organic compounds (VOCs), a necessary reactant for photochemical smog formation, are emitted from numerous sources. Limited available data suggest that dairy farms emit VOCs with cattle feed, primarily silage, being the primary source. Process-based models of VOC transfer within and from silage during storage and feeding are presented. These models are based upon well-established theory for mass transport processes in porous media with parameters determined from silage properties using relationships developed for soils. Preliminary results indicate that VOC emission by advective flow of silage gas is generally insignificant compared to emission by surface convection and diffusion from within silage. VOC emissions are dependent upon silage properties, temperature, wind speed, and exposure duration, which have implications for measuring, predicting, and controlling VOC emissions from silage. Emissions appear to be co-limited by convection and diffusion; therefore, the EPA-style emission isolation flux chamber design previously used to measure VOC emissions from silage is not suitable for this task.*

Keywords. Silage, emissions, volatile organic compound, VOC, model, simulation

Introduction

Photochemical smog is a major air pollution problem and occasional cause of premature death throughout the United States (U.S. EPA 2008a, National Research Council 2008). Volatile organic compounds (VOCs), a necessary reactant for smog formation, come from numerous sources. In the US, the largest source of VOCs is industry, followed by vehicles (U.S. EPA 2009a). Surprisingly, dairy farming may be an important source of VOCs in some areas. Most of California's San Joaquin Valley, which has a high concentration of large dairy farms, is classified as a "nonattainment area" by the US EPA based on measured ozone levels (US EPA 2009b). Ozone is the major oxidant in smog and is taken as a surrogate for the latter. The San Joaquin Air Pollution Control Board reports that agriculture is the largest single emitter of VOCs in the Valley (San Joaquin Valley Air Pollution Control Board, 2008). However, little data exist on VOC emissions from dairy farms. In order to reduce smog pollution, it is important to understand the magnitude and sources of VOC emissions from dairy farms.

Potential sources of VOCs on dairy farms include manure, feed, and cattle themselves. Several studies have identified and quantified VOCs on dairy farms to include alcohols, acids, aldehydes, ketones, and esters (Sunesson et al. 2001, Rabaud et al. 2003, Hobbs et al. 2004, Schmidt 2006, Filipy et al. 2006, Shaw et al. 2007, Ngwabie et al 2007, Alanis et al 2008, Ngwabie et al. 2008, Sun et al. 2008). However, few studies have measured VOC emissions from isolated sources on dairy farms.

Shaw et al. (2007) and Sun et al. (2008) measured emissions from cows and manure using an enclosed environmental chamber. Both of these studies found that alcohols (primarily ethanol) had higher emissions than other compounds. Other studies have shown that feed emissions of VOCs are much higher than emissions from other sources. Alanis et al. (2008) used an EPA-type emission isolation flux chamber (Klenbusch 1986) to measure VOC emissions from several potential sources at the California State University Fresno dairy facility. They found that fluxes of VFAs from silage and total mixed rations (TMR) were approximately one order of magnitude greater than that from other sources. Schmidt (2006) used a similar flux chamber to measure VOC emissions from six different sources on two California farms. VOC fluxes from exposed silage (grass and corn) were more than two orders of magnitude greater than fluxes from non-feed sources. Given these high VOC fluxes, the estimated contribution of silage and feed to total farm VOC emissions was high on both farms studied by Schmidt (2006). Although few studies have measured VOC emissions from silage (and those that have done so have limitations) they provide strong evidence that silage is an important source of VOC emissions on dairy farms. Clearly, more work is needed on this topic.

Silage contains many VOCs that have the potential to enter the atmosphere. Organic acids and alcohols produced by fermentation during the ensiling process (Rooke and Hatfield, 2003) are important because of their volatility and high concentrations in silage (acetic acid plus ethanol generally exceeds 3% of the dry mass of corn silage). About 100 million Mg of corn is used annually as silage in the United States (USDA National Agricultural Statistics Service, 2009). Assuming a dry matter content of 32%, total loss of 20%, and ethanol and acetic acid concentrations of 1% and 2%, respectively, total annual VOC production from corn silage in the US is around 0.8 million Mg. For comparison, all transportation in the U.S. is estimated to contribute 7.6 million Mg of VOC annually (US EPA, 2003). Clearly, emissions of all VOCs present in silage would be a major national source of VOC emissions. However, it is likely that only a fraction of this total is actually emitted to the atmosphere. Even if this is the case, silage may still be an important local or regional source of VOCs.

A process-based model of VOC emissions from silage would be useful for estimating emissions, directing experimental research design, and evaluating potential mitigation strategies. Considering that biological, chemical, and physical processes are responsible for VOC emissions from silage, one would expect emission rates to be highly variable and dependent on weather, crop characteristics, and silage production practices. Development of a process-based model provides a means of evaluating the effect of many parameters simultaneously—a task that would be difficult to carry out experimentally or with an empirical model.

The goal of this work was to develop a process-based model of VOC emissions from silage and silage-containing feeds. Our objectives were to: develop models for the most important pathways of silage VOC emissions; compare the magnitude of VOC emissions from competing pathways; and quantify the effect of important parameters on VOC emissions. Although there are a myriad of VOCs that may be emitted from silage, we focused on two representative VOCs: ethanol and acetic acid. In the few studies that have measured VOC emissions on dairy farms, these compounds have been important (Card & Schmidt, 2006; Schmidt, 2006; F. Mitloehner, personal communication, 2009). Additionally, the physical behavior of these compounds may be representative of other alcohols and organic acids.

Methods

Mechanisms of VOC production and emissions

During the fermentation stage of silage production, organic acids, alcohols, and other metabolic end products are generated by anaerobic bacteria (Rooke & Hatfield, 2003). Once the main fermentation phase is complete (after 1 week to 1 month) little microbial activity takes place (Pahlow et al., 2003) and therefore the concentration of these compounds is expected to be relatively stable (assuming the silo is sufficiently sealed). Once a silo, silage pile, or silage bag is opened, these compounds have the potential to escape into the atmosphere. The models presented in this work focus on predicting emissions of these compounds from fermented silage and not the production of these compounds during fermentation. These models focus on VOC emissions from the exposed face of silage storages that can be applied to silage piles, bunker silos, silo bags, or any other exposed silage. Although not included in this paper, the convection-diffusion model can also be applied to mixed rations in a feed bunk.

Transfer of VOCs from the exposed surface of silage to the atmosphere will take place by convection. There are at least four potential pathways that may be responsible for transferring VOCs to the surface of a silage pile: 1) advective flow of water, 2) advective flow of silage gas, 3) diffusion through aqueous phase, and 4) diffusion through gaseous phase.

Diffusion of VOCs occurs in response to concentration gradients. Diffusion of VOCs in geologic material has been extensively studied and modeled (see reviews by Hu & Wang, 2003; Ho & Webb, 2003). The importance of both aqueous and gaseous diffusion of VOCs through these media has been recognized (Jury et al., 1990; Ho and Webb, 2003). In silage, oxygen diffusion (presumably gas-phase) has been studied because of its importance to silage spoilage. Oxygen and CO_2 diffusion in silage has been measured by Rees et al. (1983a, 1983b) but no measurements of aqueous-phase diffusion coefficients for silage are available.

Advective flow of gases through porous media occurs due to differences in pressure over space or in response to the force of gravity. Advective flow of gases in geologic materials has been extensively studied and modeled (Massmann and Farrier, 1992; Seely, 1994; Ho and Webb, 2003). In silage, pressure differences between gas in silage pores and the atmosphere are generated by density differences between silage gas and external air or by net production of

CO_2 by fermentation (see Williams (1994) for more information on changes in silage gas over time). Modeling work by Parsons (1991) demonstrated that advection was probably important for O_2 infiltration into silage. Parsons' predictions were supported by later observations of gas profiles in silage (Muck and Huhnke, 1995; Williams et al., 1997).

Description of models

To assess the importance of both advection and diffusion in VOC emissions from silage, we developed two numerical models: one for advective gas flow within silage and one for VOC diffusion and convection from the surface of silage. Although it is artificial to separate these processes into two separate models, it is useful for evaluating their relative significance. Moreover, since VOCs are minor components of silage gas, advection is independent of VOC diffusion and convection. Advective flow can influence VOC diffusion, but if this flow is insignificant for VOC transport, it is reasonable to exclude it from a model of VOC emissions.

In both models, silage porosity is estimated from (dry) density, assuming a particle density of 1500 kg/m^3 (Rees et al., 1983b). Water-filled porosity is determined from total porosity and water content (assuming a water density for pure water based on temperature), and gas-filled porosity is calculated by difference.

Assuming that VOC sorption to particulate matter is insignificant, partitioning of VOCs between an aqueous and gaseous phase is based on Henry's law:

$$K_{H,i} = \frac{\gamma_i m_i}{P_i}$$

(1)

where $K_{H,i}$ = Henry's constant for species *i* (mol/kg-atm), m_i = molal concentration of species *i* in solution (mol/kg), γ_i = activity coefficient of species *i*, and P_i = partial pressure of species *i* in equilibrium with the solution. In this work, activity coefficients for all uncharged species were assumed to equal unity. Henry's constant is assumed to be temperature dependent:

$$\ln(K_{H,i}) = a + \frac{b}{T}$$

(2)

where, *a* and *b* are empirical parameters, and *T* = temperature (K). Values for the coefficients in Eq. (2) were calculated from Khan and Brimblecombe (1992) for acetic acid and Warneck (2006) for ethanol.

In the two-dimensional advection model, gas composition and pressure may vary with height and distance from the exposed silage surface, but are constant across the width of a silage pile. The primary components of silage gas are N_2, CO_2, and O_2 (Williams, 1994). In this model, silage gas was represented by a mixture of N_2 and CO_2, with any O_2 that entered silage pores converted to CO_2 (through respiration). Since O_2 is quickly converted to CO_2 in silage and O_2 concentrations are generally very low (Muck and Huhnke, 1995; Williams et al., 1997) this approximation is expected to have a minor effect. Gas flow in this model is based on Darcy's law (Bird et al., 2002):

$$v_z = -\frac{\kappa}{\mu}\left(\frac{dP}{dz} + \rho g\right)$$

(3)

where v = gas flux (m^3/m^2-s), κ = permeability (m^2), μ = viscosity (kg/m-s), ρ = gas density (kg/m^3), and g is force of Earth's gravity (9.807 N/kg). Equation (3) is for vertical flow; for

horizontal flow the term $+\rho g$ is excluded. Dispersion and diffusion of N_2 and CO_2 are assumed to play a minor role and are not included. Gas density is calculated from the ideal gas law. Silage permeability and porosity are estimated from density and dry matter content based on relationships derived for grass silage (Williams, 1994). Net production of CO_2 via fermentation is included based on estimates of fermentation loss (McGechan, 1990).

In the one-dimensional convection-diffusion model VOC concentrations and silage properties may vary with depth from the exposed surface but are constant for all points located at the same distance from the exposed surface. The mass transfer coefficient for VOC removal from the surface was calculated from wind speed, air viscosity, and the free fluid VOC diffusion coefficient in air using a correlation for laminar flow (Perry et al., 1997):

$$Sh = 0.646 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \tag{4}$$

where Sh = Sherwood number, Re = Reynold's number, and Sc = Schmidt number.

VOC diffusion through both solution- and gas-filled pores was based on Fick's law (Bird et al. 2002):

$$j_i = -D_{i,b} \frac{dc_i}{dx} \tag{5}$$

where j_i = the flux of species i (g/m²-s), $D_{i,b}$ = effective diffusivity of i through b (where b is silage gas or silage solution) (m²/s), c_i = concentration of VOC i in the gaseous or aqueous phase (g/m³), and x denotes relative position (m). Diffusion coefficients were adjusted from clear fluid values based on silage porosity. Previous models of gas diffusion in silage have generally used the Penman (1940) model for predicting diffusion coefficients from clear fluid values (Pitt, 1986; Pitt and Muck, 1993; McGechan and Williams, 1994; Ruxton and Gibson, 1994), where clear fluid diffusion coefficients are multiplied by 2/3θ, where θ is the volumetric gas content (m³/m³). To our knowledge, the only measurements of gas diffusion in silage were made by Rees et al. (1983a, 1983b). Measured values were much lower than that predicted by the Penman model, as noted by McGechan and Williams (1994) and McGechan (1990). To calculate gas-phase diffusion coefficients in our model, the Millington and Quirk (1961) model was used, which was more consistent with measurements from Rees et al. (1983a, 1983b):

$$D_{i,sg} = D_{i,air} \frac{\phi^{10/3}}{\Phi^2} \tag{6}$$

where $D_{i,air}$ = diffusivity of VOC i in clear air, ϕ = gas-filled porosity (m³/m³), and Φ = total porosity (m³/m³) = $\phi + \theta$, where θ = water-filled porosity (m³/m³). For aqueous phase diffusion, the Penman-Millington-Quirk model (Moldrup et al., 1997) with m = 1 is used (Eq. 7). Diffusion coefficients in clear air were taken as 1.2 × 10⁻⁵ m²/s and 1.1 × 10⁻⁵ m²/s for ethanol and acetic acid, respectively (Winkelmann, 2007; U.S. EPA, 2006), and in clear water as 1.3 × 10⁻⁹ m²/s and 1.2 × 10⁻⁹ m²/s for ethanol and acetic acid, respectively (U.S. EPA, 2006).

$$D_{i,ss} = D_{i,water} \frac{\theta^{11/3}}{\Phi^{3.06}} \tag{7}$$

The complete convection-diffusion model requires values for ten parameters: diffusion coefficient in clear air, diffusion coefficient in clear water, Henry's law parameters, dry matter content, silage density, characteristic length, temperature, VOC concentration, and wind speed. Both the advection and convection-diffusion models were implemented using the finite

difference method with the deSolve package (Soetaert et al. 2009) in R v. 2.8.1 (R Development Core Team, 2009). In addition to the numerical convection-diffusion model, an analytical version was developed. All models will be described in more detail in a future publication.

Model simulations

To assess the importance of advection for VOC emissions from silage, we calculated total gas emissions for a range of conditions. For the advection model, a range of geometries were used: 3 m by 6 m, 3 m by 60 m, 5 m by 30 m, 12 m by 30 m, and 12 m by 60 m. Tested silage dry densities were 150, 250, and 350 kg/m^3, dry matter content was 25, 35, and 50%, and fermentation loss was 1%, 2.5%, and 4%. All combinations of these parameter values were used to generate emission predictions. To estimate total VOC emissions from advective gas flow, ethanol was used as a representative VOC, with a concentration of 1% (dry matter basis).

To generate predictions from the convection-diffusion model to compare to those from the advection model, the same set of parameter values were used for density and dry matter as given above. Additionally, wind speed was varied from 0.1 to 5 m/s. All combinations of these parameter values were used to generate predictions. The concentration of ethanol in these simulations was fixed at 1%.

To explore the importance of parameter values on VOC emissions, the convection-diffusion model was used with a wide range of parameter values. Simulations are described in detail in the following sections. For all simulations with both models, temperature was fixed at 20°C unless specified.

Results and discussion

Importance of advective gas flow for VOC emissions

Predictions from the advection model show an initial period of gas flow out at all heights due to CO_2 production by fermentation. This period is then followed by establishment of a circular flow pattern. This pattern, which has been predicted previously by Parsons (1991), is the result of dense silage gas flowing out of the bottom of the exposed face due to gravity, and fresh air flowing in at the top to replace the denser silage gas (Fig. 1). Flow declines over time as the CO_2 content of silage gas declines to 20%. Even at 20% CO_2, advective flow of silage gas continues indefinitely, since the mixture remains more dense than air. The pattern of silage gas emissions over a one-year period is shown in Fig. 2 for four different scenarios. Low density and low moisture content (high dry matter) both increase porosity and permeability and therefore silage gas emissions. Advective flow of silage gas continues as long as organic substrate exists. Predicted ethanol emissions for the range of parameter values described in the Methods section are shown in Fig. 3A.

Convective loss of VOCs from an exposed silage surface is a short-term process. Every time silage is removed from a silo (e.g. once or more per day) a new surface with bulk concentrations of VOCs is exposed (assuming that VOC depletion does not extend beyond the depth of silage removed at each feeding). Therefore, simulations with the convection-diffusion model were carried out for a 24-hr period. Emissions over a longer period of time are the sum of 24-hr emissions, if feeding is once daily. Predicted cumulative ethanol emissions over a one-year period using the range of parameter combinations given in the Methods section are shown in Fig. 3B.
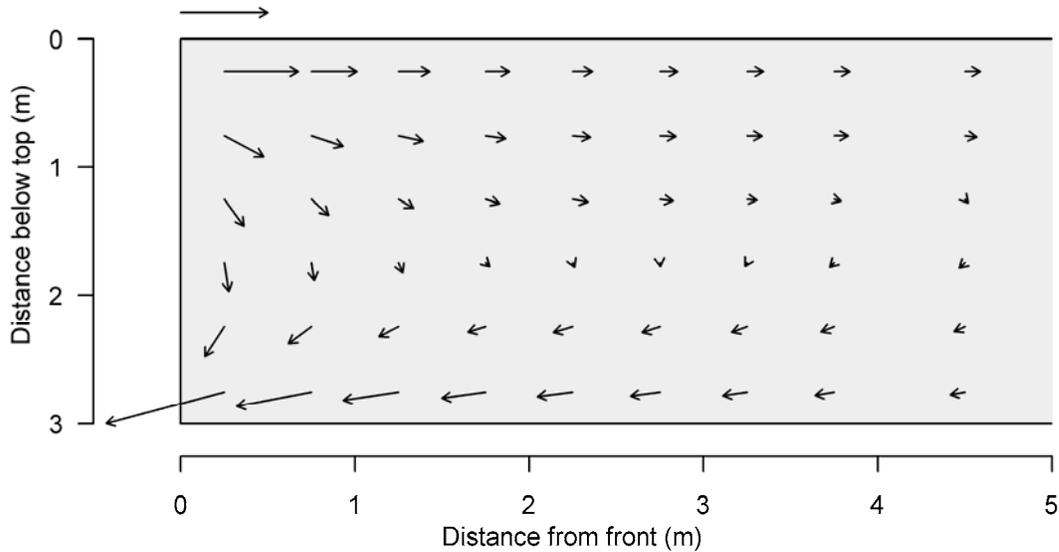
Figure 1. Simulated advective gas flow in a bunker silo or silage pile 15 days after exposing the surface (left side) to the atmosphere. Arrow length represents silage gas flux; the scale bar (upper left) represents 0.1 m^3/m^2-d. Note that the right side of the plot is truncated. For this simulation, silage density(250 kg/m^3) and dry matter content (35%) were intermediate.
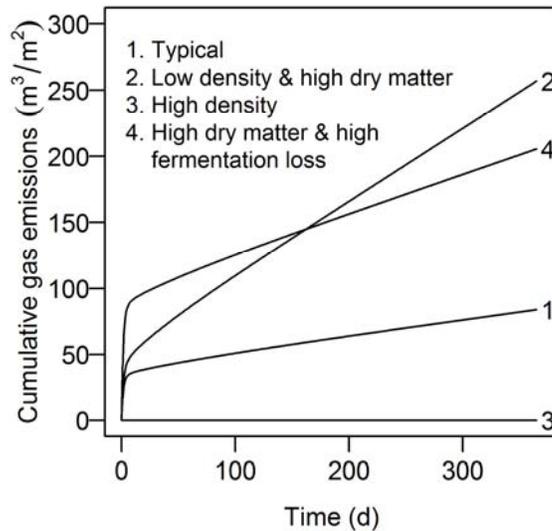

Figure 2. Cumulative silage gas emissions via advective flow as predicted by the advection model for four scenarios. All predictions were for a 5 m (height) by 30 m (length) bunker silo or silage pile. The "typical" scenario uses intermediate parameter values and the other scenarios use parameters at the low or high values given in the Methods section.

A comparison of emissions predicted with the advection and convection-diffusion models strongly suggests that convection and diffusion more important for predicting VOC emissions from silage than is advective flow of silage gas (Fig. 4). The maximum predicted ethanol emission via advective flow is 600 g/m^2 over a one-year period. Predicted ethanol emissions from the convection-diffusion model ranged from 7 to 36 g/m^2 over a 24-hr period, representing 2.6 to 13 kg/m^2-yr. Moreover, predicted ethanol emissions from the advection model are overestimates for two reasons. First, removal of silage (which is not included in this model)

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would be expected to reduce advective gas flow. Second, VOC concentrations in silage increase during the fermentation phase, so silage gas emitted during this phase (primarily CO_2 produced via fermentation) actually contains lower VOC concentrations than is assumed here. However, short-term advective gas flows have the potential to be important (i.e. the left-most portions of the results shown on Fig. 3A), and more work is needed to assess these. This potential importance is buffered by lower VOC concentrations at the start of the ensiling process.
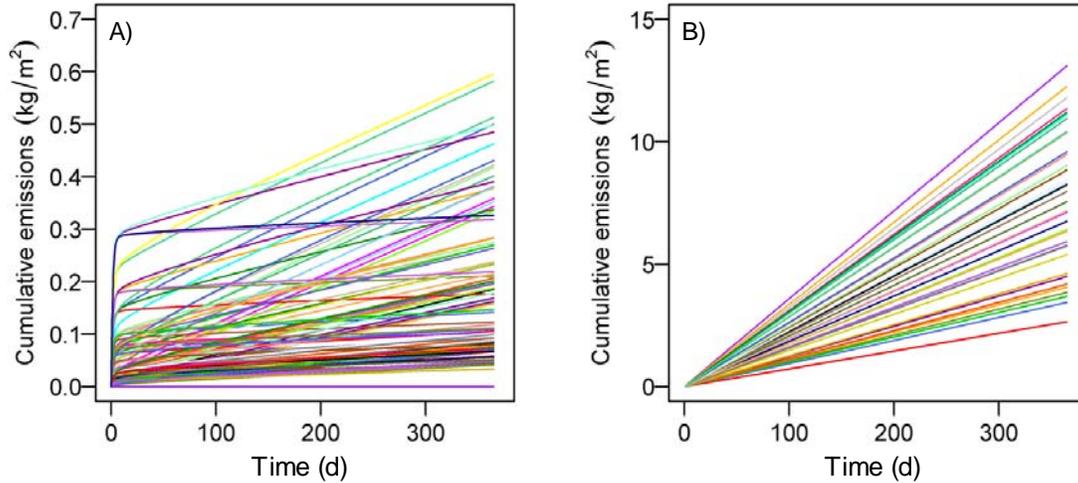

Figure 3. Simulated ethanol emissions from the advection model (A) and the convection-diffusion model (B) over a one-year period. Each single line represents an individual scenario with a unique combination of parameter values, as described in the Methods section.
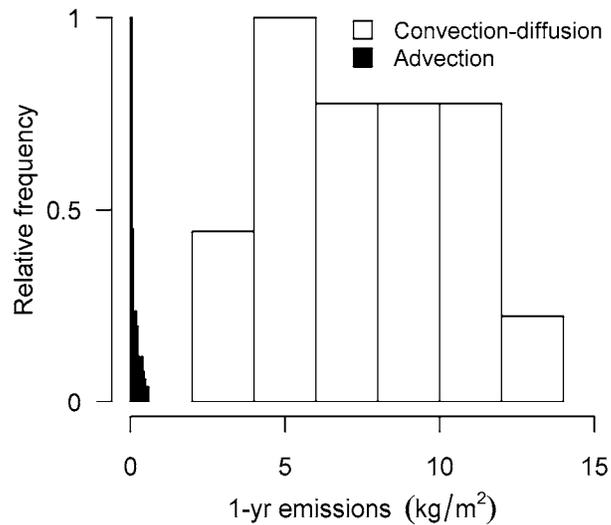

Figure 4. Histograms of annual ethanol emissions predicted by the advection and convection-diffusion models. Values represent the final cumulative emissions (i.e. at the end of day 365) shown in Fig. 3. In this plot, the x-coordinate is the predicted annual ethanol emission and the y-coordinate is proportional to the number of model simulations with a given emissions rate.

Convection and diffusion of VOCs

Ethanol and acetic acid emissions predicted by the convection-diffusion model for silage with typical parameter values are shown in Fig. 5. Predictions from the model show some important trends. In general, the surface flux declines during a 24-hr period. However, the rate of decline differs between ethanol and acetic acid. The overall magnitude of emissions is clearly dependent on VOC characteristics, since acetic acid emissions are much lower than ethanol emissions despite lower concentrations for ethanol (1% vs. 1.8%).
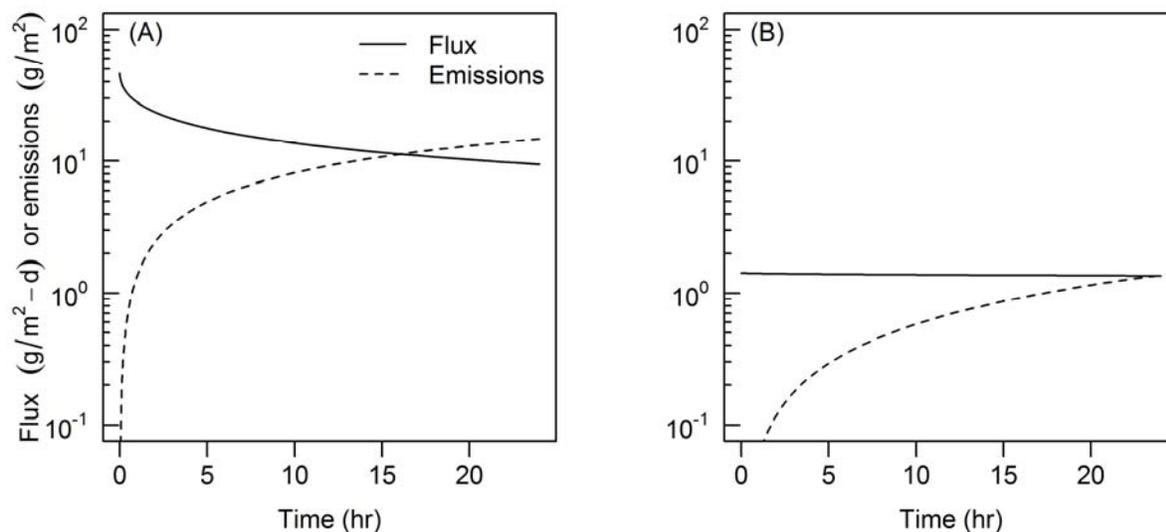

Figure 5. Cumulative emissions and instantaneous surface flux of ethanol (A) and acetic acid (B) simulated by the convection-diffusion model for typical silage (dry density = 250 kg/m^3, dry matter = 30%, wind speed = 0.5 m/s, temperature = 20°C, ethanol = 1%, acetic acid = 1.8%).

The decline in surface flux over time seen in Fig. 5 is due to the depletion of VOCs near the exposed surface. When a fresh silage surface is first exposed to the atmosphere, convection is the only mass transport process that occurs, since no concentration gradient exists within the silage before any VOC loss has occurred. In this situation, emissions are clearly convection limited, and a change in wind speed over the exposed surface will result in a change in surface flux, while diffusion has no impact on the surface flux at this time. As VOC molecules are removed from the exposed surface, the surface concentration declines. This results in a reduced surface flux and a concentration gradient within the silage, which initiates diffusive transport to the surface. Through the remainder of the exposure period, surface flux is controlled by both diffusion and convection, i.e. a change in either the convection coefficient or the effective diffusion coefficient (e.g. by changing porosity) will change the surface flux. Through time, the effect of convection declines and that of diffusion increases. This is demonstrated in Figs. 6 and 7 for ethanol and acetic acid respectively.

The results shown in Figs. 6B and 7B demonstrate where and to what degree surface flux is controlled by diffusion. Because individual silage properties, such as density or dry matter content, may influence multiple chemical and physical properties (e.g. gas- or aqueous-phase concentration, porosity, diffusion coefficients) changes in silage properties may not have the expected effect, and nonlinear responses and interactions between parameters are likely. Ethanol surface flux and cumulative emissions shown in Fig. 8 demonstrate all three of these qualities. An example of a nonlinear response can be seen in the effect of silage density. Reducing silage density slightly increases surface flux (scenario 1 vs. 4) due to higher gas-

phase diffusion, resulting in a slight increase in 24-hr emissions. Increasing density decreases gas-phase diffusion, but it increases aqueous-phase diffusion, as well as the initial concentration of ethanol, resulting in a large increase in 24-hr emissions (scenario 1 vs. 5).
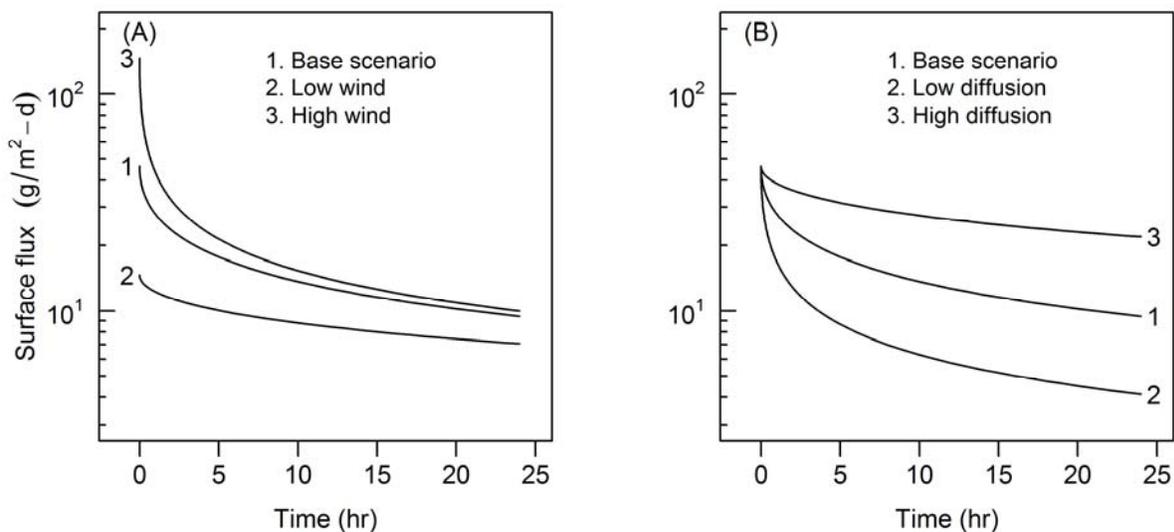

Figure 6. The effect of changes in wind speed (A) and effective diffusion coefficient (B) on predicted instantaneous surface flux of ethanol. Wind speeds are 0.5, 0.05, and 5.0 m/s, while the effective diffusion coefficient is changed by a factor of 10 from the base case for the low and high scenario. All scenarios use the same ethanol concentration (1%).
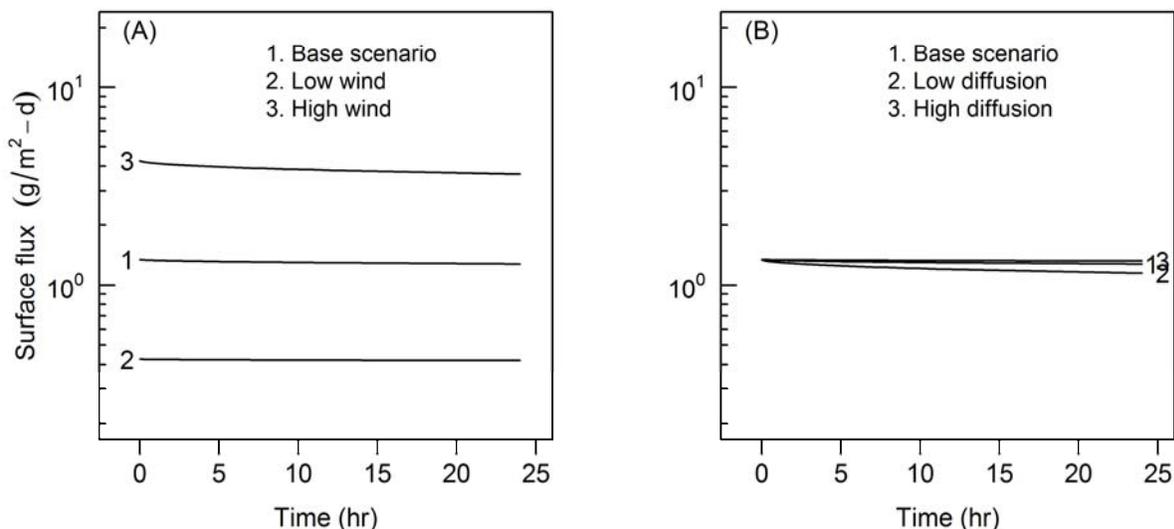

Figure 7. The effect of changes in wind speed (A) and effective diffusion coefficient (B) on predicted surface flux of acetic acid. Wind speeds and changes in the diffusion coefficient are the same as in Fig. 6. Note that the scale for the y axes differ from Fig. 6. All scenarios had the same acetic acid concentration (1.8%)
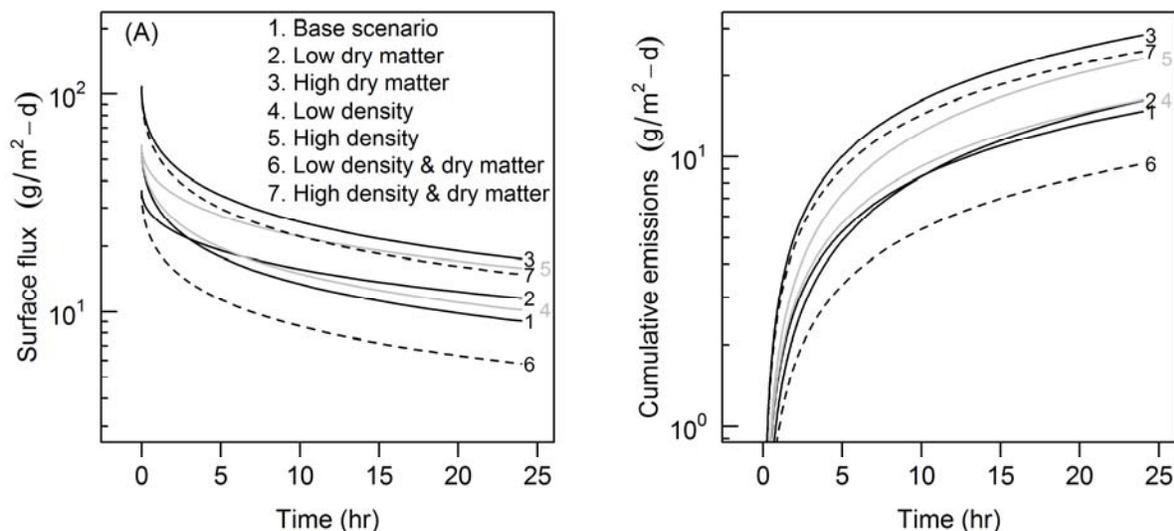
Fig. 8. Predicted ethanol surface flux and cumulative emissions for several combinations of dry matter content and density. Density values were 150, 250, and 350 kg/m^3, while dry matter was 25%, 35%, and 50%.

It is clear from the results shown in Figs. 5-7 that different VOCs may have very different behavior. The large differences in emissions between ethanol and acetic acid are due to differences in partitioning. At 20°C, Henry's law constants are approximately 250 and 7400 mol/kg-atm for ethanol and acetic acid, respectively. For a given solution concentration (molal concentration of uncharged species), the equilibrium gaseous concentration of ethanol is about 30 times that of acetic acid. Since not all acetic acid in silage is present in the uncharged form, this difference is even greater in practice. Therefore, at comparable solution concentrations, convective losses of ethanol proceed much more quickly than those for acetic acid. For the same reason, a change in gas-filled pore space (through a change in density or dry matter content) will have a larger effect on ethanol diffusion.

This difference in partitioning also explains the different trajectories seen for ethanol and acetic acid. With a lower rate of loss by convection, acetic acid is depleted from a surface more slowly, resulting in less change in surface flux over time than would be experienced for ethanol (compare Figs. 6 and 7). However, acetic acid generally will be more responsive to changes in wind speed, since convective losses are not limited by depletion to the degree of that of ethanol (compare Figs. 6 and 7).

Temperature is expected to have substantial effects on VOC emissions, with warmer conditions increasing emissions. The aqueous solubility of most compounds decreases with temperature, with a typical factor of 2 decline per 10°C increase in temperature (Staudinger and Roberts, 2001). Near 20°C, ethanol and acetic acid both follow this response closely. Therefore, with an unlimited VOC supply in cases where gas-phase diffusion is dominant, a 10°C increase in temperature doubles emissions. In practice, a doubling is not expected, since depletion occurs. Simulations for ethanol and acetic acid confirm this expectation (Figs. 9 and 10).

Implicit in the above results and discussion is the concept that parameter interactions are strong in the results from the convection-diffusion model. For example, the effect of wind speed on 24-hr emissions is different for ethanol than it is for acetic acid, due to differences in partitioning, as seen by comparing Figs. 6 and 7. Similarly, we would expect that the effect of changes in silage density is dependent on dry matter content, and that its effect will be different for different VOCs. These complicated responses may obscure potential mitigation strategies, but they also

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highlight the utility of a process-based modeling approach. It would be difficult to use either an empirical model or an experimental program to predict the interactions that can readily be predicted using a process-based model. One parameter that has a very clear effect on emissions is VOC concentration; all else being equal, a given increase in VOC concentration results in a proportional increase in surface flux and emissions.
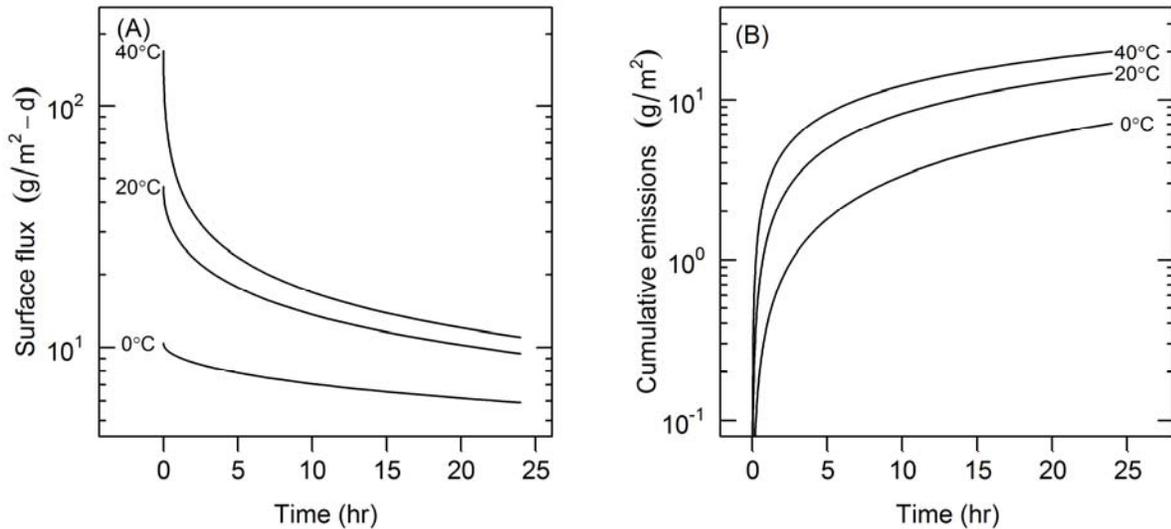

Figure 9. Predicted surface flux (A) and cumulative emissions (B) of ethanol from the convection-diffusion model at three temperatures.
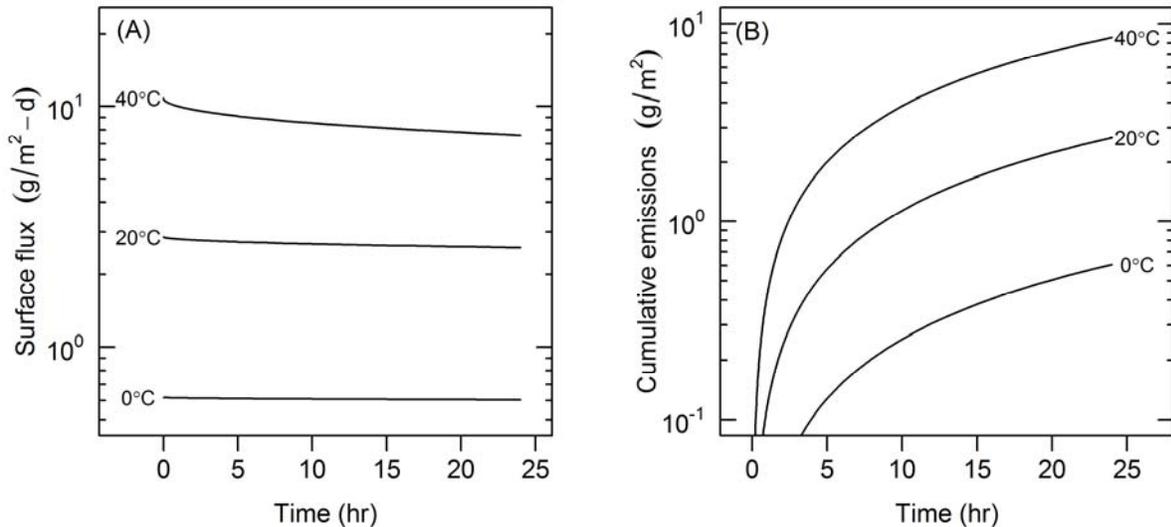

Figure 10. Predicted surface flux (A) and cumulative emissions (B) of acetic acid from the convection-diffusion model at three temperatures. Note that the y axis scale differs from Fig. 9.

Implications for measurement and control

It should be stressed that these results are preliminary. Although the individual components of the convection-diffusion model have been tested in other media, they have not previously been applied to silage. We are currently in the process of developing techniques for measuring VOC emissions from silage (Montes et al., 2009), and will present comparisons between model predictions and measurements in a future publication. Preliminary results support the effects of wind speed, exposure duration, and differences between ethanol and acetic acid. Additionally, it is possible that other transport processes (such as transport in flowing liquid water) play a role in VOC transport within silage. We are evaluating this possibility through our research.

A common approach for measuring VOC emissions from soils is to use the EPA-style emissions isolation flux chamber. This system has also been used for measuring VOC emissions from silage (Schmidt, 2006; Alanis et al., 2008). Since soil-VOC systems are typically diffusion-limited, this system was designed for diffusion-limited emissions where wind speed does not influence emission rate (Klenbusch, 1986). Perhaps the most obvious implication of the model results discussed above is the unsuitability of the EPA-style emission isolation flux chamber for measuring VOC emissions from silage. Since silage emissions are, at least to some degree, convection-limited, measurements with an emission isolation flux chamber will underestimate emissions, given the very low air flow rate used. A more suitable measurement approach represents the *in situ* air flow pattern to the degree possible. Another option is to use a wind tunnel, which has been shown to result in higher emission rates as compared to the emission isolation flux chamber for other agricultural materials (Sohn et al., 2005).

The surface flux of a VOC declines over time, where the magnitude of the decline is dependent on silage and environmental parameters. It is clear that VOC emission from silage is a transient process, and, in many cases, cannot be measured by a short-term process. In the least, it is important to recognize that emissions from a freshly exposed surface are much higher than that from a surface exposed for 24 hr. This response has implications for measurement, predictions, and mitigation. For example, farms that remove silage three times daily would be expected to have higher emission rates than those that remove silage only once per day. With regard to measurement, it is likely that short-term trials (e.g. a few hours) will not reflect cumulative emissions over longer time periods. In general, measured emissions will be dependent on wind speed, temperature, and exposure duration, in addition to silage characteristics, and this should be recognized in the design of measurement approaches.

At this stage in the development and testing of our models, it is premature to suggest that any particular mitigation strategies should be implemented. However, model results do suggest some mitigation strategies that could be the topic of future research. Reducing the degree of exposure of silage would be expected to reduce emissions. Without estimates for VOC emissions from covered silage, it is not possible to determine how much this would reduce emissions. Although ethanol and acetic acid are not the only VOC's emitted by silage, they are two of the most important compounds on the basis of emission rates. Therefore, any steps that reduce ethanol and acetic acid emissions would be expected to reduce VOC emissions in general. Any process that reduces ethanol and acetic acid concentrations within silage would be expected to cause a proportional reduction in the emissions of these two compounds. Fortunately, neither compound is a desirable component of silage, and some practices may reduce their concentrations in silage. For example, inoculation appears to reduce ethanol concentrations in silage (Driehuis and van Wikselaar, 2000; Rodrigues et al., 2004). Without more information on the effect of silage density on gas- and aqueous-phase diffusion, it is not clear how density will impact VOC emissions; model simulations suggest a nonlinear response. Regardless, changes in density will likely have differing effects on different VOCs.

Research needs

Several areas are in need of additional research to improve or understanding of VOC emissions from silage and assist with model development. Some of the more important experimental needs are: 1) measurement of VOC emissions for all likely routes from storage through feeding, 2) determination of the degree of VOC sorption to silage particulate material, 3) measurement of VOC emissions for a wide range of silage types using a wind tunnel method, 4) determination of rates of microbial oxidation of VOCs, and 5) development of a database on silage composition. We are currently addressing some of these areas in our own research including the development of a silage composition database, measurement of emissions from different silage types, and the evaluation of effects of silage characteristics and the environment on emission rates through the measurement of VOC emissions from silage under controlled conditions.

Conclusions

In some locations, dairy farms may contribute to smog formation through the emission of VOCs from silage. Preliminary results from the models developed in this work show that:

- VOC emissions can occur by multiple pathways, but advective flow of silage gas is much less important than combined convection and diffusion.

- Exposure duration, wind speed, and temperature all have a substantial effect on ethanol and acetic acid emissions, and measurement approaches should take this into account. In particular, the commonly-used EPA-style emission isolation flux chamber is not suitable for measuring VOC emissions from silage.

- VOC emissions are sensitive to silage characteristics, and emissions will vary substantially among and within silage types and locations.

- VOC emissions show complicated responses to model parameter values with nonlinear responses and parameter interactions common.

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