Final Report

Quantification of the Emission Reduction Benefits of Mitigation Strategies for Dairy Silage

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Disclaimer

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A, B, C	Compound-specific constants in calculating saturated vapor pressure
A_{sur}	Area of emitting surface (m^2)
C_{air}	VOC concentration in ambient air (g/m^3)
C_{lyr}, C_{lyr-1}	VOC concentrations for simulated lower and upper layers, respectively (g/m^3)
C_{sur}	VOC concentration in silage surface layer (g/m^3)
C_{VOC}	Measured hourly VOC concentration in headspace (ppm)
D_b	Effective bulk diffusion coefficient (m^2/s)
D_{ss}	Diffusion-dispersion coefficient for aqueous phase (m^2/s)
f_{emis}	Fraction of VOC lost over time
h_m	Surface mass transfer coefficient
IA	Index of agreement
j_{lyr}	Hourly mass transfer of VOC from the adjacent lower layer (g/m^2-hr)
j_{sur}	Simulated hourly VOC emission (g/m^2-hr)
$j_{sur,m}$	Measured hourly VOC emission (g/m^2-hr)
K	Overall mass transfer coefficient (m/s)
K_H	Henry's law constant (mol/kg-atm)
k_{sg}	Diffusion-dispersion coefficient for gaseous phase (m^2/s)
l	Distance from center to the upper edge of a simulation layer (m)
L	Thickness of simulation layer (m)
$lyr, lyr-1$	Lower and upper layers, respectively
m_i	Molal concentration of VOC *i* (mol/kg)
MAE	Mean absolute error
MW_{VOC}	Molecular weight of VOC of interest (g/mol)
P_i	Partial vapor pressure of VOC *i* (atm)
P_{sat}	Saturated vapor pressure of VOC *i* (atm)
P_T	Total vapor pressure of solution (atm)
$R_{s/m}$	Ratio of simulated to measured emissions
$RMSE$	Root mean square error
t	Cumulative exposure time (s)
T	Silage temperature (°C)
TMR	Total mixed ration
u_*	Friction velocity (m/s)
V_{flow}	Hourly flow rate of air through the sampler (m^3/hr)
VOC	Volatile organic compound
x_i	Mole fraction of VOC *i* in aqueous phase
y_i	Mole fraction of VOC *i* in gaseous phase
α	Effective surface mass transfer coefficient (m/s)
ρ_{dry}	Dry bulk density (kg/m^3)
$f_{1,s}(\rho_{dry})$	Represents the first term in calculating surface layer depth for silage storages, a function of dry bulk density
$f_{1,f}(\rho_{dry})$	Represents the first term in calculating surface layer depth for feed lanes, a function of dry bulk density
$f_{2,s}(\rho_{dry})$	Represents the second term in calculating surface layer depth for silage storages, a function of dry bulk density

$f_{2,f}(\rho_{dry})$	Represents the second term in calculating surface layer depth for feed lanes, a function of dry bulk density
$f_{3,s}(\rho_{dry})$	Represents the equation in calculating the depth of second simulation layer for silage storages, a function of dry bulk density

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Abstract

Our previous work (Chapter 1) has shown that dairy silages are a major emission source of volatile organic compounds (VOCs) and to some unknown degree of oxides of nitrogen (NOx), both contributing to the San Joaquin Valley's (SJV) ozone challenges. In general, emission of VOCs from silage can be mitigated by either 1) reducing VOC production in the liquid/solid phase of the silage pile, or 2) reducing relative emission from the face of the silage pile or the feedlane. While NOx mainly forms in the initial phase of ensiling, the current research focused on the later stages of storage and feedout of silages; therefore, the NOx picture of the present report is incomplete and requires further research. The focus of the present research was on monitoring and modeling of VOC production using silage additives (Chapter 2), as well as emissions mitigation via various silage storage methods, de-facing practices, and feed management approaches (Chapters 3 & 4). Microbial and chemical silage additives were investigated using bucket silos, to reduce the production and emissions of volatile organic compounds in corn silage. The VOC concentrations were measured using headspace gas chromatography method. For the field monitoring of emissions from different silage storage and defacing methods, we used flux chambers and wind tunnels that were attached vertically on the silage face, immediately after de-facing. These sampling devises were attached to a fully equipped mobile air quality lab, in which concentrations of all relevant gases were analyzed in situ. This set-up allowed us to compare different storage methods (i.e. conventional standard pile vs silage bag), and defacing methods (e.g., perpendicular, lateral, and rake extraction), as well as various water inclusion rates for the feed all aiming at reducing emissions. The monitoring data was used to inform and validate a new VOC process-based model that was developed to predict VOC emissions from silage sources on farms using theoretical relationships of mass transfer and parameters determined through our earlier (published) laboratory experiments and numerical modeling. The results for the silage additive studies showed, that most microbial and chemical additives actually increase VOC production and emissions. Only one chemical additive used at one particular concentration, reduced VOCs. The results for silage storage indicated that silage bags vs. conventional silage piles emit considerably fewer emissions. Furthermore, lateral defacing versus perpendicular- and rake defacing reduced emissions of most gases. Finally, reducing of emissions in the feed lane seems to be possible via inclusion of water to the TMR. Simulations of all relevant silage mitigation options that were studied on the commercial dairies, were conducted using the VOC modeling tool. These simulations clearly showed that most of the reactive VOC emissions on a California dairy occur from feed lying in feed lanes during feeding as opposed to the silage storage pile or bag. In conclusion, regulations aimed at reducing VOC emission could be ineffective or even increase emission if they promote silage additives without recognition of different types of additives. The monitoring results of the storage and defacing study results point at certain practices as being advantageous. However, one shall not view those monitoring results in isolation, because only the integration of other parts of the feed's life cycle, using whole farm modeling, explains not just the relative- but also the absolute effectiveness of mitigation techniques in reducing VOCs and NOx on the entire dairy. The whole farm modeling clearly showed that mitigation efforts should be applied to reducing emissions from feeding rather than focusing solely on those from the exposed face of silage piles.

Executive Summary

Our previous work has shown that dairy silages are a major emission source of volatile organic compounds (VOCs) and to some unknown degree of oxides of nitrogen (NOx), both contributing to the San Joaquin Valley's (SJV) ozone challenges. Most recent studies on emission of silage VOCs and NOx have sought to identify and quantify the major VOC and NOx components of silage emissions through field or laboratory measurements (Alanis et al., 2008; Chung et al., 2009; Howard et al., 2010; Montes et al., 2010; Hafner et al., 2010; Malkina et al., 2011; Hafner et al., 2012), while two studies have looked at ozone formation through computer simulations (Howard et al., 2010; Hu et al., 2012). Literature on mitigation strategies for environmental pollutants from silages is extremely sparse and mainly related to minimizing dry matter losses and deterioration of feed quality. Most is known on the use of silage covers and additives to maintain high quality of silage and to reduce DM losses. In general, emission of VOCs from silage can be mitigated by either 1) reducing VOC production in the liquid/solid phase of the silage pile, or 2) reducing relative emission from the face of the silage pile or the feedlane. Therefore, the focus of the present research was on monitoring and modeling of VOC production using silage additives (Chapter 2), as well as emissions mitigation via various silage storage methods, de-facing practices, and feed management approaches (Chapters 3 & 4). The present research primarily addressed mitigation techniques and technologies outlined in SJVAPCD Rule 4570 addressing VOC and NOx production and emissions.

Chapter 1 of the present report is a comprehensive review of the literature around various topics as they relate to the air impacts of silage and, to the extend available, possible mitigation. The chapter clearly shows the considerable complexity and heterogeneity of processes leading to emissions and the need to assessing the topic of silage air emissions using a holistic life cycle approach. The four main phases of silage production, storage, and use are distinctively different from each other and addressing only one phase via mitigation, might likely lead to emissions downstream. Furthermore, it is apparent that while the body of literature on the ensiling process is rich, hardly any work has been reported on emission mitigation from a dairy farm.

Chapter 2 shows the effectiveness of various microbial and chemical silage additives in reducing gaseous emissions from silage. The research found that the addition of the chemical silage additive potassium sorbate may substantially reduce production of ethanol and other important volatile organic compounds. Two of the most widely used microbial additives as well as a commercial buffered propionic acid-based product, strongly stimulated VOC production and emissions from silages. Regulations aimed at reducing VOC emission from silages via use of additives could be counterproductive if they promote silage additives without recognition of different types of additives and their course of action.

Chapter 3 provides monitoring data for a variety of silage mitigation techniques. One major aspect of this monitoring research is to provide gaseous emissions data to inform and validate the concurrent silage air emission modeling study (i.e. Chapter 4). The present monitoring study conducted alongside with the concurrent modeling study, shows that emission reduction potentials of one phase of silage management might be offset throughout later phases throughout the life cycle of the feed. For example, one might reduce emissions at the silage face through lateral- versus perpendicular defacing, but the compounds one might prevent from volatilizing at the face, might become airborne later during feeding in the feedlane. Similarly, silage bags have a much smaller face compared to the conventional silage pile; thus, emissions of the former are considerably lower. However, to benefit from these emission reductions, one must also devise a proper strategy to reduce emissions after feed-out from the bag or else, mitigation effects will be diminished in the feed-out phase. Overall, it is apparent that the most effective VOC mitigation efforts are those that minimize the air exposure time of freshly extracted- as well as freshly mixed feed to the atmosphere (e.g., silage face and feed-lanes).

In Chapter 4, the modeling aspects of the present work are presented. Using ethanol and methanol emission measurements from conventional silage piles, silage bags and feed lanes on a dairy farm in California (i.e., data presented in Chapter 3), evaluation showed that the former silage VOC emission modeling component of the Integrated Farm System Model (IFSM) performed inadequately. A new process-based model was then developed for predicting VOC emissions from silage sources on farms using theoretical relationships of mass transfer and surface emission, with simulation parameters refined through laboratory experiments and numerical modeling. Simulating emissions measured from the California dairy farm, the model worked well in predicting ethanol emissions but underpredicted methanol emissions. With a better performance, the new silage VOC emission model was incorporated as a component of the IFSM, where it was used to evaluate management and climate effects on VOC emissions along with other aspects of farm performance, environmental impact and economics. Simulations of a representative dairy farm in California indicate that most of the reactive VOC emissions occur from feed lying in feed lanes during feeding rather than from the storage pile. This implies that mitigation efforts should focus on reducing emissions during feeding rather than those from the exposed face of silage piles.

Chapter 1 - Background Literature on the Dairy Industry, Silage Practices, and Related Mitigation of Air Pollutants

United States Dairy Industry

The United States is home to 9,257,000 dairy cows and each cow produces on average 10,096 kg of milk per year. California accounts for twenty percent of the US milk production contributing 21 million tons of milk per year (Hoskin, 2014). The San Joaquin Valley (SJV) in California alone houses three quarters of California's dairy cow population. The combination of numerous emissions sources, including dairies, in the SJV and its topography present environmental and in particular air quality concerns because air pollutants remain within the airshed for prolonged periods of time. Along with numerous other sources of air pollution, the dairy industry contributes to the SJV as having one of the worst air quality conditions throughout the US (Garcia et al., 2013).

The dairy industry in the SJV is a contributor of ozone precursors, such as (VOCs) and (NOx). According to earlier estimates, the California Air Resources Board (CARB) listed dairy farms and associated waste as the second largest contributors to these ozone precursors (Chung et al., 2010). However, research discovered that the CARB estimations were approximately 9 times greater than the true ozone production from dairy animal waste (Shaw et al., 2007, Hu et al., 2012), which led to corrections of the inventory. The majority of the earlier emissions research on dairy farms encompassed manure, lagoons, animals, and heavy machinery (Schmidt, 2009). Animal feed was discovered to produce both VOCs and NOx (Maw et al., 2002). Animal feed includes, but is not limited to, a variety of products such as dried distiller grains (DDGs), almond hulls, cereals, hays, and fermented feed (silage).

A dairy farm typically has three types of production stages: calves, heifers, and dry and lactating cows. Diets fed reflect the production stage and associated nutrient requirements for the animal. Lactating dairy cows have one of the most demanding diets. Their energy demand supports pregnancy, lactation, and body maintenance. A total mixed ration or TMR is often used to fulfill their requirements and to maximize milk production efficiency (Driehuis and Elferink, 2000). A TMR is composed of cereal grains, fats, minerals, vitamins, forage, and a wide array of byproduct feedstuffs. The bulk of the costs associated with dairy farms is related to feed. Fermented feed such as silage, has a long shelf life, and can sustain the herd throughout the year. As such, most TMRs include silage, as a form of forage, as part of a balanced diet. Silage can compose of up to 60% of the total TMR and therefore is a major component of dairy cow diets. In addition to its many benefits as feed, it also has some consequences associated with it, namely the fact that it produces ozone precursors, which make it an environmental concern (Maw et al., 2002). With a majority of California dairies storing and feeding silage, research has been conducted to quantify their contribution to ozone forming potential (OFP). The VOC emissions were measured from animal feeds and the results showed that feeds had significantly higher emissions than other sources on a dairy, for example animal waste (Alanis et al., 2010, Malkina et al., 2011). Volatile fatty acids (VFAs), alcohols, and aldehydes make up the majority of VOCs found on dairy farms. However, silage has been shown to emit not just VOCs but also multiple species of NOx (Howard et al., 2010). The resulting emissions cause dry matter (DM) loss, environmental, and human health consequences. Mitigation and management of fermented feed can result in a win-win situation for both the environment and the dairyman's financial viability (Hafner et al., 2014).

Factors such as wind speed, temperature, moisture, and extraction methods can strongly alter emissions. Prior to ensiling, other production factors such as crop maturity, crop species, moisture content, and storage method affected the profile of compounds emitted (Rossi and Dellaglio, 2007). Each dairy varies in storage, extraction, and general silage management. Accurate emission projections can best be achieved through modeling of the important factors and management strategies present at a specific farm (Hafner et al., 2012); however, measurements under field conditions are needed to validate model predictions (Hafner et al, 2012).

Air Quality Regulations for the California Dairy Industry

As discussed above, the SJV is home to both the largest dairy herds and some of the worst air quality in the United States. The SJV experiences high levels of ozone and particulate matter pollution. According to National Ambient Air Quality Standards, mitigation techniques and technologies from all sources of pollution need to be managed and evaluated (Shaw et al., 2007). Ozone can affect day-to-day quality of life because of its potential to cause respiratory and cardiac diseases. California's air regulatory agencies consider dairies as a contributor to ozone pollution. Fermented feedstuff such as silage, rather than animal manure, were found to be the greatest source of ozone precursor gases from dairy farms (Alanis et al., 2010, Malkina et al., 2011, Hafner et al., 2013).

The San Joaquin Valley Air Pollution Control District (SJVAPCD) implemented rule 4570 in 2006 to limit emissions of VOCs from confined animal facilities (i.e. dairies, feedlots, layer houses etc.). For example, dairy mitigation strategies first revolved around fresh and stored manure management but in 2011, an amendment was added to include feed and silage emission management. The amendment mandates that farmers choose several mitigation measures to reduce gaseous losses from silages. A more detailed explanation of the rule can be found in the appendix of the present report along with specific examples of mitigation techniques. Rule 4570 not only provides regulatory restrictions but an opportunity to simultaneously minimize dry matter (DM) losses from feedstuff. A serious limitation of Rule 4570 is that many of the mitigation options contained therein have never been assessed for their efficacy in reducing gaseous emissions.

Over the past century, dairy farms in California have decreased and the number of milking cows per farm has increased (USDA, 2015). Silage is one of the main feed sources used in the dairy sector (Cherney and Cherney, 2003). In California, corn is typically chopped and ensiled in late summer to early fall for ensiling (Schukking, 1976). As previously mentioned, the summer schedule of corn ensiling coincides with the ideal conditions for ozone formation. The environmental impact of silage is 2-fold. The early ensiling process contributes NOx and the continued feed-out phase VOCs into the atmosphere (Maw et al., 2002, Chung et al., 2010). Dairy farms in the summer are potentially emitting both VOCs and NOx simultaneously and in close spatial proximity.

Silage

Silage Preservation

Entire crops such as corn, sorghum, and other forages can be chopped, compacted, and preserved as silage, a fermented feed, to be fed to animals throughout the year. Silage is less weather dependent than hay making and is mechanized more easily. Silage is better suited than hay to large-scale livestock production systems and is adapted to a wider range of crops (Bolsen and Heidker, 1985). Criteria for a crop to ensile properly include knowledge of DM content, moisture, buffering capacity (resistance to acidification), plant maturity, plant species, and sugar content (Zaunmüller et al., 2006). Corn is an ideal silage crop because of its sugar content, buffering ability, and DM content; whereas alfalfa is more difficult to preserve as silage (Blezinger, 2000). Grasses generally contain more water soluble carbohydrates (WSC) and have less resistance to acidification than legumes (Bolsen et al., 1996).

Prior to harvest, chemical properties such as plant maturity and moisture content are important to measure. If maturity and moisture conditions are met, the plant is chopped and ensiled. Various forages such as alfalfa may be left in the field to wilt to 50-60% moisture before ensiling (Pitt, 1990). The amount of time needed for the crop to wilt is dependent on the plant species, environment, and desired moisture content (Nash, 1959). Not all plants require time to field wilt before ensiling, as can be seen in the case of corn, which has a whole crop moisture range of 55-75% (Johnson et al., 1999). Generally, the higher the moisture content the faster the forage ensiles. The abundant supply of water soluble carbohydrates (WSC) is utilized by micro-organisms and the metabolism of WSC causes a rapid pH drop (Perry et al., 1967, Coblentz et al., 1998). In silage making, plants are first chopped to desired particle size. Particle size is important in obtaining optimal compaction rates and nutritional digestibility (Yang et al., 2001). Chopped feed is then placed into its respective storage containers and compacted in layers. In California, compaction is mainly achieved by two methods. The first method involves a tractor rolling over the transverse plane of the pile in layers, a process that generates the "conventional standard pile". The second method uses a conveyer belt to feed the chopped forage in a horizontal fashion into a 'silage bag" (aka "Ag bag") followed by pressure compaction (Johnson et al., 1982). Compaction is essential in removing as much oxygen as possible from the silage, thus reducing porosity. Compaction is inversely linked to porosity, which decreases as compaction increases (Hafner et al., 2010). Pores are areas where oxygen can pool, slowing down the ensiling process and decreasing the silage quality (Stadhouders and Spoelstra, 1990). A swift transition from an aerobic to anaerobic environment minimizes nutritional loss and maximizes preservation (Jaster, 1995). If the transition of an aerobic to anaerobic environment is slow, it can harbor the growth of unfavorable micro-organisms, clostridials, which are capable of causing secondary fermentation (Spoelstra, 1983, Leibensperger and Pitt, 1987). Quickly creating and maintaining an anaerobic environment are critical factors in producing high quality silage and avoiding the negative impacts of plant respiration, plant proteolysis, and aerobic microbial activity (Muck, 1988). Any delays in covering the ensiled material or inadequate sealing, negatively impacts silage quality (Denoncourt et al., 2007). A delay in covering causes the retardation of temperature and pH changes necessary for fermentation. Quality silage preservation is most susceptible during the first and final phase of silage making (phases outlined below). Knowledge of how to minimize the effects of the driving forces of emissions such as air speed, temperature, porosity, and surface roughness will improve management decisions to improve silage quality, the ensiling process, and as a result, lower the emission profile. An increase in any of these physical properties will result in excessive gas loss and DM loss (Hafner et al., 2012).

Silage Production Phases and Gas Production

The ensiling process undergoes four distinct phases. Each phase has unique characteristics and differs by pH, temperature, microbial populations, and gas production.

Phase 1 - Aerobic Phase

Phase 1 represents the chopped plants being compacted and covered with gas tight plastic tarp. This aerobic phase lasts for approximately two days. Major gaseous losses of NOx and CO_2 occur during Phase 1 (Burger and Jackson, 2003) in which cellular respiration breaks down plant sugars causing the production of CO_2, NOx, heat, and water (Hopkins and Hüner, 1995). Plant respiration eliminates oxygen from the pile contributing to the anaerobic environment inside the silage pile. Plant proteases simultaneously break down proteins into amino acids, ammonia, peptides, and amides (Johnson et al., 2002). The conversion of sugar to acid is vital for the preservation and fermentation of silage. Sugars are the main substrate for lactic acid bacteria to produce the acids needed to preserve the crop as silage (Bolsen et al., 1996). Plant enzymes and microorganisms, such as aerobic fungi and spoilage bacteria, remain active because the pH is still within their favorable conditions (i.e. 6.0-6.5) (McGarvey et al., 2013). Toward the end of this phase, temperature increases and pH begins to decline. The low pH limits a majority of enzymatic activity (Vuuren et al., 1989).

Phase 2 - Fermentation Phase

During phase 2, lactic acid, acetic acid, and ethanol are produced. The production of acids and alcohols causes the pH of the silage to drop and the temperature of the silage to increase. Yeast fermentation of the ensiled plant material produces the alcohols needed for preservation (Ranjit et al., 2002). The ensiled forage heats up to 32 °C and pH levels drop to 5.0 (temperature and pH ranges are unique and specific to plant type and effective storage system). The fermentation phase lasts approximately 21 days, facilitating the growth of anaerobic micro-organisms (Seglar, 2013). The organisms compete with lactic acid bacilli (LAB) for the remaining fermentable carbohydrates. All soluble carbohydrates are believed to be metabolized to lactic acid, mannitol, ethanol, and acetic acid after 44 days (Neureiter et al., 2005). The end products of LAB are desired for their preservation characteristics, while the former organisms yield no preservation properties. Enterobacteria can no longer replicate when the pH drops below 5 and as a result, most enterobacteria are depleted with in the first three days of ensiling (Lin et al., 1992). If a rapid transition to an anaerobic environment fails to occur, clostridial growth occur. Clostridials cause the forage to undergo additional fermentation yielding the production of butyric acid, which leads to DM and digestible energy (DE) loss, which reduces silage quality that contributes to lowered DM intake by cows. Silage core sampling may be used to monitor the favorable microorganism population.

Most dairy producers observe their silage piles for the production of what is commonly known as “silage gas” (i.e. NOx), which causes the gas tight barrier to expand and if not released, tear the plastic cover, making the silage susceptible to aerobic deterioration (Seglar, 2013). Once the majority of NOx has left the pile, the storage pile is resealed from the environment for storage. Ideal conditions after the fermentation phase will render the corn silage pile at a pH of about 4 (Pahlow et al., 2003).

Phase 3 - Storage Phase

During the storage phase, the microbial community is dominated by lactic acid bacteria (LAB) effectively lowering the pH and stabilizing the silage (Driehuis et al., 2001). During this phase, silage has become preserved and will remain in storage until feed-out to animals. The pH range remains around 4 and silage temperature (species dependent) averages at 30°C. The low pH prevents the growth of most fungi and spoilage bacteria. Some undesirable micro-organisms, such as clostridia and bacilli, can remain present in the storage phase but continue to lay dormant until phase 4, aka the feed-out phase. The storage phase is of lesser importance with respect to air emissions due to minimal occurrence of physical and chemical changes. Routine inspection of the pile for oxygen exposure is important to the continued preservation of quality silage. Re-exposure to oxygen, leaks, and tears, will promote yeast and mold populations and some pathogens such as Listeria *monocytogenes* (Perry and Donnelly, 1990, Duh and Schaffner, 1993). Micro-organisms such as clostridial spores, yeasts, molds, and *enterobacteriaceae* negatively impact the quality of silage (Dunière et al., 2013).

Phase 4 - Feed-out Phase

The feed-out phase leads to aerobic deterioration (aka spoiling of the feed), due to the re-exposure to oxygen, and is the major phase of VOC gas losses (Courtin and Spoelstra, 1990). Oxides of nitrogen emissions are also lost from the feed-out phase and any further agitation of silage prior to reaching the feed lane (Maw et al., 2002). Oxygen activates the production of aerobic bacteria, mold, and yeast activity at the exposed silage face. The silage face increases in temperature (>43°C) and pH (pH of 7) (Borreani and Tabacco, 2010). The change in temperature and pH makes the environment favorable to the undesired micro-organisms. These micro-organisms consume the nutrient rich lactic acid, acetic acid, and other soluble products. The consumption of these soluble products leads to the production of CO_2 and water, which causes the temperature increase at the face of the pile (Pitt et al., 1991). Caution should be given to yeasts and bacteria if they reach a population of 10^7-10^8 colony forming units per gram (cfu/g) of silage, or molds reach 10^6-10^7 cfu/g. High bacterial and yeast populations cause the digestible components that can be utilized by cows including sugars and fermentation products to be rapidly lost (Dolci et al., 2011). Time required for heating to occur depends on four factors: number of aerobic microorganisms in the silage, time exposed to oxygen prior to feeding, silage fermentation characteristics, and ambient temperature (Bolsen et al., 1996). These four factors vary even between silage piles with the same forage and management. Woolford (1990) quantified under laboratory conditions that a rise in 8-12°C above the ambient temperature causes DM losses at approximately 1.5-3.0% DM.

Silage Air Emissions

Volatile Organic Compounds (VOCs)

Dairies emit VOCs from many sources including animal waste, bedding, flush lanes, and free stalls. Little is known about VOCs from animal feeds and how they compare with other VOC emitters such as light duty vehicles. In 2010, research was conducted on six dairies in the California's SJV with six locations within each dairy being tested (Chung et al., 2010). The locations measured were the silage storage pile, TMR within the free stall barns, the bedding, the flushing lanes, the open lots, and the lagoon to create an emissions profile. A total of 48 VOCs were identified with substantial variation across and between dairies and sources within a dairy. Silage and TMR (containing silage) were the greatest contributors to VOCs amongst the six locations (Chung et al., 2010). Compounds found in silage included but were not limited to alkanes, alkenes, aromatics, carbonyls, alcohols, and halogenated organics. Ethanol made up the majority of the VOC profile from silage followed by ethyl acetate, acetone, and 2-propanol. Compounds such as alkanes and aromatics also contributed to the emissions profile of silage, but were still several orders of magnitude smaller than ethanol.

The reactivity of these VOCs can also be expressed as ozone formation potential (OFP). The OFP from animal feed can be quantified and compared with other pollution sources on similar scale. Howard et al (2010) conducted a study evaluating seven common animal feeds: cereal silage, alfalfa silage, corn silage, high moisture ground corn, almond shells, almond hulls, and TMR (55% corn silage, 16% corn grain, 8% almond hulls, 7% hay, 7% bran and seeds, and 5% protein, vitamins, and minerals). The objective of that work was to measure the OFP of these animal feeds and provide estimations for the source of VOCs and their ozone formation compared with light duty vehicles. Alcohols accounted for about half of the ozone formation for the measured feed types. Alkenes were significant in corn silage, alfalfa silage, and TMR. Acetaldehyde contributed about 25-30% of ozone formation in cereal silage. The OFP of these feeds range from 0.4 g-O_3 per g-VOC to 0.2 g-O_3 per g-VOC. Light duty vehicles in comparisons have an OFP of 0.7 g-O_3 per g-VOC. The OPF of animal feed on confined animal facility (CAF) is 25 ± 10 t O_3 day^{-1} was estimated compared with 13 ± 1.3 t O_3 day^{-1} of light duty vehicles. The consumption of these feeds was also evaluated and although almond hulls may have a larger OFP they make up a smaller contribution in a TMR as compared with silages. Based of the Department of Agriculture's census for animal numbers and the ozone production of corn silage, total emissions were calculated to be approximately 20 ± 9.5 t day^{-1} (Census of Agriculture, 2007, Howard et al., 2010) .

Ethanol is a major contributor at >70% of VOCs from animal feed; therefore the flux of ethanol's emission rate becomes a crucial part of the problem (Howard et al., 2010, Malkina et al., 2011). Based on plant maturity at harvest, ethanol ranged from 0.45 to 2.7 % of DM in the subsequent corn silage (Sheperd and Kung Jr, 1996). As much as 40% of the ethanol emissions were lost from recently extracted silage piles within the first 5 hours (Shaw et al., 2007). The percent lost between silage piles varied and could be attributed to packing density of the silage pile. Poor packing density caused the silage pile to sustain a semi-aerobic environment. Sufficient acid production was still observed under semi-aerobic environments, but there were fewer formed metabolites (Neureiter et al., 2005, Hafner et al., 2010).

Studies have then translated packing density to measured emissions from silage faces, i.e. extracted and exposed silage. The high variation of measured emissions from feed sources presents challenges when using traditional models. Process-based models incorporate parameters that influence VOC emissions and have more accurately quantified emissions from silage (Zhang et al., 2009, Hafner et al., 2012). Additional variations were present in the mode of transport of VOCs from the silage into the atmosphere (Hafner et al., 2012). The mass transfer model of ethanol emissions developed from a convective transport model, and it addresses the pathway of ethanol emissions from the liquid to gaseous phase in thin layers of corn silage. The final mathematical model for ethanol emissions can predict ethanol emissions in the silage as a function of initial ethanol concentration and exposure time (Hafner et al., 2012). The mass transfer coefficient of ethanol was also calculated against temperature and air velocity. The results illustrate, two orders of magnitude greater mass transfer coefficient of ethanol from 15 °C at 0.2 m s^{-1} to 35 °C at 2.5 m s^{-1}. Ethanol contributes as much as 10 g m^{-2} h^{-1}, the majority of the compound released within 10h, and follows an exponential emission decay curve over time (hours) (Hafner et al., 2012, Hafner et al., 2013).

Oxides of Nitrogen (NOx)

The oxides of nitrogen emissions present an environmental concern, a potential parameter for quality silage (i.e. progression of fermentation and overall quality), and a worker health hazard.

Oxides of nitrogen are a precursor in ozone formation. Documented animal feed related emission sources of NOx are not as well defined as those for VOCs. The NO_2 is the only compound of the NOx family that the EPA regulates because of its prevalence and it is both an air pollutant and a precursor to ozone and acid rain. The EPA has created NAAQS for the tropospheric ozone. The primary and secondary standard for NO_2 is 0.053 ppm (Lyndon Cox, 1999).

Nitrogen dioxide in the atmosphere reacts with air and UV radiation to create nitric oxide (NO) and ozone (O_3). The UV radiation releases free radicals from VOCs that can react with NO. Free radicals can then recycle the newly formed NO back to NO_2. The recycling of NO to NO_2 continues until the carbon chains in the VOCs are no longer photo sensitive. Typically, five rotations of the recycling process can occur, providing many opportunities for ozone formation (Grano, 1997). The NO_2 can also be readily absorbed in atmospheric moisture to produce acid rain and undesirable environmental effects.

There are seven NOx species: nitrous oxide (N_2O), nitric oxide (NO), dinitrogen dioxide (N_2O_2), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5). With regards to silages, the main species of interest are NO (colorless gas/slightly water soluble), NO_2 (red-brown gas/water soluble and decomposes in water), and N_2O (colorless gas/water soluble) (Ataku, 1982). According to the EPA, mobile sources account for 50%, electric power plants 20%, and “everything else” 30% of the NOx emitted in the US. Identifying the sources emitted from the “everything else” category could help the nation reduce overall NOx emissions and achieve proposed NAAQS standards (EPA, 2015).

The process of ensiling is one of the unaccounted sources of NOx emissions. Nitrate is found in plants naturally and also in other anthropogenic sources i.e. fertilizers (Lindsay et al., 1981). The majority of nitrate is broken down in the feedstuff during the ensiling process. The degradation of nitrate is related to high pH levels and high ratios of NH_3-N to total N. A high pH and high ratio of NH_3-N to total N constitute unfavorable conditions in the ensiling process and retard the rapid transition to an acidic anaerobic environment (Spoelstra, 1985). The ensiling process causes the reduction of nitrate and starts producing nitrite, nitrogen oxides, and ammonia within the first week (Ohshima et al., 1978, Spoelstra, 1985, McDonald et al., 1987, Henderson, 1993, Petersen et al., 2006). The first phase of ensiling contains microbes such as *enterobacter sp., lactobacillus plantarum*, and *clostridium tyrobutyricum.* These microbes can all reduce nitrate (Ohshima et al., 1978, Spoelstra, 1983, Bolsen et al., 1996) and lead to the reduction of nitrate to nitrite, nitrite to ammonia, and the release of nitrogen oxides (Hasan and Hall, 1975). The nitrogen oxides can be formed from the interaction of nitrate and organic acids with by-products of water (Grayson, 1956). Research has been conducted to correlate the reduction products of nitrate to overall improved silage quality (Ohshima et al., 1978, Ataku, 1982, Spoelstra, 1983, Spoelstra, 1985).

Oshima et al., (1978) characterized high quality silage by having low pH, high lactic acid content, low VFA concentration, and low volatile basic nitrogen (VBN). Their research compared two experiments of ensiled ladino clover. Each experiment had silage enriched with a glucose additive and silage without additive. Silage with glucose added had a pH range of 3.96-4.02 compared with the silage without added glucose, which showed pH values of 4.55-4.62. Silage with glucose added had almost twice as much lactic acid present and half the percentage of VFAs and VBNs. High-sugar crops have reported low pH levels that plateau for quality preservation and low ammonia production. Low-sugar crops are not able to reach similar acidic conditions, increase pH over days ensiled, and yield high ammonia production (Wilkins, 2013). Oshima et al., (1978) also found that density had no effect on nitrite content but nitrogen oxide gas production increased with density (with and without glucose added). A greater density may be correlated to a better compaction rate and oxygen expulsion and the compaction minimized the activity of aerobic bacteria (Ohshima et al., 1978). Ataku et al. (1982) found that the majority of nitrate was reduced in the first phase of ensiling and no additional reduction of nitrate was found in the remaining stages of ensiling. Further research showed that nitrate reduction could be completed by both aerobic and anaerobic microorganisms throughout the phases despite low pH levels and an anaerobic environment (Henderson, 1993).

Recent research has been conducted measuring the oxides of nitrogen throughout the ensiling phase, storage phase, feed-out phase, and associated agitations prior to reaching the feed lane (i.e. mixer wagon, extraction from pile, etc.) (Maw et al., 2002). These workers also reported that the majority of NOx measured at the face of the silage was approximately 95% NO and 5% NO_2. Peak concentrations of NOx in corn silage ranged from 460-2137 ppbv (Maw et al., 2002). The variation was likely due to the seasonality effects of ambient temperatures (e.g. warmer temperatures increase NOx). In addition, NOx emissions increased as the exposed silage face area increased and time exposed to air increased (Maw et al., 2002, Montes et al., 2010). Maw et al., (2002) reported that after seven months of ensiling, corn silage placed in the mixer wagon and agitated produced significant amounts of NOx, approximately 1700 ppbv compared with background levels of 21 ppbv. Maw et al., (2002) reported that the NOx emissions that were lost, posed minimal effects on nutritional content, but instead presented a health risk to people as well as animals, and were an environmental pollution concern (i.e. ozone production).

Silo-filler's disease, a health condition caused by a reddish brown (i.e. NO_2) gas, is responsible for pulmonary injury (Fleetham et al., 1978). Silo-filler's disease is a result of the fermentation process of silage. As previously mentioned, crops contain nitrate, and nitrate is converted to nitrites with organic acids to make nitrous acid. The transition from phase 1 to phase 2 of ensiling incorporates rising temperatures. The temperature increase caused nitrous acid to decompose into water and NOx (Ramirez and Dowell, 1971). Nitrogen dioxide (NO_2) is the reddish brown gas with its pungent odor. The NO_2 concentrations in phase 1 of ensiling increase with fertilization, lack of water, and immature plant harvest (Fleetham et al., 1978). Inhalation of NO_2 is toxic and can be fatal depending on the dose and duration of exposure. The NO_2 readily reacts with water in the respiratory epithelium to form nitric- and nitrous acids. The resulting acid formation can cause severe burns, pulmonary edema, bronchoconstriction, and inflammation (Jiang et al., 1991, Zwemer Jr et al., 1992). The toxic gas appears within the first couple days and can last up to a week (Reid et al., 1984). Nitrogen dioxide was reported to be a dense cloud of orange gas covering the silage or pooling in silo buildings (Wang and Burris, 1960, Zwemer Jr et al., 1992). Ramirez and Dowel (1971) illustrated the partitioning of NOx within a silo. Nitrous acid occurs toward the base of the silage, whereas NO, the colorless gas, travels toward the silage surface. Once in contact with air, the NO becomes NO_2, the reddish brown gas, settling on the surface. The N_2O_4 is present within the proximal head space of the silo, characterized by a yellow gas. Symptoms from Silo Filler's Disease can be the result of acute exposure and/or chronic low-level exposures (Goldstein et al., 1977). Symptoms of the disease could be overlooked and unaccounted for because of the rare prevalence of the disease. Silo-Filler's disease is also common to industrial exposure of nitrous fumes. Silage consequently presents a risk to workers and animals acutely when ensiling occurs and with chronic low level exposure in poorly ventilated buildings (Ramirez and Dowell, 1971).

Mitigation Strategies for Gas Emissions and Nutritional Losses in Silage

In general, mitigation strategies for environmental losses from silages is sparse and mainly related to minimize DM losses and deterioration of feed quality. Most is known on the use of silage covers and additives to maintain high quality of silage and to reduce DM losses.

Silage Covers

Silage making reduced farmers' dependency on the weather and minimized potential losses when harvesting grasses. However, the storage of silage presents a large initial investment. Silos and silage bunkers are well established storage venues for ensiled material across the United States but may present feasibility challenges for a farm to be profitable (Savoie, 1988). The agricultural industry has also adopted the use of low density polyethylene (LDPE), high density polyethylene (HDPE), and linear low density polyethylene (LLDPE) in their operations (Briassoulis, 2007). Polyethylene (i.e. plastic film) provides farmers an alternative storage system to silage management. The plastic film can vary in composition and layers, but typically provides UV resistant, specific thickness, and gas-tight properties for proper ensiling.

Savoie (1988) researched the costs associated with plastic covers, optimal thickness, and DM losses. He devised several modeling equations to quantify the optimal characteristics to ensile high quality feed. The equations involved the cost of the plastic, which increased with size and thickness, the permeability and volumetric infiltration rate of oxygen, oxygen consumption of carbohydrates, and DM losses. Oxygen consumption rate was determined as a gram of oxygen needed by microbes to consume 0.9375 g of soluble sugars and was reported as DM loss (Wood and Parker, 1971). Thickness varied from 25 μm to 400 μm with a corresponding permeability of 1.95-0.12 cm atm^{-1} h^{-1}. The DM losses were reported as a percent (%) per 30-day period. Dry matter losses during the 30-day period were between 0.16 and 2.44% with the 400 μm polyethylene cover. Monthly intervals accounted for temperature differences and their influence on DM loss. Polyethylene cover thickness recommendations for a 120-day storage period were 0.0120 cm and for 360-day storage a thickness of 0.0200 cm. Additional cover thickness should be factored for pest control and environmental damage (Savoie, 1988).

Gaseous emissions and nutrient losses were affected by plant species, chemical composition of the forage, oxygen, physical preparation, preservatives, temperature, storage, and moisture content (Gordon, 1967). The most common way to determine total DM losses is the comparison between amount of feed ensiled and removed silage for feed-out. The three main routes for total DM constituents losses were: effluent or liquid loss, spoilage or unsafe to feed, and gaseous loss (Gordon, 1967). Controlling moisture levels and crop maturity prior to ensiling minimized DM loss. Recommended moisture levels for a specific crop facilitated favorable conditions for lactic acid bacteria, but the duration of wilting required could influence the cost benefit (i.e. DM loss) (Wilkinson, 1981).

Emissions from silage were largely driven by air velocity, temperature, porosity, and surface area (Alanis et al., 2010, Chung et al., 2010, Montes et al., 2010). Hafner et al. (2010) provided estimates of the rate of ethanol emissions from loose corn silage, quantifying the effects of temperature, air velocity, and exposed surface area on ethanol emission rates, and assessed the accuracy of the US EPA emission isolation flux chamber method for measuring VOC emissions from loose silage. Hafner et al. (2010) concluded that the VOC emission rate from loose corn silage was high initially and declined rapidly to plateau over time. Temperature, air velocity, and different silage types had significant effects on the overall emissions of ethanol (Muck, 1988, Elferink et al., 2000, Alanis et al., 2008, Hafner et al., 2010). Temperature and air velocity had the largest effects on VOC emissions (Montes et al., 2010). Emissions increased by a factor of 4 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 (Hafner et al., 2010, Hafner et al., 2013). Low density or high porosity silage, increased surface area between silage particles for oxygen and aerobic bacteria to negatively impact silage quality and promote VOC emissions (Hafner et al., 2013). The resulting VOC emission losses continued with loosely packed silage piles post-extraction, excess mixing time in the TMR wagon, and prolonged exposure time in the feed lanes (Hobbs et al., 2004, Hafner et al., 2010).

Silage Additives

The fermentation process can vary based on silage moisture, maturity, nitrate levels, and storage type. Research on silage additives has been conducted in order to minimize variability of the above mentioned parameters and enhance the ensiling process for the production of quality silage (Buxton and O' Kiely, 2003). In the 1970s, the addition of glucose was reported to improve silage quality and depress the nitrate reduction process. The glucose treated silages yielded lower pH values (Ohshima et al., 1978). The use of additives were further studied to minimize DM loss, rapidly lower pH, support desired microorganisms, limit secondary fermentations, and maximize quality and preservation (Merensalmi and Virkki, 1991). Enzyme inoculant mixtures of cellulose, xylanase, cellobiase, and glucose oxidase were reviewed to ascertain their effects on ensiling corn. The inoculant mixture had no effect on silage pH but did increase titratable acidity, reduced fiber components, and promoted partial degradation of structural carbohydrates. The reduction of fiber components improved nutritional value of the silage and subsequent animal performance (Stokes and Chen, 1994).

The factors influencing the preservation of crops as silage include enzymes and micro-organisms. The enzymes involved are respiratory, proteolytic, and polysaccharide-degrading enzymes. Major micro-organisms that can alter crop preservation, emissions, and nutrient quality are lactic acid bacteria, enterobacteria, clostridia, fungi (yeasts and molds), bacilli, listeria, acetic acid bacteria, and propionic acid bacteria (Henderson, 1993). Most forage crops other than corn should be harvested at the driest time of day and field wilted for approximately 24 hours. Research is still required to reduce DM loss, improve animal performance, and reduce losses throughout the ensiling phases (Henderson, 1993).

While numerous microbial additives have been reported to improve silage quality, research on decreasing gaseous emissions is at a nascent stage. Many of the microbial additives that have been studied (including *lactobacillus buchneri*, *lactobacillus plantarum*, and propionic acid mixtures) were originally believed to reduce the production of VOCs emissions but the following chapter is the first work that shows actual efficacy of that claim.

Chapter 2 - Effects of Silage Additives on Gaseous Emissions[1]

Task 1: To investigate the effects of selected microbial and chemical silage additives on air emissions

Abstract

The objective of this chapter was to evaluate the effects of microbial and chemical silage additives on the production of volatile organic compounds (VOC) (methanol, ethanol, 1-propanol, methyl acetate, and ethyl acetate) within corn silage. Recent work has shown that silage VOC can contribute to poor air quality and reduce feed intake. Silage additives may reduce VOC production in silage by inhibiting the activity of bacteria or yeasts that produce them. We produced corn silage in 18.9 L bucket silos using the following treatments: 1) control (distilled water); 2) *Lactobacillus buchneri* 40788, 400,000 colony-forming units (cfu) per g wet forage; 3) *Lactobacillus plantarum* MTD1, 100,000 cfu/g; 4) a commercial buffered propionic acid-based preservative (68% propionic acid, containing ammonium and sodium propionate and acetic, benzoic, and sorbic acids), 1 g per kg wet forage (0.1%); 5) a low dose of potassium sorbate, 91 mg per kg wet forage (0.0091%), 6) a high dose of potassium sorbate, 1 g per kg wet forage (0.1%); and finally, 7) a mixture of *L. plantarum* MTD1 (100,000 cfu/g) and a low dose of potassium sorbate (91 mg/kg). VOC concentrations within silage were measured after ensiling and sample storage using a headspace gas chromatography method. The high dose of potassium sorbate was the only treatment that inhibited the production of multiple VOC. Compared to the control response, it reduced ethanol by 58%, ethyl acetate by 46%, and methyl acetate by 24%, but did not clearly affect production of methanol or 1-propanol. The effect of this additive on ethanol production was consistent with results from a small number of earlier studies. A low dose of this additive does not appear to be effective. While it did reduce methanol production by 24%, it increased ethanol production by more than two-fold, and did not reduce ethyl acetate. All other treatments increased ethanol production at least two-fold relative to the control, and *L. buchneri* addition also increased 1-propanol to approximately 1% of DM. No effects of any treatments on fiber fractions or protein were observed. However, *L. buchneri* addition resulted in slightly more ammonia compared with the control. If these results hold under different conditions, a high dose of potassium sorbate will be an effective treatment for reducing VOC production in and emission from silage. Regulations aimed at reducing VOC emission could be ineffective or even increase emission if they promote silage additives without recognition of different types of additives.

Introduction

Silage contains numerous volatile organic compounds (VOC), including organic acids, alcohols, esters, aldehydes, and ketones (Hafner et al., 2013). Volatile organic compounds present in silage can contribute to poor air quality (Howard et al., 2010), and reduce feed intake by livestock (Weiß and Auerbach, 2012; Gerlach et al., 2013). Both problems could be addressed through the use of silage additives if VOC production can be reduced by inhibiting the activity of the bacteria or yeasts that produce them. Both biological additives (usually consisting of lactic

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[1] The present chapter has been published in the peer reviewed literature: Hafner, S.D., R. B. Franco, L. Kung Jr, C.A. Rotz, and F.M. Mitloehner. 2014. Potassium sorbate reduces production of ethanol and 2 esters in corn silage. *Journal of Dairy Science*. 97:7870-8.

acid bacteria) and chemical additives are commonly used to reduce fermentation losses, improve silage quality, and improve aerobic stability (Duniere et al., 2013). In general, effects of these additives on VOC have not received much attention, but several studies have reported effects of additives on ethanol production during ensiling. Ethanol may be produced by at least four groups of microorganisms present within silage: lactic acid bacteria, enterobacteria, clostridia, and yeasts (Hafner et al., 2013). Excluding acetic acid, it is generally the most concentrated VOC present in corn silage (Hafner et al., 2013) and contributes to the production of additional VOCs—ethyl esters (Weiß and Auerbach, 2009, 2012, 2013), and possibly acetaldehyde (Hafner et al., 2013). Biological additives have been reported to increase or decrease ethanol production in silage, or even have no effect (see review in Hafner et al., 2013). However, a small number of studies have reported large reductions in ethanol production with the addition of potassium sorbate. Teller et al. (2012) found that 0.1% addition of potassium sorbate (fresh mass basis) reduced ethanol production in corn silage by at least 70%. Kleinschmit et al. (2005) reported that 0.1% of a 1:1 mixture of potassium sorbate and ethylenediaminetetraacetic acid (EDTA) (fresh mass basis) reduced ethanol production in corn silage by 80%. Weiß and Auerbach (2012) reported a 70% reduction in ethanol by addition of a commercial mixture of sodium benzoate and potassium sorbate (21.9% sodium benzoate, 13.2% potassium sorbate, applied at 0.2% (Kirsten Weiß, Humboldt Universität Berlin, Germany, personal communication)) to corn silage. Furthermore, production of two esters (ethyl lactate and ethyl acetate) was reduced by at least 45%. In another study, Queiroz et al. (2013) found that 0.1% addition of sodium benzoate (fresh mass basis) reduced ethanol production in corn silage by 68%. Auerbach and Nadeau (2013) found reductions of 73% to 85% in ethanol production in corn silage treated with two commercial products containing potassium sorbate, sodium benzoate, and, in one product, sodium nitrite (potassium sorbate application ranged from 130 to 300 mg/kg, while sodium benzoate application ranged from 250 to 515 mg/kg). Most recently, Bernardes et al. (2014) evaluated two doses of potassium sorbate or sodium benzoate (0.1% and 0.2%). All treatments reduced ethanol by at least 54%, and the high dose of potassium sorbate was most effective, reducing ethanol by 85%.

The protonated form of the sorbate ion, sorbic acid, is toxic to many microorganisms (Lambert and Stratford, 1999). This uncharged molecule diffuses through cell membranes, and may acidify the cytosol, which would interfere with the proton gradient used for ATP production and with other cellular processes (Beek et al., 2008). Natural acidification of silage increases the ratio of sorbic acid to sorbate, and therefore, would be expected to increase this inhibitory effect. Yeasts, molds, and most Gram-negative bacteria are generally sensitive to sorbic acid, but lactic acid bacteria are not (Emard and Vaughn, 1952; Woolford, 1975). Because yeasts and enterobacteria may be responsible for production of many silage VOC, their inhibition would be expected to reduce VOC production (Hafner et al., 2013).

Confirmation of the effects of potassium sorbate on ethanol and ester production is needed. Furthermore, it is important to determine the effect of potassium sorbate on other important VOC. In the present study, our objective was to evaluate the effect of potassium sorbate and other additives on the production of three alcohols and two esters: methanol, ethanol, 1-propanol, methyl acetate, and ethyl acetate. These compounds were selected because they are among the most significant silage VOC from an air quality perspective (Hafner et al., 2013), and are relatively easy to measure. Ethanol is generally the single most important compound emitted from corn silage, based on its relative effect on air quality (Hafner et al., 2013). However, other compounds that may have a significant effect on air quality under some conditions, such as some aldehydes, were not included.

Materials and Methods

Silage production

Corn silage was made from a single batch of forage collected from a commercial dairy farm. Each silage additive was applied to a single subsample of forage that was divided among six replicate buckets after mixing. The process of applying additives and mixing was done by the same people using the same method all on a single day to minimize confounding handling effects, so differences were expected to have a negligible effect on measured variables. Corn forage, at approximately 25% DM, was harvested from a commercial dairy farm in Elk Grove, CA on September 22, 2012 and chopped in the field to a nominal length of 10-15 mm. Treatments were applied in 1.0 L of distilled water applied to 75 kg of wet forage using spray bottles, and the forage was thoroughly mixed using shovels and rakes on the top of plastic tarps. To avoid cross-contamination, tarps were either new or disinfected with a 10% bleach solution, thoroughly washed, and then dried for each treatment.

Treatments were: 1) control (distilled water only); 2) LB: *Lactobacillus buchneri* 40788 (Lallemand Animal Nutrition, Milwaukee, WI) 400,000 colony-forming units (cfu) per g wet forage; 3) LP: *Lactobacillus plantarum* MTD1 (Ecosyl Products Ltd., Stokesley, UK), 100,000 cfu/g; 4) PA: a commercial buffered propionic acid-based preservative (68% propionic acid, containing ammonium and sodium propionate and acetic, benzoic, and sorbic acids; total concentrations of acids 82% by mass; Kemin Americas, Des Moines, IA), 1 g per kg wet forage (0.1%); 5) PSL: a low dose of potassium sorbate, 91 mg per kg wet forage (0.0091%); 6) PSH: a high dose of potassium sorbate, 1 g per kg wet forage (0.1%); and finally, 7) M: a mixture of *L. plantarum* MTD1 (Ecosyl Products Ltd., Stokesley, UK) (100,000 cfu/g) and the low dose of potassium sorbate (91 mg/kg), added separately. Potassium sorbate was 99.0% pure (Sigma-Aldrich, Germany). Twelve kg of each treated forage was then manually compressed in 18.9 L buckets. Buckets were covered with tight-fitting lids, which were installed with silicone caulk to ensure a gas-tight seal. Excess silage gas accumulated in 5 L tedlar gas bags (SKC-West Inc., Fullerton, CA) attached to the bucket silo lids using a plastic through-wall connector sealed with a rubber o-ring. Each treatment was replicated six times and all bucket silos were stored inside an unheated building with air conditioning in summer months. The temperature inside the building was not monitored during the entire trial but based on limited measurements ranged from approximately 15°C to 27°C. Outside temperature during this period ranged from 3°C to 43°C.

Bucket silos were opened after 303 days, and the top 10 cm of silage was removed and discarded as a precaution in case any air infiltration had occurred. Samples (approximately 100 g) were collected from a depth of 10-20 cm and immediately (within 5 min.) vacuum packed in polyethylene/nylon bags (FoodSaver, Sunbeam Products, Jarden Consumer Solutions, Boca Raton, FL) where they remained until analyzed. Vacuum-packed samples were stored under refrigeration (about 4°C), apart from one week at about 20°C due to an equipment failure. Five of the six replicates were analyzed for VOC over a period of 66 d after opening the silos, and the last set of replicates were analyzed 170 d after opening the silos. A second set of vacuum-packed samples were shipped on ice to a commercial laboratory and analyzed for all other analysis within four weeks of opening the silos.

Silage analysis

Concentrations of methanol, ethanol, 1-propanol, methyl acetate, and ethyl acetate were measured using a headspace gas chromatography procedure. About two hours prior to analysis, vacuum-packed bags were removed from refrigeration, N_2 gas was added using a needle, bags were resealed with tape, and the samples were allowed to warm to room temperature. Then, a 1.0 mL gas sample was removed using a gas-tight syringe and manually injected in a Varian CP 3800 GC with an 0.53 mm (inner diameter) capillary column with an 0.5 µm SPB-1000 coating (Supelco Analytical, Bellefonte, PA, US). Split injection was used, with a split ratio of 5:1 and an injector temperature of 75°C. Carrier gas was N_2 at 10 mL/min. The oven temperature was 35°C, and the flame ionization detector temperature was 250°C. Standards were produced by mixing a stock mixture of pure compounds in water, and were equilibrated with an air phase in 125 mL jars with a septum in the cover (I-Chem Septa Jars, Fisher Scientific, Hampton, NH) alongside bagged silage samples. Standard solutions were made using pure compounds (methanol, ethanol, 1-propanol, and methyl acetate were ≥99.9% pure; ethyl acetate was 99.8% pure; all Sigma Aldrich, St. Louis, MO, USA) in 18 MΩ-cm deionized distilled water. Chilled pure chemicals were originally combined in a stock mixture with no water, which was stored below -18°C, and added to water to make standards each time the GC was used. Headspace samples from the standards were removed and injected as with silage samples. Compounds were identified based on retention time relative to ethanol. Retention times within 2.5% of expected values were accepted (based on results from the standards), although 6% was allowed for two injections where carrier gas flow appeared to differ slightly from the standards), and were quantified using peak height to minimize the influence of overlapping peaks. Typical relative standard deviation for the method was 2-10%, depending on the compound and the sample. The underlying mechanism of this headspace method is a fixed aqueous-gas partitioning coefficient (i.e., concentration ratio) for each individual compound at a given temperature. If the partitioning coefficient is identical in solution standards and silage solutions, a calibration curve determined from headspace samples taken from aqueous standards can be used with the FID response from silage samples to directly calculate aqueous-phase concentrations without determining gas-phase concentrations. These aqueous phase concentrations can be converted to a dry mass basis using the corrected DM. Evaluation of this headspace method is described in the online data supplement.

Silage dry matter content, fiber fractions, crude protein, organic acids, 1,2-propanediol, pH, and yeast counts were determined by a commercial laboratory (Cumberland Valley Analytical Services, Cumberland, MD, USA). Dry matter was determined by oven drying at 60°C for 4.5 h in a forced-air oven, followed by grinding and then additional drying for 2 h at 105°C. Dry matter values were corrected for loss of volatile compounds by assuming that 8% of lactic acid and 95% of the acetic acid (based on Weißbach and Strubelt, (2008)), 100% of NH_3 (based on Porter and Murray (2001)), and all VOC mass (based on the 100% estimate made by Weißbach and Strubelt, (2008) for alcohols) was volatilized during drying). For determination of pH, ammonia-N, organic acids, and 1,2-propanediol a 25 g sample of silage was mixed with 200 mL of deionized water. The sample mixture sat overnight, was blended for 2 min and then filtered through coarse filter paper (20-25 µm particle retention). Sample pH was measured using a 30 mL subsample. Ammonia-N was measured by distillation and titration. L-Lactic acid was measured with a YSI 2700 Select Biochemistry Analyzer (YSI Inc., Yellow Springs, Ohio), and multiplied by two for an estimate of total lactic acid. For determination of 1,2-propanediol and acetic, propionic, and butyric acids, 3 mL of extract was filtered through a 0.2 µm filter membrane and a 1.0 µL sub-sample was injected into a Perkin Elmer AutoSystem gas chromatograph (Perkin Elmer, Shelton, Connecticut) using a Restek column packed with Stabilwax-DA (Restek Corporation, Bellefonte, Pennsylvania) and a flame ionization detector. Helium was used as the carrier gas, and injector, oven, and detector temperatures were 225°C, 150°C, 150°C, respectively. Nitrogen content was determined by total combustion of the sample using a LECO CNS 2000 Analyzer (LECO Corp., St. Joseph, MI) and was multiplied by 6.25 to obtain crude protein. Soluble protein content was determined using the borate-phosphate buffer procedure by Krishnamoorthy et al. (1982). Samples were analyzed for neutral detergent fiber (NDF) using sulfite and amylase (Van Soest et al., 1991) and acid detergent fiber (ADF) was determined using the AOAC Official Method 973.18 (AOAC, 2000a). Starch was measured using the procedure described by Hall (2009). Yeast and mold counts were measured using the AOAC Official Method 995.21 (AOAC, 2000b). The detection limit for yeast and mold was 1000 cfu/g (wet mass basis).

Data analysis

Linear regression with dummy variables to represent the treatments was used in R (v. 3.02, R Core Team, 2013) for data analysis. “Treatment” coding was used with the control group as the baseline. Each treatment was compared to the control response using separate *t* tests with a single pooled estimate of the standard error of the difference (calculated using the “summary” method for “lm” objects). The type I error rate α was set at 0.05, and the Bonferroni adjustment was applied for the comparison, resulting in an α of 0.00833. All VOC concentrations were log-$_{10}$-transformed to account for error distributions closer to log-normal than normal and to eliminate heteroscedasticity. Means of VOC concentrations presented below are back-transformed values, and standard errors were also back-transformed and expressed as a relative value, using the formula $10^{SE_l} - 1.0$ where SE_l is the standard error of $\log_{10}$-transformed data. Standard errors were not expressed as a percentage to avoid confusion with units of % of DM. Because of values below the detection limit for yeast count, these results were analyzed using a nonparametric approach, the Wilcoxon Rank Sum Test, with the Bonferroni correction. Analysis of covariance was used to assess the effect of storage duration at 4°C on VOC concentrations. The lm function was used as above for this analysis, but storage duration was included as a covariate. For each compound, both the overall effect of duration and separate effects for each treatment were evaluated using *t*-tests, with α = 0.05 and no adjustment for multiple comparisons. Lastly, multiple linear regression (also with the lm function) was also used to assess correlation between esters, alcohols and acetic acid.

Results

Fresh forage composition and typical silage properties are summarized in Table 1. Dry matter content was lower than recommended values for corn silage (typically 30-40%). Silage pH, lactic acid, and acetic acid were within the range of typical corn silage with DM of 30%-40% (Kung and Shaver, 2001), with some exceptions: lactic acid was above 7% in the control (7.87%) and PSL (7.18%), and acetic acid was well above 3% in LB (5.73%). Additionally, propionic acid was above 0.1% in PA (0.18%), presumably due to addition of the compound, and also very high in LB (1.3%). The LB treatment markedly increased acetic acid production, markedly reduced lactic acid, and increased pH ($P < 0.001$ for each). All other treatments moderately reduced lactic acid production, and apparently did not change acetic acid production, resulting in a decline in lactic acid:acetic acid ratio for all treatments relative to the control. The LB treatment slightly increased production of ammonia (by 0.026% of DM, $P < 0.001$). Additives did not affect the concentrations of total or soluble crude protein, fiber fractions, or starch.

Table 1. Characteristics of corn silage treated with biological and chemical additives[1]

	Treatments							*Pooled*
Item	*C*	*LB*	*LP*	*PA*	*PSL*	*PSH*	*M*	*SE*
DM	27.5	26.7	26.8	27.4	26.6	27.5	27.0	0.255
pH	3.68	4.08***	3.70	3.69	3.68	3.77*	3.75	0.022
CP	7.66	7.67	7.67	7.83	7.67	7.45	7.67	0.127
NH_3	0.134	0.16***	0.129	0.145	0.128	0.127	0.126	0.00342
ADF	30.7	31.2	30.5	30.9	31.7	30.6	32.4	0.545
NDF	45.6	47	46.8	46.6	47.6	46.9	48.2†	0.708
Starch	22.3	21	22.2	22.1	20	21	19.8	0.846
Yeasts[2]	<3.70	<3.00	6.88*	6.46*	6.67*	<3.00	6.73*	0.278
Lactic acid	7.87	1.8***	6.87**	5.97***	7.18*	6.57***	6.41***	0.173
Acetic acid	1.14	5.73***	1.22	1.26	1.26	1.31	1.25	0.105
Lactic:acetic	6.95	0.324***	5.64***	4.76***	5.74***	5.05***	5.18***	0.255
Propionic acid	n.d.	1.28	n.d.	0.179	n.d.	n.d.	n.d.	n.d.

[1] Abbreviations used for means are: C, control; LB, *Lactobacillus buchneri 40788*, 400,000 cfu/g; LP, *Lactobacillus plantarum MTD1*, 100,000 cfu/g; PA, buffered propionic acid-based preservative; PSL, potassium sorbate, 0.0091% of wet forage mass; PSH, potassium sorbate, 0.1%; M, *Lactobacillus plantarum MTD1*, 100,000 cfu/g, plus potassium sorbate, 0.0091%. Number of replicates was 6 for all groups. The symbol n.d. indicates no detection. 1,2-Propanediol was detected only in silage treated with *L. buchneri*, where it was 1.01% of dry matter. All results are given as percent of DM except pH and yeasts. Ammonia is expressed as % of DM as N. Statistical significance is based on comparisons of each group to the control with the Bonferroni adjustment: †$P < 0.10$, *$P < 0.05$, **$P < 0.01$, ***$P < 0.001$.

[2] Units are $\log_{10}$(colony-forming units/g) on a wet mass basis, and the detection limit was 3.0. All replicates for PSH and all but one replicate for C and LB were below the detection limit. Asterisks show results of comparisons to C, with the single high value excluded, or LB or PSH (identical results for each).

Mold counts were below the detection limit (10^3 cfu/g) for every sample. Additives appeared to have effects on yeasts, but it was difficult to conclusively detect differences using the control group in comparisons, since one of the six replicates had a high yeast count and the remaining five replicates were at or below the detection limit. Counts in both LB and PSH were below the detection limit (10^3 cfu/g) for almost all samples, and it was not possible to determine if these results were any different from the control treatment. But all other treatments appeared to increase yeast counts by at least 2800-fold whether compared to the control samples with the high value omitted or to LB and PSH samples

The most concentrated VOC present in the silages (Table 2) was ethanol, which ranged from 1,440 to 10,100 mg/kg (0.15 to 1.0% of DM) based on mean values. The LB samples, where 1-propanol reached 10,200 mg/kg (1.1% of DM), were an exception. Silage additives had clear effects on production of some VOC, but in many cases additives actually stimulated their production (Table 2). *Lactobacillus buchneri* stimulated production of all three alcohols and both esters relative to the control treatment. The largest relative increase due to an additive was seen in this treatment, where 1-propanol was approximately 400-fold the control mean ($P < 0.001$). Additionally, 1,2-propanediol was about 1% of DM in these samples, but was not detected in any others. All additives except PSH substantially increased production of ethanol. The increase ranged from 2.0-fold ($P < 0.001$) by LB to 3.0-fold ($P < 0.001$) by PA. Conversely, all treatments except LB and PSH reduced methanol production, albeit slightly—the largest reduction was 24% by PSL ($P < 0.001$).

Table 2. Mean concentrations of volatile organic compounds (mg/kg, DM basis) in corn silage treated with biological and chemical additives, measured using a headspace gas chromatography method[1]

	Treatments							*Pooled*
Item	*C*	*LB*	*LP*	*PA*	*PSL*	*PSH*	*M*	*SE*[2]
Methanol	538	696***	415***	450**	409***	470†	402***	0.0368
Ethanol	3450	6810**	8400***	10100***	7780***	1440***	9420***	0.138
1-propanol	25.6	10200***	43.3	47.7	42.3	14.1	38.6	0.309
Methyl acetate	9.91	28.9***	8.52	8.63	7.83	7.48*	8.85	0.0713
Ethyl acetate	20.5	168***	38.5**	61.8***	29.1	11.1**	47.7***	0.132
TOFP[3] (O_3 mg/kg DM basis	5421.0	16529.5	12588.7	15111.3	11672.9	2428.5	14072.4	0.5

[1] Abbreviations used for means are: C, control; LB, *Lactobacillus buchneri 40788*, 400,000 cfu/g; LP, *Lactobacillus plantarum MTD1*, 100,000 cfu/g; PA, buffered propionic acid-based additive; PSL, potassium sorbate, 0.0091% of wet forage mass; PSH, potassium sorbate, 0.1%; M, *Lactobacillus plantarum MTD1*, 100,000 cfu/g, plus potassium sorbate, 0.0091%. Number of replicates was 6. Statistical significance is based on comparisons of each group to the control with a *t* test using the pooled standard error (*SE*) and the Bonferroni adjustment: †$P < 0.10$, *$P < 0.05$, **$P < 0.01$, ***$P < 0.001$.

[2] Pooled *SE* was calculated from $\log_{10}$-transformed values, and the values here are relative values calculated by $10^{SE_l} - 1.0$, where SE_l is the standard error of the $\log_{10}$-transformed values.

[3] Total Ozone Forming Potential (TOFP) was the sum of the 4 VOC concentrations multiplied by their Maximum Incremental Reactivity (MIR) values.

The high dose of potassium sorbate (PSH) was the only treatment that reduced concentrations of multiple VOC: it reduced ethanol by 58% ($P < 0.001$), ethyl acetate by 46% ($P = 0.0014$), and methyl acetate by 24% ($P = 0.0068$). Conversely, the low potassium sorbate treatment (PSL) increased ethanol production and did not reduce ethyl acetate concentration (42% increase, $P = 0.052$). Ethanol concentrations were more variable in the control samples than in most other groups, which affected the precision and power of all estimates of relative effects on production of this compound. The control sample with the highest ethanol concentration (9120 mg/kg, about 2.7-fold the mean value) was also the one with the most yeasts ($\log_{10}$ cfu/g = 7.20), but other variables were similar to mean values. To determine if the apparent reduction in ethanol by PSH was caused by a small number of particularly high samples in the control treatment, a comparison was made without this highest and without the control sample with the second-highest ethanol concentration (7460 mg/kg, about 2.2-fold the mean value). In this case the mean concentration in the control group was 2230 mg/kg, for an apparent reduction by PSH of 36% instead of 58% (95% confidence interval: 15% to 53% from a two-sample *t*-test).

It is possible that potassium sorbate can reduce production of other alcohols as well. The mean methanol concentration for PSH was slightly lower than the control, but the *P* value (0.014) was above the critical value. However, PSL did reduce methanol (described above). For 1-propanol, the PSH mean was about 50% smaller than the control mean, but there was some overlap between the two groups, and the comparison *P* value (0.13) was much higher than the adjusted critical value. Additional experiments will be needed to assess effects on these compounds. Importantly, there is no evidence that PSH increased production of any VOC.

Ester concentrations were strongly correlated with their respective alcohols and acids. Based on least-squares regression using results from individual samples, the concentration of ethyl acetate could be related to ethanol (e) and acetic acid (a) concentrations (all in mg/kg) by: $-31.6+0.00465e+0.00291a$ (adjusted $R^2 = 0.958$, $P < 0.001$ for each term). Similarly, methyl acetate could be related to methanol (m) and acetic acid by: $-4.11+0.0194m+0.000338a$ (adjusted $R^2 = 0.957$, $P < 0.001$ for each term).

Only one bucket showed signs of air infiltration: mold was present at the surface of a low potassium sorbate replicate, but measured variables for this silage were similar to the other replicates and it was not excluded. In general, there was little evidence that storage duration of vacuum-packed samples at 4°C affected VOC concentrations. Only ethyl acetate in the control ($P = 0.007$) and PSL ($P = 0.024$) treatments, and ethanol in the control treatment showed significant responses to storage duration (all positive, 0.96% d^{-1} or less). An overall effect of storage duration was detected for ethyl acetate only ($P = 0.0046$), but this appeared to be due to the apparent responses in the control and PSL samples. There were no clear trends with storage duration for other treatments.

Discussion

With the exception of PSH, the additives evaluated here were not effective at reducing VOC production under these ensiling conditions. It is useful to understand why these additives increased VOC production. Ethanol is the single most important VOC, but understanding effects of additives on production of this alcohol can be challenging, since it is produced by at least four groups of microorganisms present in silage: lactic acid bacteria, enterobacteria, clostridia, and yeasts (Hafner et al., 2013). Increases in ethanol production by LP, PA, PSL, and M are difficult to explain. Yeast activity may have played a role because, except for LB, all treatments resulted in higher yeast counts than PSH. But why yeasts may be stimulated, or less inhibited, when these additives are used is not clear. Alternatively, the ethanol increase due to LP and M treatments could be due to direct production through the facultative heterolactic fermentation by *Lactobacillus plantarum*. An increase in ethanol production due to addition of bacterial additives is not uncommon (Steidlová and Kalac, 2003; Kleinschmit et al., 2005; Tabacco et al., 2009; Queiroz et al., 2013). Increased ethanol production has also been reported in response to addition of a formic and propionic acid mixture (Weiß and Auerbach, 2012), but the mechanism is not clear.

The strong correlations between the acetate esters and alcohols and acetic acid suggest that reducing alcohol production will reduce ester production also, and so effects of additives on esters can largely be explained by effects on alcohols and acids. Correlation between ethyl esters and ethanol has been observed before and has been cited as evidence of abiotic esterification reactions in silage (Weiß and Auerbach, 2009; 2012; 2013). However, PSH reduced methyl acetate production without a clear change in methanol, which is not consistent with this explanation. Limited statistical power for detecting an effect on methanol may underlie this apparent inconsistency. Implications of alcohol conversion to esters for air quality are probably insignificant. The tendency of esters to form ozone is less than for alcohols, and so production of esters at the expense of alcohols would actually reduce effects on air quality. However, the low concentrations of esters compared to alcohols, shown here for just two esters but for other esters for corn silage in general (Hafner et al., 2013; Weiß and Auerbach, 2009; 2012; 2013; Gerlach et al., 2013) limit the impact of this conversion.

Concentrations of alcohols measured in these silage samples are within the wide range of values reported in earlier studies, as summarized by Hafner et al. (2013). But ester concentrations measured in this study are lower than those reported in other studies summarized in this work (Hafner et al., 2013) and reported since then (Gerlach et al., 2013). Gerlach et al. (2013) found mean ethyl acetate concentrations of 138 to 400 mg/kg in corn silage made with different chopping lengths and densities. In our measurements, the mean methyl acetate concentrations ranged from 7.5 to 29 mg/kg, and mean ethyl acetate ranged from 11 to 170 mg/kg. Variability in VOC concentrations among silages can be very high; based on empirical tolerance intervals for a set of silage samples from within the US, Hafner et al. (2013) estimated that 25% of silage samples will have ethanol and ethyl lactate concentrations more than a factor of 2.4 of the median value. The differences between the concentrations we measured and those reported in previous studies may be the result of this variability, but may also be due to biases of the measurement techniques.

The primary sources of methanol in silage have not been identified, but this compound may be produced from pectin demethylation catalyzed by plant enzymes (see review in Hafner et al., 2013). It is not clear why additives would affect this process, which can occur after harvest before additives are added.

In contrast with the other additives, the effects of LB on silage composition are consistent with the current understanding of this bacterium. *Lactobacillus buchneri* is added to silage to improve aerobic stability, which is thought to be a result of the higher acetic acid concentrations resulting from conversion of lactic acid to acetic acid (Oude Elferink et al., 2001) but could be due to other substances as well. However, *L. buchneri* is not recommended for wet silages, where it grows particularly well and can consume so much lactic acid that pH is substantially elevated (Nishini and Touno, 2005; Schmidt et al., 2005). This additive was probably not appropriate for the wet silage used in this work. *Lactobacillus buchneri* can produce ethanol directly through heterolactic fermentation of carbohydrates (Oude Elferink et al., 2001). Additionally, it produces 1,2-propanediol (Oude Elferink et al., 2001), which can result in propionic acid and 1-propanol production by the *Lactobacillus diolivorans* (Krooneman et al., 2002). Therefore, the increases in ethanol, 1,2-propanediol, propionic acid, 1-propanol compared to the control group, along with the effects on lactic and acetic acid described above, are consistent with high activity of *L. buchneri*. However, some of these effects are not typically observed for this inoculant. Conversion of lactic acid to acetic acid is generally more limited, propionic acid increases are typically not observed, and ethanol is not typically elevated when *L. buchneri* is used for corn silage (Kleinschmidt and Kung, 2006). Effects on ethanol and the organic acids are probably due to the stimulation of *L. buchneri* by high moisture. Whether the high moisture also affected the activity of *L. diolivorans* and therefore production of propionic acid and 1-propanol, or the population of this or related bacteria was particularly high for this forage is unknown. Effects of *L. buchneri* addition on 1-propanol have generally not been reported, but in at least two studies, addition of ≥ 100,000 cfu/g of *L. buchneri* led to large increases in production of the compound, up to 7160 mg/kg (Kristensen et al., 2010), and 14200 mg/kg (Driehuis et al., 2001), which encompass the mean observed in the LB samples. The reactivity of 1-propanol is higher than for ethanol (Carter, 2009), so effects of *Lactobacillus buchneri* on air quality will depend on 1-propanol production. For the LB samples, the potential effect of 1-propanol on air quality is about twice the effect from ethanol (based on the product of concentration and EBIR from Carter (2009)). At least for the wet silage used here, *L. buchneri* appears to be a very poor additive for the purpose of reducing VOC production. Additionally, the effects of this additive provide an example of potential complexities of additive effects on air quality. If 1-propanol were not measured, the potential effect of this treatment on air quality would be substantially underestimated, and in cases where ethanol production was suppressed, the direction of the estimated effect could be wrong.

The only treatment we evaluated that could reduce VOC emission under conditions of this study was PSH. The 58% reduction in ethanol based on all data is comparable to other studies summarized in the introduction (Kleinschmit et al 2005; Teller et al., 2012; Weiß and Auerbach, 2012; Queiroz et al., 2013; Auerbach and Nadeau, 2013; Bernardes et al., 2014), although smaller. The response of ethyl acetate to PSH was nearly identical to the result from Weiß and Auerbach (2012) in response to a sodium benzoate and potassium sorbate mixture. Our results provide further evidence that a sufficient dose of potassium sorbate can reduce ethanol production and the production of two esters, even under wet conditions. The mechanism behind the reduction in ethanol and ethyl acetate is probably inhibition of yeasts, although inhibition of enterobacteria could also play a role. It is surprising that the effect of a lower dose of this additive (PSL), which approximates the concentration most commonly used in practice, appeared to stimulate ethanol production.

It will be important for future research to evaluate the effect of PSH on production of these, and, ideally, other VOC. There were features of this study that may affect VOC production, and so other studies may find different VOC concentrations and possibly different effects of silage additives. The DM content, chemical composition, and composition of the native microbial population all could influence VOC production. And in this particular experiment, the ensiling period (303 days) was relatively long, which could influence both total production of different VOC and also relative effects of additives, since at least ethanol can be produced by multiple groups of microorganisms. The type of water used to dilute the microbial additives could affect their activity—here, we used distilled water, while tap water is typically used in the field. Additionally, microbial activity could have continued in vacuum-packed samples after the bucket silos were opened. The small amount of oxygen present in the samples immediately after vacuum packing could have stimulated growth of yeast or other microorganisms, which might have increased or decreased VOC concentrations through partial or complete oxidation, and also increased yeast counts. Gerlach et al. (2013) reported that ethanol and ester concentrations increased during storage of corn silage at room temperature in vacuum-packed samples, but increases were only observed for samples initially exposed to air for more than four days (Katrin Gerlach, University of Bonn, Bonn, Germany, personal communication). The samples in this work were exposed for less than five minutes. Some oxygen exposure usually occurs during full-scale silage production, so these conditions were not unlike typical silage production, but a more typical ensiling period and more controlled storage conditions would be better.

Conclusions

Silage additives can reduce production of volatile organic compounds in corn silage, but not all additives are equivalent. Addition of potassium sorbate at 0.1% (fresh forage mass basis) can substantially reduce production of ethanol, methyl acetate, and ethyl acetate, but a lower dose (91 mg/kg fresh weight) can increase VOC production. A commercial propionic acid-based product and the biological additives evaluated here can stimulate production of ethanol and ethyl acetate (and possibly 1-propanol) in corn silage. Regulations aimed at reducing VOC emission could be ineffective or even increase emission if they promote silage additives without recognition of different types of additives. Future work should be carried out to evaluate the effectiveness of potassium sorbate under different conditions, and at different doses. Additionally, it will be important to evaluate the effect on production of aldehydes.

Chapter 3 - Measurements of the Emission Reduction Benefits of Mitigation Strategies for Silage

Task 2: Emissions of VOCs and NOx from various defacing methods
Task 3: Emissions of VOCs and NOx from storage types
Task 4: Emissions of VOCs and NOx from TMR treated with water vs raw silage

Abstract

Silage management continues to be critical component of the dairy industry both economically and environmentally. The purpose of the present study was to identify air emission mitigation options for the silage storage and feed-out phases. The three main tasks were 1) to evaluate the emissions of VOCs and NOx from different silage storage types (conventional silage piles vs. silage bags), 2) to study the emissions of VOCs and NOx from different silage defacing methods, 3), and to reduce emissions of VOCs and NOx from a total mixed-ration (TMR) in the feedlane through the addition of water[2]. Experiments were conducted comparing emissions between conventional silage piles and silage bag using flux chambers that were attached vertically on the silage face immediately after de-facing (aka extraction) of silage material. Furthermore, different de-facing methods such as perpendicular, lateral, and EZ rake extraction, were compared to quantify the effects of extraction method on air emissions. Finally, the inclusion of water into the TMR at 0%, 5%, and 10%, aiming at emission reduction, were tested using flux chambers and monitored for 23 h. Overall, the scope of the present monitoring study was to measure emission losses from storage, and feed-out processes and to generate data to inform and validate a prediction model for silage air emissions (see chapter 4). The results indicated that silage bags vs. conventional silage piles emit fewer emissions when comparing the total exposed silage faces. When comparing different types of defacing methods, the lateral defacing technique appeared to emit fewer emissions compared to the EZ rake and perpendicular defacing. Finally, reducing emissions in the feedlane is possible by use of water to the TMR. Overall, the results of the present Chapter 3 shall not be viewed in isolation, because only the integration with the modeling results from Chapter 4 explain not just the relative- but also the absolute effectiveness of mitigation techniques in reducing VOCs and NOx on California dairies.

Introduction

Central California's San Joaquin Valley (SJV) has the highest concentration of dairy cows (Agricultural Statistics Board, 2008) in the United States. The SJV has long suffered from some of the country's worst air pollution (US EPA, 2008), and in particular high tropospheric ozone levels. The US Environmental Protection Agency (EPA) has designated the SJV as an "extreme non-attainment" area based on the federal 8-hour ozone standard. In order to attain the standard, the reduction of the ozone precursors including VOCs and NOx from all major sources is imperative.

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[2] Many oxygenated VOCs have a high affinity to stay in the liquid vs. the gas phase. The application of water to the feed is intended to make the VOCs stay in the liquid phase and to prevent them from volatilization into the atmosphere.

Silage is among the leading operational costs and a critical feed commodity on dairies and its continued use is essential to a highly productive and economically viable dairy industry. It is natural to assume that environmental gains can and must be made from mitigation research relating to VOC and NOx emissions from silage on dairies. There are also highly compelling economic reasons to pursue mitigation research, as the reduction of VOC emissions from silage can reduce the loss of nutrients and increase cow productivity and thus, the industry's economic potential. Emission losses are economic losses.

Our previous work conducted at UC Davis, showed that among various emission sources on dairies, silages were the largest source of both VOCs and NOx, posing a significant source of ozone precursors in the San Joaquin Valley (Howard et al. (2010). Alcohols, VFA, aldehydes, and multiple species of NOx were shown to be emitted from silage sources. Ethanol and methanol accounted for the majority of total VOCs emitted from silage sources but isopropanol, acetic acid, and acetyl-aldehyde were other major compounds emitted (Malkina et al., 2010, Zhang et al., 2010).

The VOCs and NOx gases are emitted during the distinct phases of the silage/feeding process, which include:
- The aerobic phase: when chopped material is piled, compacted, and covered,
- The fermentation phase: when silage material is sealed and fermented,
- The storage phase: when silage material is sealed and few emissions released,
- The feed-out phase: during which silage material is removed from the face daily,
- The daily mixing phase: when silage is mixed with other feedstuffs in a mixer wagon, and
- The daily feed-lane phase: during which feed is placed in the feed lanes.

For the purpose of the present study, the silage life cycle is defined by four production phases (aerobic, fermentation, storage, and feed-out phase, the latter including defacing, TMR mixing, and feed-lane feeding. Our recent research (see page x of the present report for a listing of peer reviewed papers related to silage topics) revealed the initial ensiling phase as the time of significant NOx release, yet its measurement is highly complex and even dangerous due to the toxic properties of these NOx gases and related safety concerns to the investigative team. The closed storage phase at which the pile is covered, produces minimal gaseous losses because the pH is too low for microbial activity. The open-face storage phase in which silage is extracted to feed cows, is clearly the major VOC loss phase of the pile: compounds are exposed to the atmosphere for many hours and dependent on the wind, temperature, and volatility of the compound, losses can occur rapidly. Finally, the mixing and feeding phases significantly contribute to losses of VOCs from dairies. Indeed, the actual feeding of cows at which feed is spread out over a relatively large area (i.e. feedlane in front of the cows) is the greatest contributor to gaseous losses on dairies (as shown in Chapter 4 of this report).

Earlier published work from our lab on monitoring and modeling of different silage types during numerous phases, showed high concentrations of emitted alcohols and other oxygenated species and lower concentrations of highly reactive alkenes and aldehydes (Malkina et al., 2011). Emission profiles also differ distinctively across silage/feeding phases. To complement our understanding of the complex issues around silage emissions on dairies, additional monitoring and modeling of these emissions throughout the entire life cycle of the feed were essential to be conducted on commercial dairies for the assessment of, and response to, the specific needs of the regional air quality in the SJV.

The present research for monitoring in described in Chapter 3 (and for modeling in Chapter 4) primarily addresses mitigation techniques/technologies outlined in SJVAPCD Rule 4570, addressing VOC and NOx emissions. The research was largely conducted on commercial dairy farms and assessed the effectiveness of Rule 4570 mitigation practices: namely different pile storage methods, de-facing practices, and feed moisture management.

Materials and Methods

General

Corn silage was made from the fields neighboring a dairy farms in the SJV of California. The chopped corn was placed in two types of storage systems: a conventional silage pile and a silage bag. Whole-plant corn was harvested at approximately 30% dry matter using a commercial flail chopper, providing a chop forage material with a cut length between 1 and 2 cm. The commercial flail chopper excavated an area of approximately 7.0 km for a week. Trucks drove adjacent to the chopper to facilitate continuous operation and transport the chopped forage to the silage storage site. Transport trucks reversed into the LX1214 Professional Silage bagger (Ag-Bag, WI). The silage bagger simultaneously pushed the truck forward and packed the silage into the silage bag in a straight line (see Photo 1 and 2). Trucks not used for the silage bagger were sent to a nearby location on the farm to form a conventional silage pile. An area of 1,020 m^2 was designated for the conventional silage pile. Wheel tractors were used to compact the freshly unloaded chopped corn, in a drive-over fashion. The compaction continued until the apex of the pile reached a height of 6.1 m. The pile was covered with two layers of gas tight plastic cover material and the plastic held against the silage surface using recycled tires to prevent oxygen exposure. Silage bags were sealed for approximately one week. The silage bag was monitored for excessive gas build up, if notable, gaseous pressure was released via small cut in the fabric. Once the silage bag stopped releasing gas, the so-called “blow hole” was sealed and patched.

The present gas monitoring research involved three separate main aspects: collection of silage core samples for GC analysis (for use in a concurrent modeling study; Chapter 4), the inclusions of water at 0%, 5%, and 10% of the TMR, and direct air emission monitoring from the silage face.

Photo 1. Chopped corn being delivered by truck into the ensiling machine.

Photo 2. The open tray area for chopped corn collection, and the silage bags (white) being filled at the dairy.

Sampling Equipment

The Mobile Agricultural Air Quality Laboratory (MAAQ Lab) measured ethanol, methanol, ammonia, NO, N_2O, NO_2, and methane.

The following equipment was available in the MAAQ Lab for real time sample collection and analysis.

1. An automatic control and data acquisition system,
2. An automatic gas sampling system,
3. An infrared photo-acoustic multi-gas INNOVA 1412 analyzer,
4. A TEI 55C methane and non-methane hydrocarbon analyzer,
5. A TEI 17i NH3 analyzer,
6. A TEI 46i N_2O analyzer.
7. Four flux chambers,
8. Two wind tunnels,
9. An Environics 4040 Gas dilution system.

In addition to the equipment listed above, both gas and solid samples were collected using bags and sorbent tubes, respectively, for laboratory analyses to be later conducted in UC Davis laboratories using GC, GCMS, and HPLC.

Following is a detailed description of the analytical equipment that was used.

Automatic control and data acquisition system

The automatic control and data acquisition system consisted of an industrial grade desktop computer, interface hardware, and interface software based on the Labview (National Instruments, TX) program. The system controls sample collection sequence and timing, acquires data from all analyzers and sensors, and sends the images of computer screen to registered users over internet for remote review of the current operational status.

Automatic gas sampling system.

The automatic gas sampling system involved an 8-port rotary valve, a manifold, a Teflon coated sampling pump, a bypass pump, a sampling flow meter, a temperature sensor, a relative humidity (RH) sensor, a pressure sensor, Teflon tubing, and particle filters. The sampling system collected gas samples from 8 different locations in sequence controlled by the automatic control and data acquisition system. Gas samples were pulled into the system by the Teflon coated pump through the rotary valve and fed to analyzers through the manifold. Sample lines that were not currently selected by the rotary valve for analysis were connected to the bypass pump for purging to keep the air in these sample lines fresh. All sensors of temperature, RH, pressure, and flow meter were used to monitor the performance of the gas sampling system.

INNOVA 1412 analyzer

The INNOVA 1412 (LumaSense Technologies Inc., Ballerup, Denmark) analyzer is an infrared (IR) photoacoustic multi-gas analyzer, which measures up to six gases including water vapor.methanol and ethanol in sequence . In addition to its ability for multi-gas measurement, the INNOVA 1412 is a sensitive gas analyzer and has a wide dynamic measurement range. Measurement ranges for methanol and ethanol were 0-14000 ppm and 0-8000 ppm with detection limits of 0.14 and 0.08 ppm, respectively.

TEI 55C methane and non-methane hydrocarbon analyzer

The TEI 55C (Thermo, MA) is a stable gas analyzer that can accurately measure methane in a wide range from 0 to 1000 ppm with 20 ppb detection limit using a Flame Ionization Detector (FID). Although the TEI 55C can also accurately measure non-methane hydrocarbons in a wide range, the non-methane hydrocarbon data were not used because these hydrocarbons cannot be separated.

TEI 17i NH_3 analyzer

The TEI 17i (Thermo MA, USA) is a chemiluminescence NH_3 analyzer. It directly measures NO, NOx ($NO+NO_2$), NOt ($NO+NO_2+NH_3$) separately by converting both NO_2 and NH_3 to NO. The difference between NOx and NO is NO_2 (NO_2=NOx-NO) and the difference between NOt and NOx is NH_3 (NH_3=NOt-NOx). The measurement ranges for NO, NO_2 and NH_3 were 0-20 ppm and the detection limit was 1 ppb

TEI 46i N_2O analyzer

The TEI 46i (Thermo, MA) is an infrared gas analyzer that can accurately measure N_2O in the range of 0-50 ppm at 0.02 ppm detection limit using a gas filter correlation technology.

Table 3 summarizes the detection limits and measurement ranges of each gases measured by above mentioned gas analyzers.

Table 3. Measurement ranges and detection limits of gas analyzers used in this study.

Gases	Molecules	Gas Analyzers	Detection limit (ppb)	Measurement range (ppm)
Methane	CH_4	Thermo 55C	20	0 - 1000
Nitric Oxide	NO	Thermo 17i	1	0 - 20
Nitrogen Dioxide	NO_2	Thermo 17i	1	0 - 20
Ammonia	NH_3	Thermo 17i	1	0 - 20
Nitrous Oxide	N_2O	Thermo 46i	20	0 - 20
Methanol	MeOH	Innova 1412	140	0 - 14000
Ethanol	EtOH	Innova 1412	80	0 - 8000

Flux chambers

Flux chambers can be used to determine air emission rate by measuring the gas concentrations, air ventilation rate, temperature, RH, and pressure in the monitoring environment. Flux chambers are suitable for emissions from small surface areas at any location, including commercial dairies. Because the ventilation rate is low in flux chamber sampling, gas concentrations inside the flux chamber can be measured using our gas analyzers. Although the flux chamber cannot be used to simulate the wind speed over a small surface area, this method has been widely used to determine the air emission rate.

The flux chambers (Odotech Inc., Montreal, Canada; see Photo 3) are made of acrylic resin with a volume of 64.5 L and consists of a cylindrical enclosure with a spherical top. Teflon tubing (50 cm, 6.35 mm OD) is installed around the inside circumference of the chamber to allow air to circulate throughout the chamber when connected to a compressed air distribution system. An opening on top of the chamber (fitted with a stainless steel Swagelok connector) is used to sample air. Of the remaining two openings on the flux chamber top, one is used for the thermo couple, and the other allows extra air to escape and equalized inside pressure while sweeping air and sampling (Sun et al., 2008).

Gas dilution system

The Environics 4040 (Environics Inc. CT) gas dilution system is used to mix the standard calibration gas with ultra-zero air to produce variable concentration gas mixture for multi-points calibration of gas analyzers. The current dilution rate of this dilution system was 100:1.

Safety Container

To ensure that researchers could safely work without the associated risks of silage avalanche, a 3m by 2m by 2m industrial safety container was used (see Photo 4). The safety container was fitted with a 2.4m wide roll-up door on the side, a 1m man door on the end, and a 36cm turbine vent on the roof. The safety container was moved to the desired location alongside the face of the silage pile with the use of a fork lift that had fork extensions. All silage face monitoring using the flux chambers, were conducted from within the safe environment of this safety container.

Photo 3. Flux chamber and wind tunnel sampling silage face within protective shipping container.

Photo 4. Safety container positioned next to defaced conventional silage pile via forklift.

Silage Sample Preparation

Silage core samples were obtained using a drill driven spiral-assisted uni-forage sampler (Star Quality Samplers Inc. AB, Canada) at a depth of 30cm. Samples were extracted from the silage core sampler and placed immediately into an airtight plastic bag. These bags were depressed and manually evacuated prior to being placed on dry ice.

Samples on dry ice were transported back to UC Davis for silage analysis. Sample preparation included placing 10 g of silage (±0.1) into a 120 ml plastic bottle. Then, 90 g of DI water (±0.1) were added to the 120 ml plastic bottle. Bottles were tightly closed and inspected for any leaks. The plastic bottles were placed on the wrist action shaker for 30 min. Post wrist action shaker, the samples were analyzed for pH. Samples were then centrifuged for 10 min at 5000 rpm. Supernatant was filtered using a 0.45 µm. Samples were acidified using ortho-phosphoric acid (10%) to a pH <2 before the injection into the GC. The GC conditions included DB wax 530µm × 30 m. Helium was used as a carrier gas at a flow rate of 5 mL min $^{-1}$. Oven temperature increased from 40°C by 5°C min-1 to 60°C, held for 1 min, and then increased by 25°C min-1 to a final temperature of 160°C. Inlet and detector temperatures were set at 170°C and 270°C, respectively. The VFA standards used for GC analysis included acetic acid, propionic acid, butyric acid, iso-butyric acid, valeric acid, and isovaleric acid.

Silage Emission Monitoring

Dairy staff defaced the silage piles twice a day for feedings at 0300h and 1200h. The safety container was placed against the silage face immediately following extraction. The flux chambers were set up vertically against the face of the silage face (see Photo 2) and inside the shipping container, then the flux chambers were connected using Teflon tubing to the MAAQ Lab. Gas sampling began within 30 min of defacing. The safety container and related equipment were removed prior to the 0300h feeding to minimize interference with dairy farm management. Datalogger probes (HOBOs) (Onset Computer Corporation, MA) were placed inside the flux chamber and safety container to continuously monitor for temperature, relative humidity, and moisture. The analyzers in the MAAQ Lab recorded the concentration of CH_4 (ppm), N_2O (ppm), NO (ppb), NO_2 (ppb), NH_3 (ppb), MeOH (ppm), and EtOH (ppm) every minute electronically. The emission rate of CH_4 (g/hr/m$^{2)}$, N_2O (g/hr/m$^{2)}$, NO (mg/hr/m$^{2)}$, NO_2 (mg/hr/m$^{2)}$, NH_3 (mg/hr/m$^{2)}$, MeOH (g/hr/m$^{2)}$, and EtOH (g/hr/m$^{2)}$ were determined in 1h averages for 14h.

Emission Calculations

Concentration samples analyzed in the flux chambers over the 15 minute period were truncated to remove the first five minutes and last two minutes of sample to prevent carry over effects. Total flux (mg/hr) was then calculated using the following equation:

$$Total\ flux = \frac{MIX \times FL \times 60}{V} \times MW \times Conv$$

where *MIX* is the concentration in either ppm or ppb, *FL* is the ambient air flow rate at 20 L/min, 60 is the conversion from minute to hour, *MW* is the molecular weight in grams per mole, *Conv* is a conversion factor of 10^{-3} for concentration in ppm and 10^{-6} for concentration in ppb, *V* is the volume of one molar gas at temperature T in liter/mole and is calculated as:

$$V = \frac{V_s \times T}{T_s}$$

where *Vs* is the standard volume 22.4 liters at 0^{0}C, *Ts* is the standard temperature 0^{0}C that equals to 273.15 K, *T* is the air temperature in K equaling to *T* in ^{0}C +273.15.

The emission rate by surface for the flux chambers (mg/hr/m^2) was calculated by:

$$Emission\ rate = \frac{Total\ Flux}{Surface\ area}$$

Water Inclusion on TMR and Silage

The effect of water inclusion rate into the TMR was measured at 0%, 5%, and 10%, respectively (see Photo 1). Total mixed ration samples were removed from the mixer wagon after mixing was complete and measured into 2 kg samples. All samples were collected at 1215 h and placed under the flux chambers by 1230 h. Samples were treated with the above water inclusion rates and placed under flux chambers for gas monitoring. The 2 kg sample was placed immediately under the flux chamber. Water was added to the TMR or raw silage samples, respectively. The samples were hand mixed for a homogenous sample and placed under the flux chambers. Gas measurements were collected for 23 hours. Three replications were performed and each included: a control (0% water), 5% water, 10% water, and raw corn silage for comparison.

Task 2: Emissions of VOCs and NOx from various defacing methods

Emissions of VOCs and NOx from the silage defacing process were compared using three types of extraction methods. The first extraction method was using a standard front-end loader parallel to the face. The second extraction method was a standard front-end loader defacing in a perpendicular fashion to the face. The third extraction method was using a de-facer attachment that had a rake-like appendage (aka EZ rake, Hanson, MN; see Photo 5). Using the first extraction method, the standard front-end loader defaced the pile in a lateral fashion or parallel to the face (aka smoothing action; see Photo 6). For the second extraction method, the front-end loader de-faced the pile in a frontal, perpendicular fashion (aka jagged action). Finally, for the third extraction method, the front-end loader received a rake attachment and during de-facing, the vehicle approached the pile in a perpendicular fashion (similar to the first), but extracted the face by combing the surface from top to bottom effectively shaving the surface layers (again, see Photo 6). During the present study, each method was conducted and measured for three days. Immediately after silage extraction, flux chambers were placed on the freshly excavated silage surface and connected via Teflon tubing directly to the MAAQ Lab and associated analyzers for measurements.

Photo 5. Standard front-end loader with quick connect to EZ rake attachment.

Photo 6. EZ rake defaced surface on left and lateral defaced surface on right of a conventional silage pile

Task 3: Emissions of VOCs and NOx from storage types

Emissions of VOCs and NOx from conventional silage piles were compared to those of silage bags during the open-face phase. The flux chamber was placed on each open face after perpendicular extraction with the standard front-end loader. The flux chamber was also connected via Teflon tubing directly to the MAAQ Lab and associated analyzers for measurements.

Task 4: Emissions of VOCs and NOx from TMR treated with water vs raw silage

Emissions of VOCs and NOx were analyzed from the TMR with water added at 0%, 5%, and 10% inclusion rate. Raw corn silage was also evaluated for VOCs and NOx emissions but without the addition of water (see Photo 7). The TMR was removed directly from the feed wagon and measured into 2 kg samples. The 2 kg samples were adjusted to appropriately incorporate the water percentage mentioned above.

Photo 7. Flux chambers located outside the MAAQ Lab sampling water inclusion rates and silage.

Results and Discussion

The present study shows effects of numerous silage storage and management schemes on gas emissions. The results from the current study (Chapter 3) were used to refine and validate our silage emission model (see Chapter 4).

Continuous monitoring of seven key gases including methane, ammonia, nitric oxide, nitrous dioxide, nitrous oxide, ethanol, and methanol was conducted for all experiments.

Defacing Method and Emissions on Conventional Silage Pile

The effects of defacing methods on the emissions of seven key gases (Figures 1-7) were reported as g/d/m^2 or mg/d/m^2 depending on the gas per surface area covered by the flux chamber. While measurement variability (expressed as standard deviation) were sometimes considerable, Figures 1-7 seem to show that lateral vs. perpendicular de-facing lead to fewer emissions. The EZ rake treatment did not seem to offer advantages in lowering emissions when compared to perpendicular extraction. The EZ rake treatment showed particularly high variability across different sampling dates. For most gases the EZ rake showed equal or greater emissions compared to perpendicular defacing. The defacing method greatly affects the roughness of the face and lateral defacing leads to the lowest roughness when compared to perpendicular and EZ rake de-facing. The lateral defacing treatment seems to be advantageous in reducing gaseous emissions during the defacing phase.

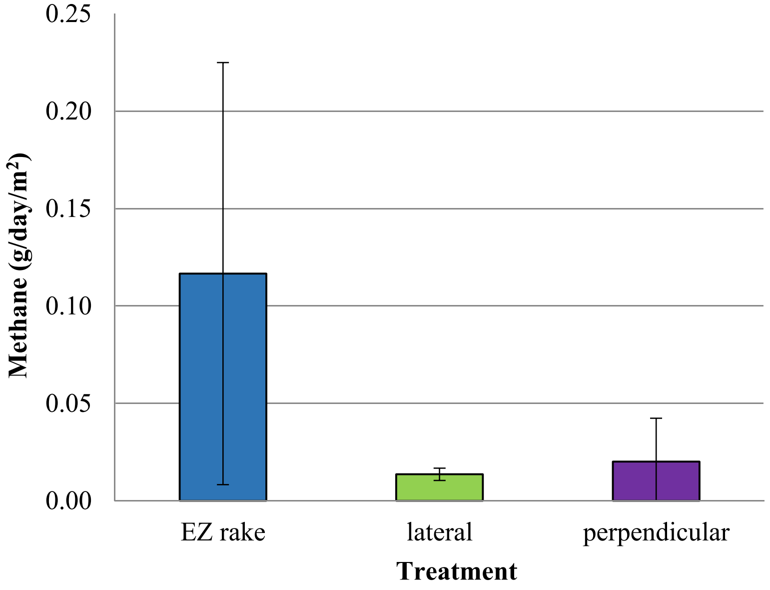

Figure 1. Means of lateral, perpendicular, and EZ rake defacing on methane (CH_4) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

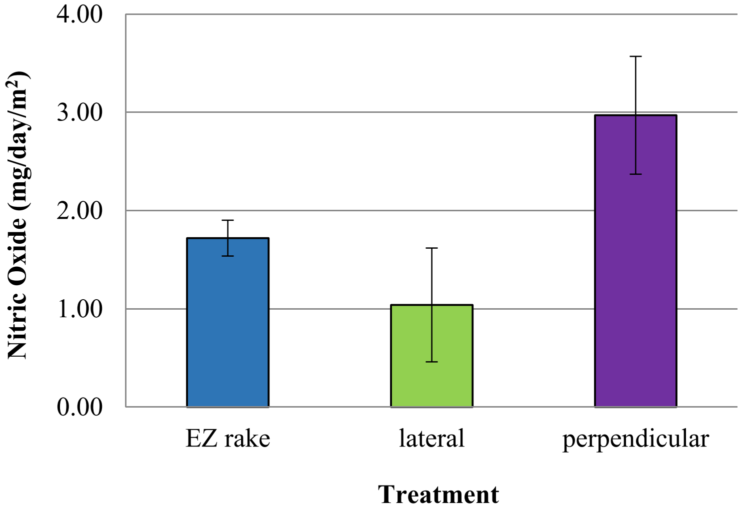

Figure 2. Means of lateral, perpendicular, and EZ rake defacing on nitric oxide (NO) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

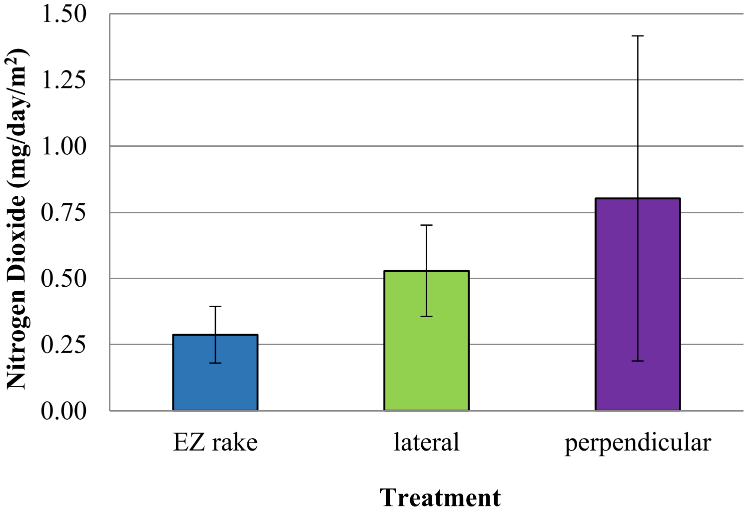

Figure 3. Means of lateral, perpendicular, and EZ rake defacing on nitrogen dioxide (NO_2) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

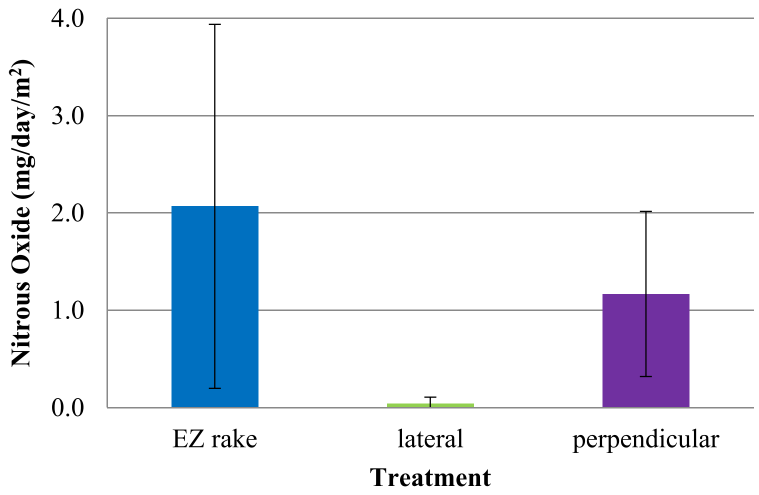

Figure 4. Means of lateral, perpendicular, and EZ rake defacing on nitrous oxide (N_2O) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

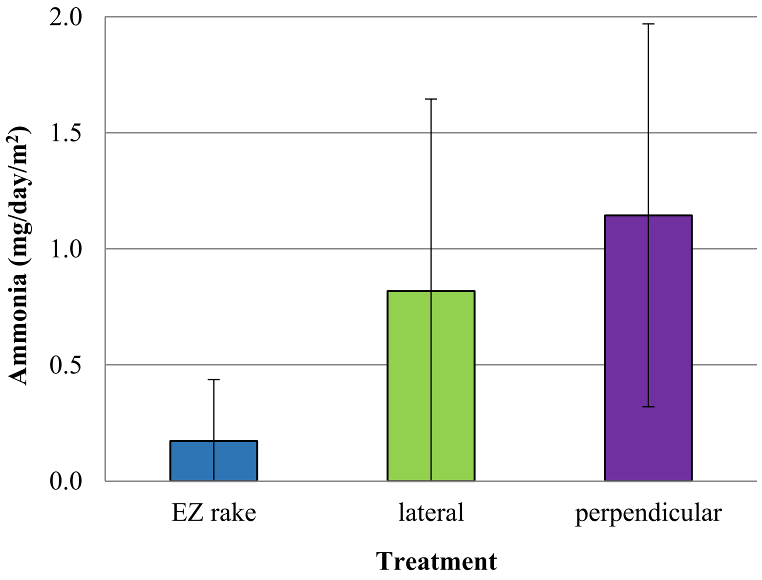

Figure 5. Means of lateral, perpendicular, and EZ rake defacing on ammonia (NH_3) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

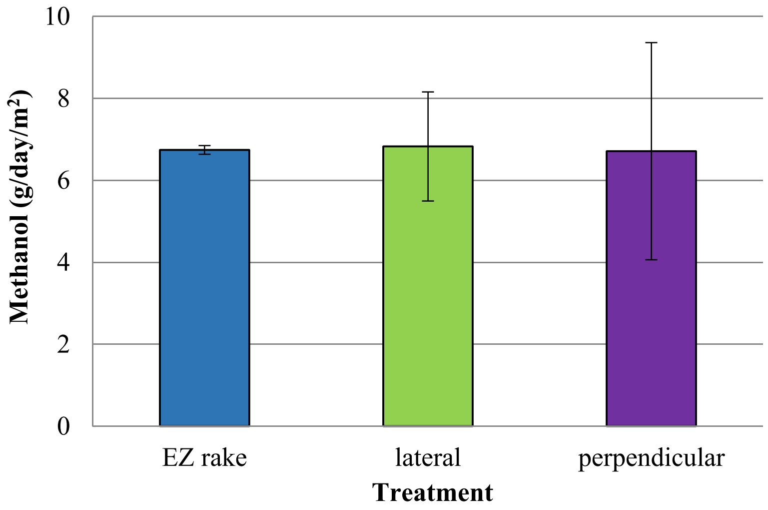

Figure 6. Means of lateral, perpendicular, and EZ rake defacing on methanol (MeOH) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

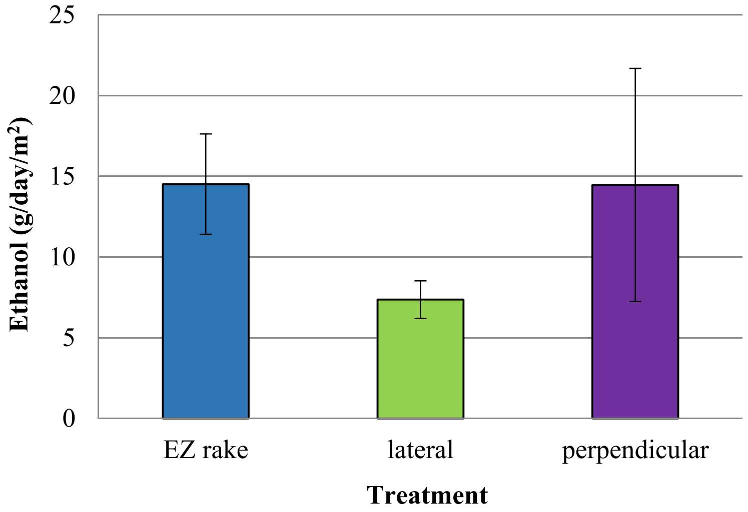

Figure 7. Means of lateral, perpendicular, and EZ rake defacing on ethanol (EtOH) emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

Table 4 summarizes the results of Figures 1-7 comparing the emissions across different defacing methods.

Table 4. Comparisons of gas emissions from different defacing methods

	Defacing treatment		
Gas Emissions	**EZ rake**	**lateral**	**perpendicular**
Methane (g/day/m^2)	0.12 ± 0.11	0.01 ± 0.00	0.02 ± 0.02
Nitric Oxide (mg/day/m^2)	1.72 ± 0.18	1.04 ± 0.58	2.97 ± 0.60
Nitrogen Dioxide (mg/day/m^2)	0.29 ± 0.11	0.53 ± 0.17	0.80 ± 0.61
Nitrous Oxide (mg/day/m^2)	2.07 ± 1.87	0.04 ± 0.07	1.17 ± 0.85
Ammonia (mg/day/m^2)	0.17 ± 0.26	0.82 ± 0.83	1.14 ± 0.82
Methanol (g/day/m^2)	6.74 ± 0.11	6.83 ± 1.33	6.71 ±2.65
Ethanol (g/day/m^2)	14.52 ± 3.11	7.36 ± 1.17	14.46 ± 7.21
TOFP[1] (O_3 g/day/m^2)	25.43	15.11	25.33

[1] TOFP: Total Ozone Forming Potential of Methane, Methanol, and Ethanol

Emissions between Face Emissions of the Conventional Silage Pile vs. Silage Bag

Figures 8-14 show measured and calculated emissions from the entire silage face of the two silage storage methods. The difference in surface area between the silage bag exposed face and conventional silage pile exposed face is approximately a factor of 10 (the exposed surface of the conventional silage face was 460m^2 compared to the exposed silage bag face was 43m^2).

Once the factor of 10 is applied (460m^2 vs. 43m^2) to correct for face area differences and the two storage methods are compared by exposed face, one can clearly see the conventional silage pile emitting far more of the seven gases compared to the silage bag (expect for N_2O). The difference in measured emissions is a function of the surface area difference between the silage storage systems.

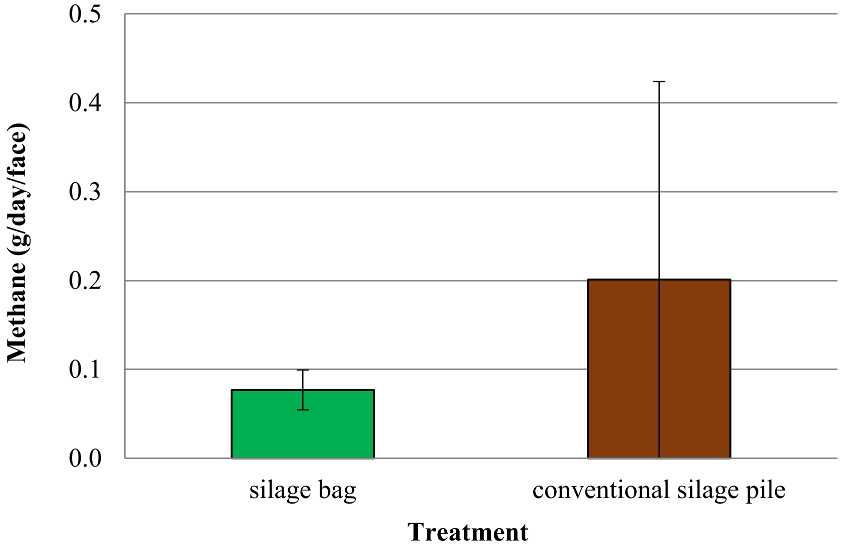

Figure 8. Means of methane emissions from the total face area of a silage bag vs. a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

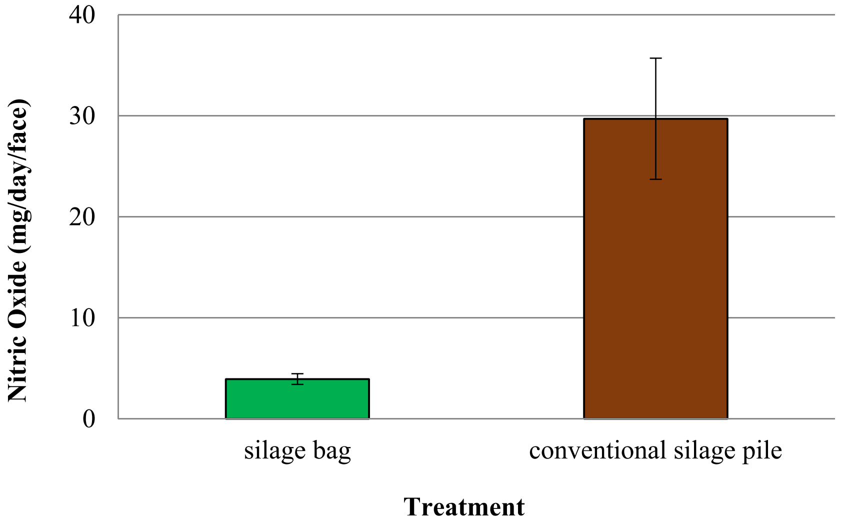

Figure 9. Means of nitric oxide emissions from the total face area of a silage bag vs. that of a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

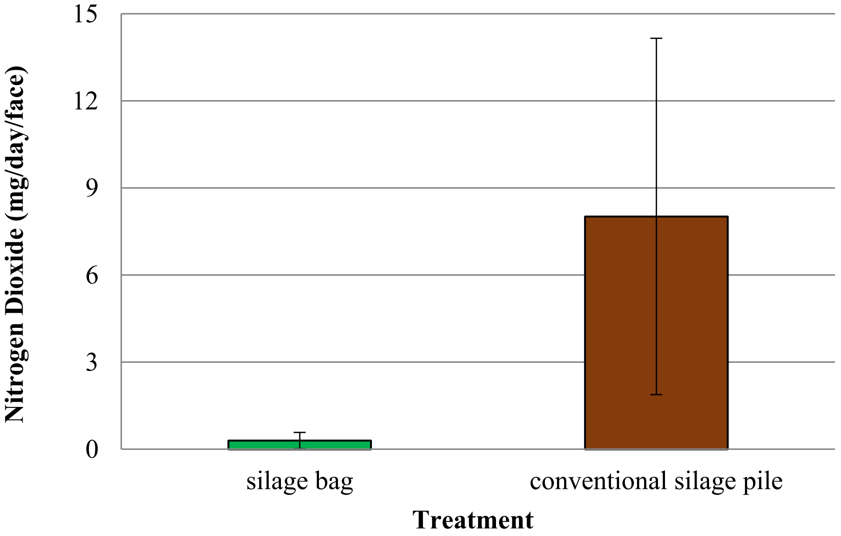

Figure 10. Means of nitrogen dioxide emissions from the total face area of a silage bag vs. that of a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

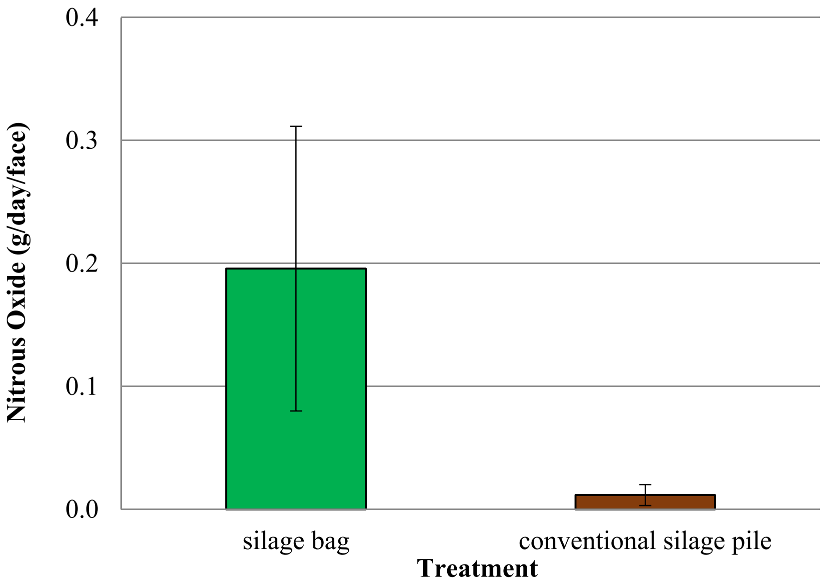

Figure 11. Means of nitrous oxide emissions from the total face area of a silage bag vs. that of a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

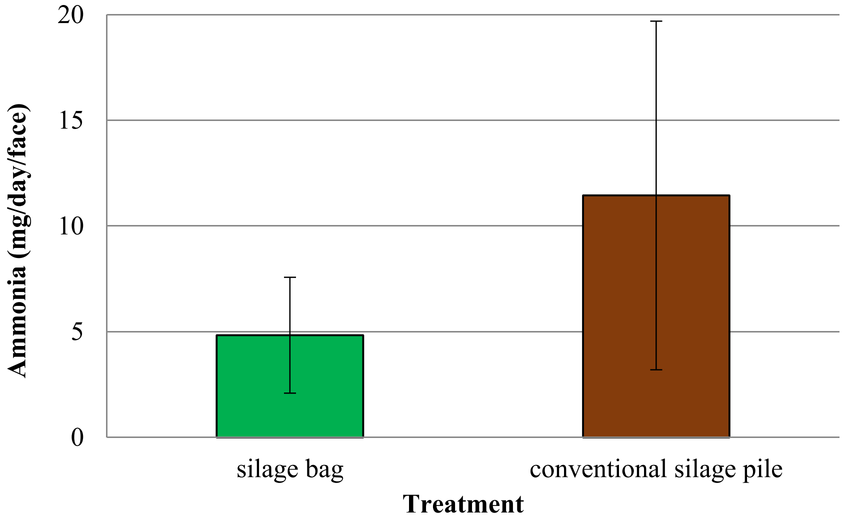

Figure 12. Means of ammonia emissions from the total face area of a silage bag vs. that of a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

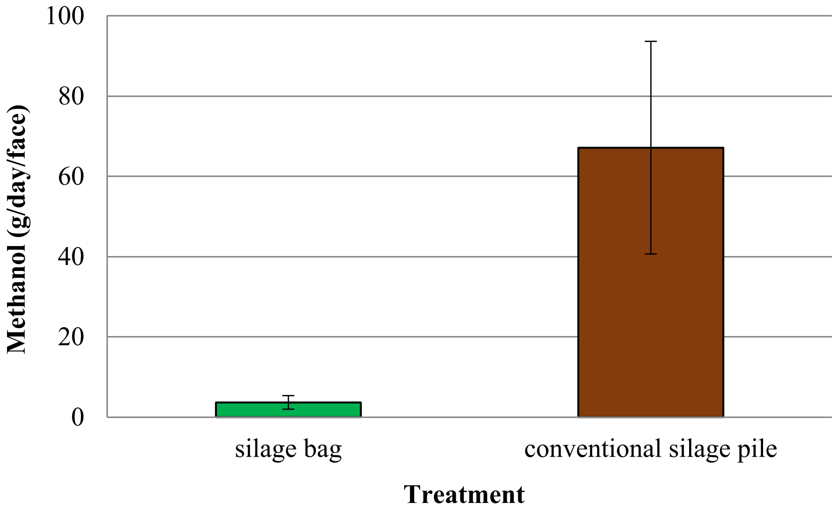

Figure 13. Means of methanol emissions from the total face area of a silage bag vs. that of a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

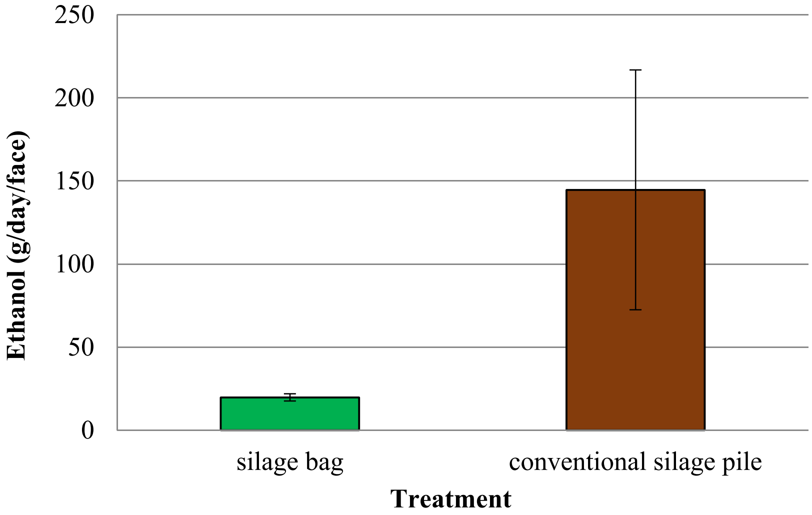

Figure 14. Means of ethanol emissions from the total face area of a silage bag vs. that of a conventional silage pile, respectively (each storage form was measured on three different days and the bars indicate the standard deviation).

Table 5 summarizes the results of Figures 8-14 comparing the between Face Emissions of the Conventional Silage Pile vs. Silage Bag.

Table 5. Comparisons of gas emissions between the faces of different silage storage methods.

	Silage storage methods	
Gas emissions	Silage bag	Conventional silage pile
Methane (g/day/face)	0.08 ± 0.02	0.2±0.2
Nitric Oxide (mg/day/face)	3.94 ± 0.53	29.7±6.0
Nitrogen Dioxide (mg/day/face)	0.30 ± 0.28	8.0±6.1
Nitrous Oxide (mg/day/face)	0.20 ± 0.12	0.01±0.01
Ammonia (mg/day/face)	4.84 ± 2.74	11.4±8.2
Methanol (g/day/face)	3.67 ± 1.71	67.1±36.5
Ethanol (g/day/face)	19.76 ± 2.20	144.6±72.1
TOFP[1] (O_3 g/day/face)	31.04	253.32

[1] TOFP: Total Ozone Forming Potential of Methane, Methanol, and Ethanol

Emissions of TMR with Water Inclusion Rates

Task 4, the evaluation of the effects of water inclusion rate on TMR on the seven gases, provided interesting data. Figures 15-21 depict the four treatments evaluated: TMR 0%, TMR 5%, TMR 10%, and raw silage. The raw silage was added to the comparison to show how loose silage differs from loose TMR. Each treatment comparison was repeated with fresh samples on three separate days.

Nitrogen dioxide, ammonia, methanol and ethanol follow the curve of a high initial gas fluxes within the first five hours followed by a gradual emission decline to zero. The curve observed is similar to the flux of ethanol measured by Montes et al. (2010), who evaluated ethanol from intact silage samples at different temperatures and wind velocities using wind tunnels. However, with the increasing percentage of water included, a reduction of the initial flux of emissions was observed. As a result, when reviewing NO_2, NH_3, MeOH, and EtOH, treatments with 10% water had the greatest decrease (compared to 5% and 0%) in total emissions, particularly during the initial period. Methane, nitrous oxide, and nitric oxide did not follow a similar curve of initial emission flux and emission plateau; instead gaseous emissions appear to be very low until 10 h, then increase until 20 h, after which their emission subsided.

Of the seven gases measured, EtOH has been the most widely documented in the literature The initial EtOH emissions in the present study were similar to measurements by Chung et al. (2010) and Malkina et al. (2011).

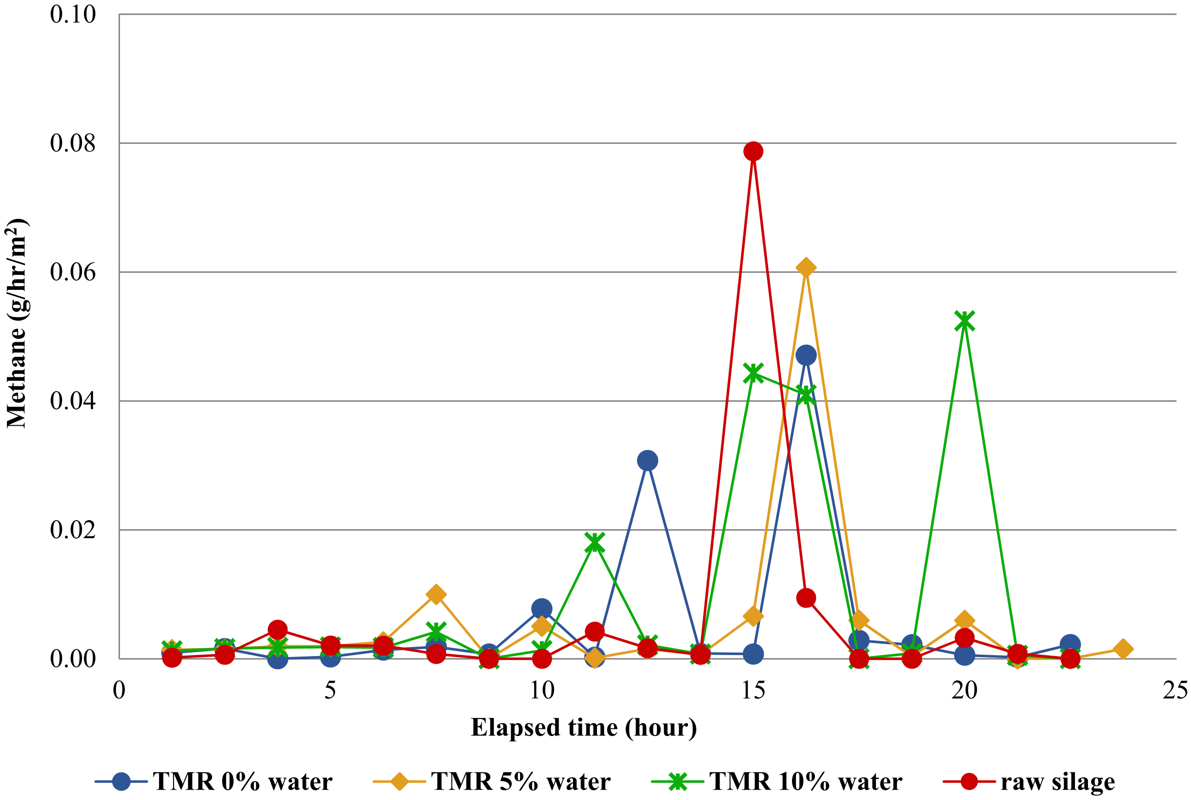

Figure 15. Means of methane (CH_4) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

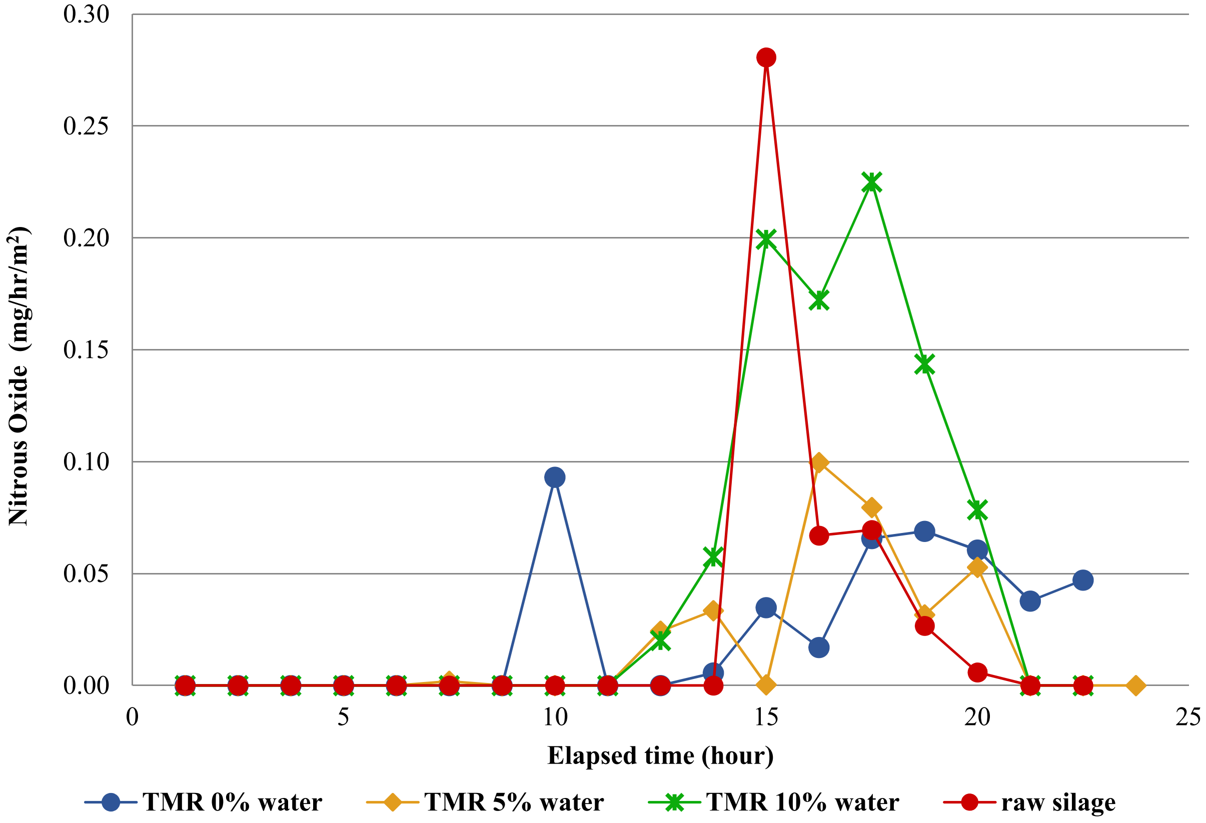

Figure 16. The effect of water inclusion into the TMR on nitrous oxide emissions. Means of nitrous oxide (N_2O) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

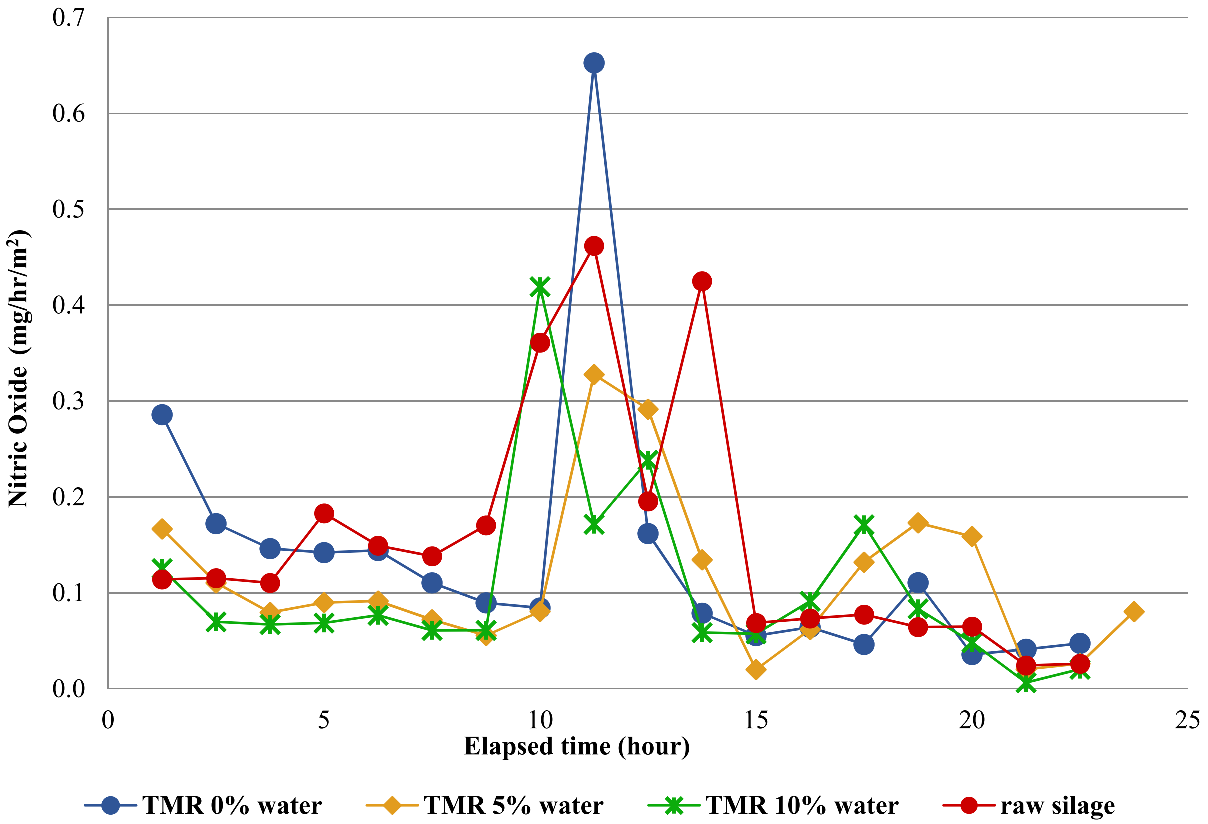

Figure 17. Means of nitric oxide (NO) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

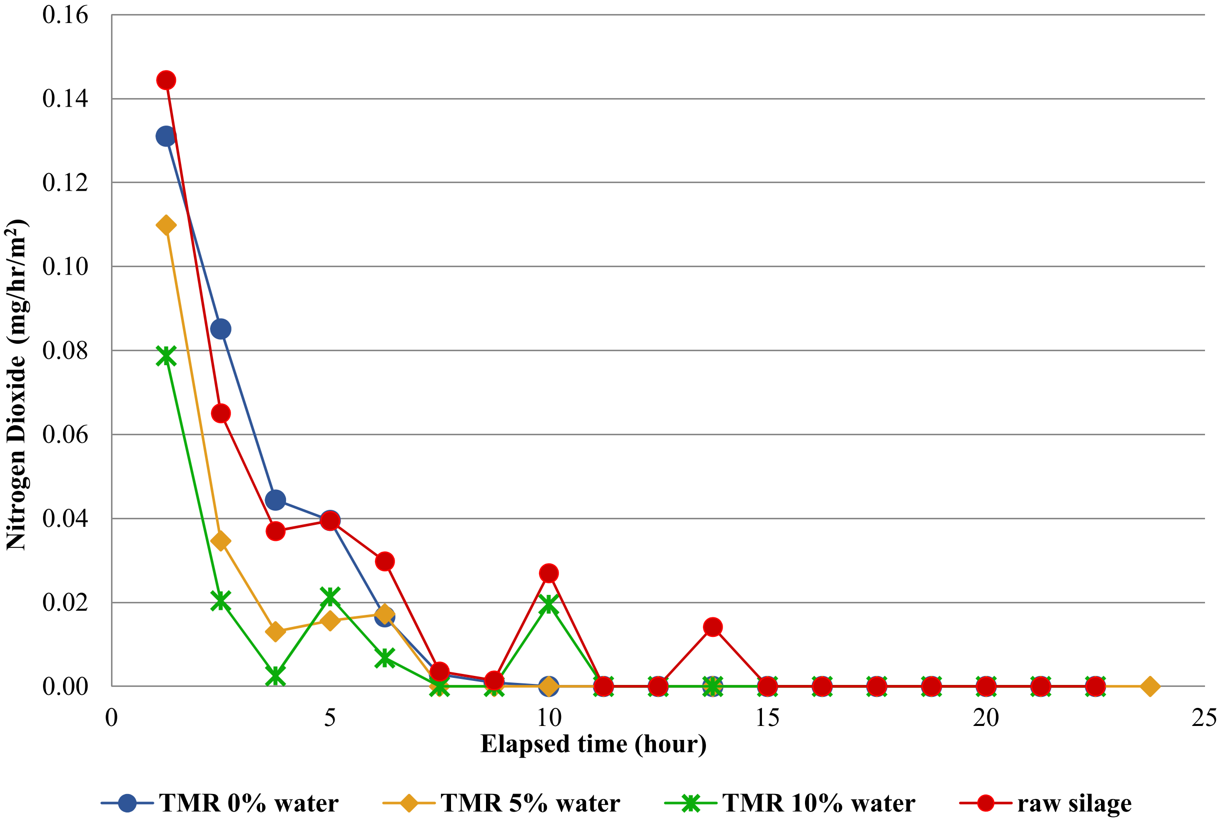

Figure 18. Means of nitrogen dioxide (NO_2) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

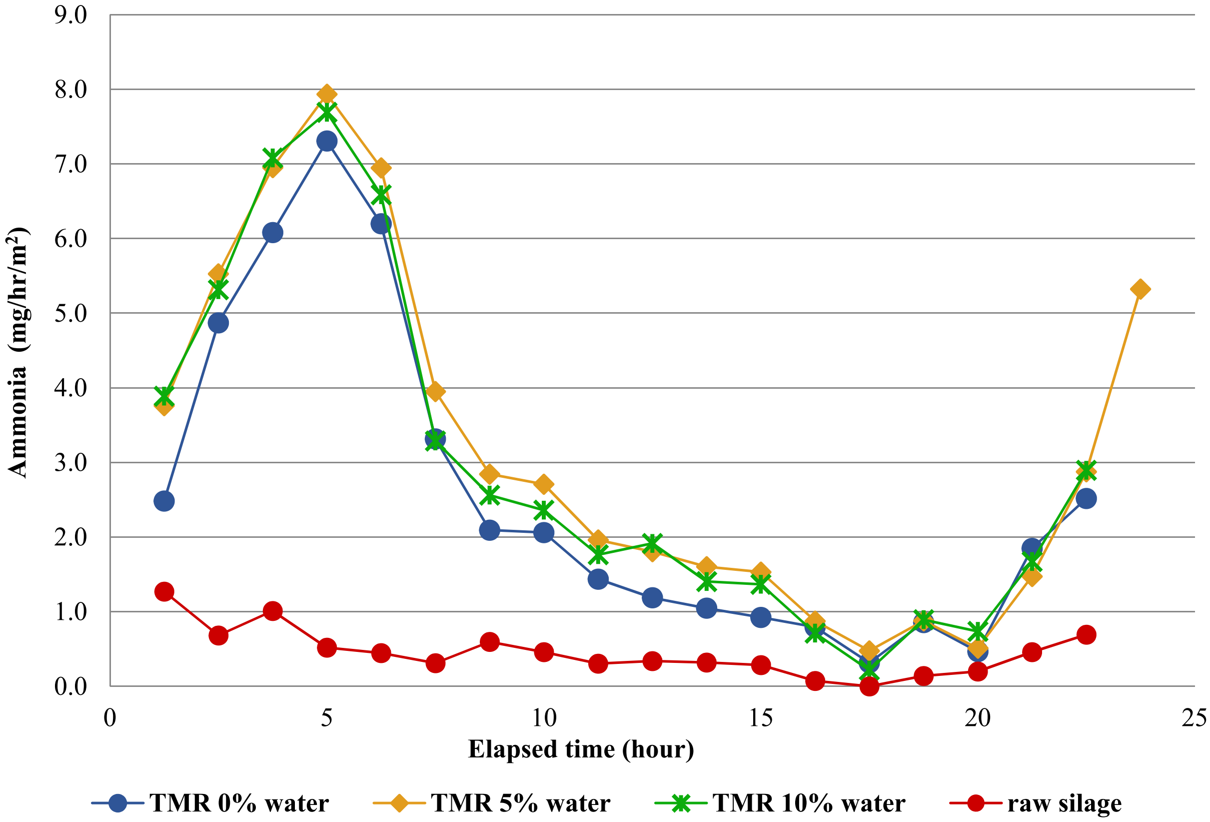

Figure 19. Means of ammonia (NH_3) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

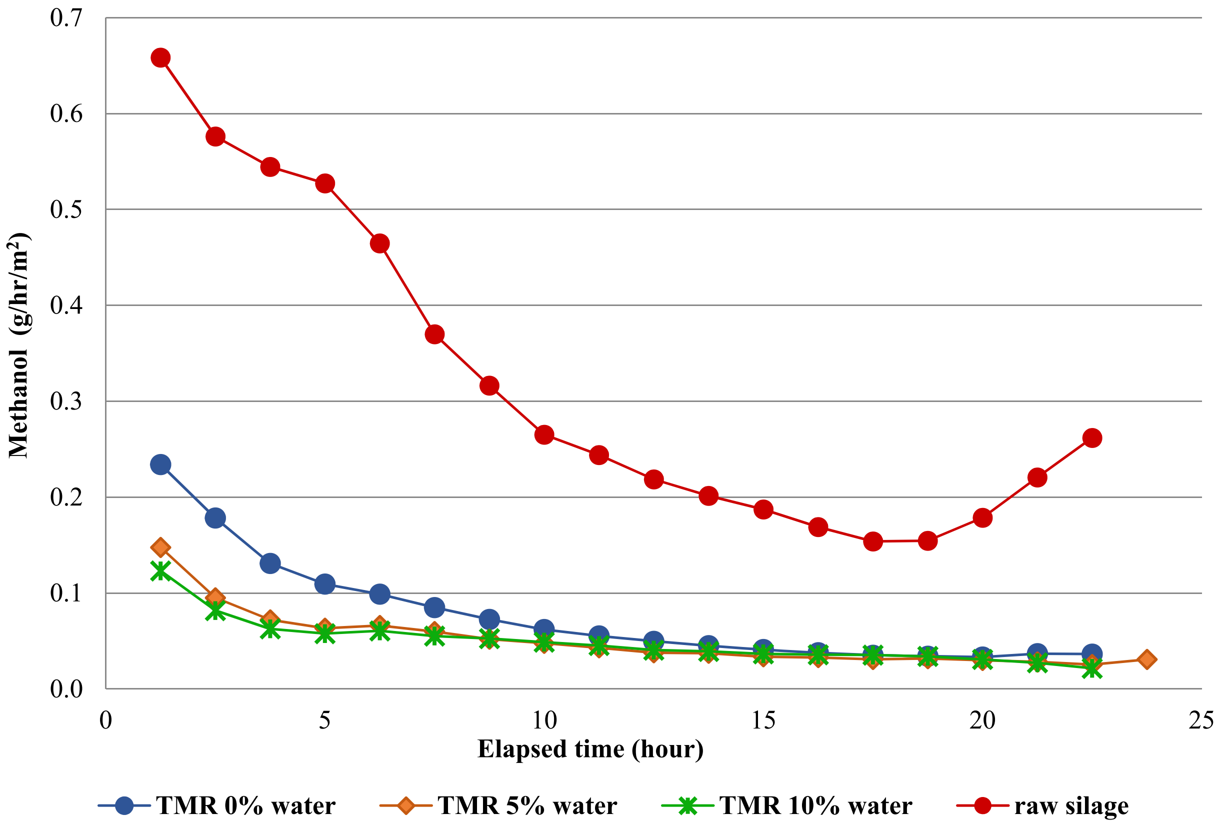

Figure 20. Means of methanol (MeOH) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

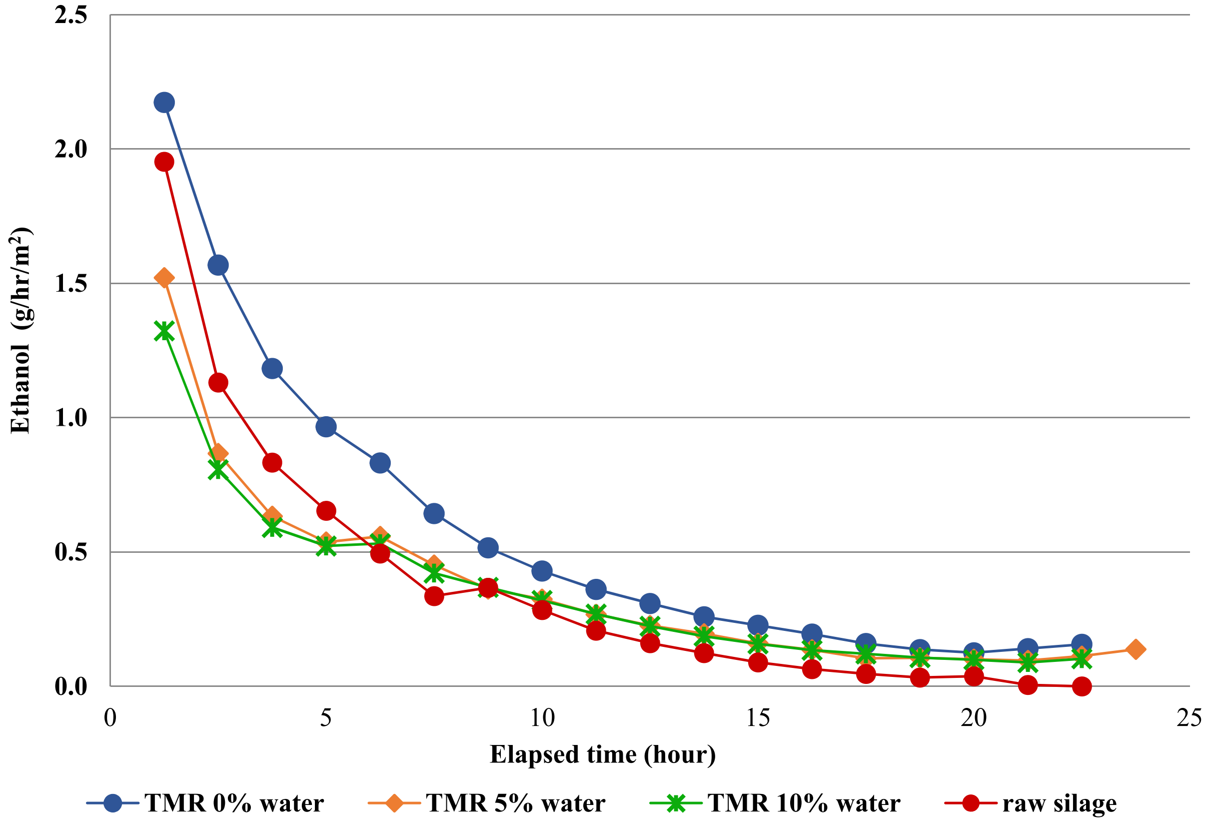

Figure 21. Means of ethanol (EtOH) emissions from TMR treated with 0%, 5% and 10% water vs. raw silage.

Table 6 summarizes the results of Figures 15-21 comparing the emissions of TMR with water inclusion rates. Because of the changes of emissions rate over time, data were averaged in 5-hr intervals for the first 20 hr and 4-hr interval in the last 4 hr. Data were also averaged over 24 hr period to make overall comparisons.

Table 6. Comparison of gas emissions of TMR between different water inclusion rates.

Emission gases	**Average over 5-hr interval elapsed from starting**											
	0-5				**5-10**				**10-15**			
	Water inclusion rate				**Water inclusion rate**				**Water inclusion rate**			
	Raw	0%	5%	10%	Raw	0%	5%	10%	Raw	0%	5%	10%
CH_4 (g/hr/m^2)	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.01	0.00	0.02
N_2O (g/hr/m^2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO (mg/hr/m^2)	0.13	0.19	0.11	0.08	0.20	0.11	0.07	0.15	0.29	0.24	0.19	0.13
NO_2 (mg/hr/m^2)	0.07	0.08	0.04	0.03	0.02	0.01	0.02	0.01	0.01	0.00	0.00	0.00
NH_3 (mg/hr/m^2)	0.87	5.19	6.04	5.99	0.45	3.42	4.11	3.70	0.31	1.15	1.73	1.61
MeOH (g/hr/m^2)	0.58	0.16	0.09	0.08	0.35	0.08	0.06	0.05	0.21	0.05	0.04	0.04
EtOH (g/hr/m^2)	1.14	1.47	0.89	0.81	0.37	0.61	0.42	0.41	0.15	0.29	0.21	0.21
TOFP[1] (O_3 g/hr/m^2)	2.03	2.24	1.35	1.23	0.77	0.93	0.65	0.63	0.35	0.45	0.33	0.33

Table 6. Continue

Emission gases	Average over 5-hr interval elapsed from starting											
	15-20				20-24				Over 24 hr			
	Water inclusion rate				Water inclusion rate				Water inclusion rate			
	Raw	0%	5%	10%	Raw	0%	5%	10%	Raw	0%	5%	10%
CH_4 (g/hr/m^2)	0.01	0.01	0.02	0.03	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
N_2O (g/hr/m^2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO (mg/hr/m^2)	0.07	0.06	0.13	0.10	0.04	0.06	0.04	0.02	0.18	0.16	0.14	0.12
NO_2 (mg/hr/m^2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.02	0.01
NH_3 (mg/hr/m^2)	0.14	0.61	0.69	0.64	0.60	3.16	3.22	3.45	0.59	3.38	3.95	3.85
MeOH (g/hr/m^2)	0.16	0.04	0.03	0.03	0.27	0.04	0.03	0.03	0.39	0.09	0.06	0.06
EtOH (g/hr/m^2)	0.05	0.15	0.11	0.12	0.01	0.16	0.12	0.10	0.43	0.67	0.44	0.41
TOFP[1] (O_3 g/hr/m^2)	0.17	0.25	0.18	0.19	0.18	0.25	0.19	0.16	0.88	1.03	0.68	0.64

[1] TOFP: Total Ozone Forming Potential ofCH_4, MeOH, and EtOH

Conclusions

The present Chapter 3 provides monitoring data for a variety of silage mitigation techniques to provide input and validation data for the concurrent modeling study (i.e. Chapter 4). The past and present research on the individual phases or processes of the silage life cycle, provide emission data on the major emissions present in each step. However, the present monitoring study conducted alongside the concurrent modeling study, show that emission reduction potentials of one phase of silage management might be negated throughout later phases of the life cycle of the feed. For example, one might reduce emissions at the silage face through lateral defacing but the compounds one might prevent from volatilizing there, might later get lost in the feedlane.

Our concurrent modeling study (Chapter 4), which received the feedlane monitoring data from the present (Chapter 3) study, showed that the TMR placed in the feedlane, has the greatest exposure to the atmosphere, resulting in the greatest emissions throughout the silage life cycle. As a result, the present Chapter 3 may guide the reader to favor specific mitigation treatments (e.g., lateral defacing and 10% water inclusion) but these mitigation steps could result in relatively insignificant overall farm effects when evaluating the entire life cycle of silage, including the feedlane phase. It is apparent that the most effective VOC mitigation effort would minimize the air exposure time of freshly extracted- as well as freshly mixed feed to the atmosphere (e.g., silage face and feed-lanes).

Chapter 4 - Modeling of the Emission Reduction Benefits of Mitigation Strategies for Silage

Task 5: To use emission data measured on the commercial farms to refine and evaluate the existing silage VOC emission model

Abstract

Using ethanol and methanol emission measurements from conventional silage piles, silage bags and feed lanes on a California dairy farm, it was found that the silage VOC emission component of the Integrated Farm System Model (IFSM), a whole farm simulation model developed by the USDA-ARS, performed poorly. In response, a new model for predicting VOC emissions from silage sources on farms was developed using theoretical relationships of mass transfer and surface emission, providing in a new process-based silage VOC emission component for IFSM. Model parameters were refined through laboratory experiments and numerical modeling. Simulating emissions measured on the California dairy farm, the new model worked relatively well in predicting ethanol emissions but underpredicted methanol emissions. With a better performance, the new process-based model was incorporated into IFSM where it was used to evaluate management and climate effects on VOC emissions along with other aspects of farm performance, environmental impact and economics. Simulations of a representative dairy farm in California indicate that most of the reactive VOC emissions occur from feed lying in feed lanes during feeding. This implies that mitigation efforts should be focused primarily on reducing emissions during feeding rather than those from the exposed face of silage piles.

Introduction

Prior to the present study, an initial VOC emission model for silage was developed and used as a component of the Integrated Farm System Model (IFSM) and the Dairy Gas Emissions Model (DairyGEM), two whole farm simulation models created by the USDA-ARS (Rotz et al., 2015a and b). This model, which simply approximated the cumulative fraction loss of VOC of interest over time, was chosen largely because of its rapid simulation, i.e. to avoid substantial slowing of the whole farm simulation (Rotz et al., 2015a and b). Other models that simultaneously simulate transport and emission of VOC from silage sources (e.g., Hafner et al., 2012) were too computationally intensive to be used in whole farm models (Rotz et al., 2015a and b). Although refined using our early experimental mass balance data presented in Hafner et al. (2012), the original VOC emission model was found to perform poorly in simulating emissions under field conditions. Using measurements obtained from commercial California dairy farms through the present project (see Chapter 3), the original model was not able to appropriately simulate emissions of ethanol and methanol from silage storages and feed lanes. Compared to measurements, the model generally predicted very high ethanol emissions and relatively low methanol emissions from both silage piles and bags. In addition, the original model did not respond appropriately to changes in simulation settings for silage bulk density and moisture content (Appendix Figures A2.1 and A2.2), two important parameters that differ among silage storage types. Inability to simulate effects of these two parameters limited the capability of the farm simulation models in evaluating changes in VOC emissions with respect to different mitigation strategies.

Through the present grant, a new VOC emission model for silage was developed to address the limitations inherent to the old model. The goal was to predict VOC emissions from silage sources by simulating emission and transport processes involved while maintaining a relatively fast simulation time. This resulted in a new silage VOC emission model that we refer to as the new process-based model. Ethanol and methanol emissions measured from silage storages and feed lanes on California dairy farms were used to evaluate and demonstrate the performance of the new process-based model in predicting VOC emissions under field conditions. With this new model incorporated, IFSM and DairyGEM provide tools for studying silage VOC emissions and evaluating VOC emission mitigation strategies from a whole farm perspective. This report provides a brief description of the process-based silage VOC emission model, the evaluation with measured farm data, and an example application of the model in evaluating mitigation strategies for a representative California dairy farm using IFSM.

Silage VOC Model Description

Rather than simulating emission and transport processes involved, the previous VOC emission model estimated the fraction of VOC loss from silage sources with respect to time (equation 1). A schematic representation of the previous VOC emission model is presented in Appendix Figure A2.3. Silage sources, which included silage storages and feed lanes, were treated as a three-pool model: surface pool, representing the first 2 cm from the surface; middle pool, representing the next 5 cm (i.e., depths of 2 to 7 cm); and a deep pool, representing the rest of the silage profile (i.e., total depth minus 7 cm) (Rotz et al., 2015b). Each pool was treated independently, composed of a gas film and a silage layer (Rotz et al., 2015b). For each pool, the fraction of a VOC lost through emission was represented using equation 1 (Rotz et al., 2015b):

$$f_{emis} = 1 - e^{-Kt/L} \tag{1}$$

where f_{emis} is the fraction of a given VOC lost at time t, K is the overall mass transfer coefficient (m/s), L is the layer thickness of the pool (m), and t is the cumulative exposure time (s). The L value was set to 0.02 and 0.05 m for surface and middle pools, respectively, while the remaining thickness was the deep pool. The total thickness was based on the calculated amount of silage needed for feeding the cows each day. Defined as the reciprocal of the sum of the two resistances to mass transfer (i.e., inverse of mass transfer coefficient), K was given by (Hafner et al., 2012; Rotz et al., 2015b):

$$K = 1/\left(1/\alpha + l/D_b\right) \tag{2}$$

where α is the effective surface mass transfer coefficient (m/s), D_b is the effective bulk diffusion coefficient (m^2/s), and l is the distance from the center of the emitting layer (pool) to the exposed surface (m). The α is computed using equation 12 of Hafner et al. (2012). The surface mass transfer coefficient (h_m) used in calculating α is based on Mackay and Yeun (1983). The value of D_b is a function of diffusion-dispersion coefficients for both gaseous (k_{sg}) and aqueous (D_{ss}) phases (Hafner et al., 2012). Because k_{sg} is several orders of magnitude higher than D_{ss} (Hafner et al., 2012), D_b is calculated as a function of k_{sg} only. From Hafner et al. (2012), k_{sg} was held constant at 2.33×10^{-5} m/s. However, using measurements obtained from California dairy farms, this original model was found to perform poorly in predicting ethanol and methanol from silage piles and bags.

Through the present project, we developed a new model where processes influencing the amounts of VOCs emitted are simulated, instead of just simply calculating the VOC fraction loss over time like in the old model (equation 1). Processes simulated include surface emission of VOCs and transport of VOCs within the silage. The governing equations describing the new model were based on the convection-diffusion-dispersion model presented by Hafner et al. (2012). But instead of using the analytical solution to these equations (i.e., which led to overestimation of VOC emissions, Hafner et al., 2012), the new model was based on numerical modeling, in which the equations for surface emission from and transport within the silage were solved numerically through discretization. Numerical models (i.e., numerical solution), however, often require very fine spatial and temporal resolution, and, consequently, a very long simulation time. As an example, model refinement performed for this study was conducted with a grid size of 1 mm, resulting in 1,000 simulation layers for a 1-m depth of silage source, and a time step of 1 second – with this very fine resolution, modeling of just 120 hourly data points (i.e., equivalent to 5 days) required more than 8 hours of simulation time. In IFSM, simulation of all farm components, which include crop production, harvesting, feed storage, animal performance, manure production and handling, etc., using daily weather conditions over a 25-year period requires a very short simulation time for any one component farm. Therefore, to be incorporated in a whole farm model, a much faster simulation was required. To achieve this, simulation layer depths for the numerical model were defined as functions of certain parameters, as discussed below, to significantly reduce spatial (e.g., 2/3 simulation layers for 1-m depth) and temporal (e.g., 1-hr time step) resolution, and simulation time. Expressions defining simulation layer depths were developed through refinement using emission profiles obtained from numerical modeling using the high spatial and temporal resolution. A detailed description of the resulting model will be presented in a future publication; a brief overview follows.

In the new process-based model, calculation of VOC emission from silage is performed on an hourly basis. The simulation domain for silage storages, such as bunkers, piles, and silage bags, has a total depth of 1 m from the exposed surface, which is divided into three layers. For feed lanes, the simulation domain has a shorter depth (0.15 m), which is modeled as two layers. As presented in Table 7, the surface layer, from which VOCs are emitted, is calculated as a function of the friction velocity (u_*) of air movement and feed dry bulk density (ρ_{dry}) for both silage storages and feed lanes. For silage storages, the second layer, which is adjacent to the surface layer, is a function of ρ_{dry}. In the new model, equations for these simulation depths were developed based on experimental data by Montes et al. (2010) and Hafner et al. (2010) and through numerical modeling. For the surface layer, simulation depth is directly proportional to u_* (i.e., more VOCs are readily available for volatilization at higher wind speeds) but inversely proportional to ρ_{dry} (i.e., more VOCs are readily available for volatilization at lower bulk densities). These depths were set using ethanol measurements. In the absence of experimental or measured data (e.g., different friction velocities), the same depths were applied for other VOCs (i.e., other alcohols, acids, aldehydes, esters, etc.).

Table 7. Depths (m) of simulation layers for silage in storages and feed lanes.

Layers	*Silage storage*	*Feed lane*
1st (surface layer)	$f_{1,s}(\rho_{dry}) + [f_{2,s}(\rho_{dry}) \times u_*]$	$f_{1,f}(\rho_{dry}) + [f_{2,f}(\rho_{dry}) \times u_*]$
2nd	$f_{3,s}(\rho_{dry})$	Remaining
3rd	Remaining	-
Total	1 m	0.15 m

In the new model, processes simulated for the 1st (surface layer) are VOC emission and volatilization. Unlike the previous model, mass transfer of VOCs between layers is simulated. A schematic representation of the new VOC emission model is presented in Appendix Figure A2.4. For VOC emission, the following assumptions were applied: the amount of VOC emitted was limited by the amount of VOC present in the 1st layer; and the mass transfer resistance due to depth of the 1st layer was neglected.

Following Hafner et al. (2012), simulated hourly VOC emission from the surface layer is given by:

$$j_{sur} = 3600\alpha(C_{sur} - C_{air}) \tag{3}$$

where j_{sur} is the hourly VOC emission (g/m^2-hr), α is the effective surface mass transfer coefficient (m/s), C_{sur} is the VOC concentration in bulk silage (g/m^3), and C_{air} is the VOC concentration in ambient air (g/m^3). The C_{air} value is assumed negligible (Hafner et al., 2012). Similar to the previous model, α is computed using eq. 12 of Hafner et al. (2012). The value of h_m used in calculating α for ethanol is based on experimental data by Montes et al. (2010), where the derived equation is a function of u_*. In the absence of data, h_m for other VOCs is based on Mackay and Yeun (1983) as implemented in the previous model.

The amount of VOC transferred from one layer to the layer above is given by Hafner et al. (2012):

$$j_{lyr} = \frac{3600 D_b (C_{lyr} - C_{lyr-1})}{l} \tag{4}$$

where j_{lyr} is the hourly mass transfer of VOC from the lower layer (g/m^2/hr), D_b is the effective diffusion mass transfer coefficient (m^2/s), *lyr* and *lyr*-1 are the lower and upper layers, respectively, *l* is the distance from the center to the upper edge of the lower layer (m), and C_{lyr} and C_{lyr-1} are VOC concentrations for *lyr* and *lyr*-1, respectively (g/m^3). Similar to the previous model, D_b is calculated as a function of k_{sg} only. The value of D_b is computed using eq. 11 of Hafner et al. (2012) with the D_{ss} term neglected. As done for h_m, an equation was derived for calculating k_{sg} as a function of u_* using ethanol data from Montes et al. (2010). This same equation was used in calculating k_{sg} for other VOCs but with the minimum value based on relationships from Tucker and Nelken (1982). With this approach, k_{sg} for all VOCs is the same at $u_* > 0.05$ m/s (i.e., 10-m height wind speed of 2.0 m/s). As k_{sg} applies to diffusion in free air, it is adjusted to represent diffusion in a porous media such as silage using the Millington-Quirk model (Hafner et al., 2012).

Both, α and D_b are functions of the Henry's law constant, bulk density, and moisture content (Hafner et al., 2012; Rotz et al., 2015a and b). To estimate K_H, equation 1 of Hafner et al. (2012) can be written as:

$$K_H = \frac{m_i}{P_i} \rightarrow K_H = \frac{m_i}{P_T y_i} \rightarrow K_H = \frac{m_i}{P_{sat} x_i} \tag{5}$$

where m_i is the molal concentration of VOC i (mol/kg solution), x_i is the mole fraction of VOC i in aqueous phase, y_i is the mole fraction of VOC i in the gas phase, P_i is the partial vapor pressure of VOC i in equilibrium with m_i (atm), P_{sat} is the saturated vapor pressure of VOC i (atm), and P_T is the total vapor pressure of the solution (atm). The value of P_{sat} is calculated using the Antoine equation:

$$P_{sat} = \frac{10^{A - \frac{B}{C+T}}}{760} \tag{6}$$

where A, B, C are compound-specific constants, and T is the silage temperature (°C). In this study, values for A, B, and C used for ethanol and methanol are based on DDBST (2015).

One shortcoming of using eq. 5 is the need to specify x_i. Based on a summary made by Hafner et al. (2013), 46 VOCs have been measured in silage. Measurement of all these VOCs to determine x_i, however, would be impractical. In this project, although silage samples were characterized in terms of seven VOCs only, the three most concentrated VOCs in silage (i.e., acetic acid, ethanol, and propionic acid; Hafner et al., 2013) were included in silage characterization. In approximating x_i, it was assumed that the moles of other VOCs not measured were negligible compared to the sum of concentrations of the seven VOCs included.

Model Evaluation Procedure

For simulating silage storages, the new VOC emission model was evaluated using the dataset of ethanol and methanol emissions measured from conventional silage piles and silage bags on the commercial dairy farm in California. In addition, performance in simulating feed lanes was evaluated using emission measurements from total mixed ration (TMR) and corn silage samples representing that spread out in feed lanes.

Emission Measurements

Measurement of hourly ethanol and methanol emissions from silage faces using flux-chambers and a wind tunnel system is described in Chapter 3. Information on measurement trials used in model evaluation are provided in Table 8, summarized according to storage type, defacing method, and measurement date.

Table 8. Measurement information on data collected from conventional silage piles and silage bags.

Trial	*Storage type*	*Defacing method*	*Measurement date*	*No. of hourly data points*	*Flux-chamber*	*Wind tunnel*
1	Conventional silage pile	Lateral	09/15/2014	13	Y	Y
2			09/17/2014	14	Y	
3			09/18/2014	14	Y	
4		Perpendicular	09/22/2014	13	Y	Y
5			09/24/2014	14	Y	
6			09/25/2014	14	Y	
7		Rake (EZ rake)	10/01/2014	14	Y	Y
8			10/02/2014	14	Y	
9			10/03/2014	14	Y	
10	Silage bag	-	10/23/2014	23	Y	Y
11			10/29/2014	21	Y	
12			10/30/2014	23	Y	

For both VOCs, measured hourly emission rate ($j_{sur,m}$) was calculated as:

$$j_{sur,m} = \frac{\left(\frac{C_{VOC} MW_{VOC}}{24.45}\right) V_{flow}}{A_{sur}} \tag{7}$$

where C_{VOC} is the hourly concentration of VOC of interest in the headspace (ppm), MW_{VOC} is the molecular weight of the VOC (g/mol), V_{flow} is the hourly flow rate of air through the chamber (i.e., 1.2 m^3/hr for flux-chambers and 5.94 m^3/hr for the wind tunnel), and A_{sur} is the area of the emitting surface (i.e., 0.196 m^2 for flux-chambers and 0.23 m^2 for the wind tunnel).

In evaluating the performance in simulating VOC emissions from feed lanes, ethanol and methanol emissions measured from corn silage and TMR samples were used. To examine whether water application could lower VOC emissions (see Task 4 in Chapter 3), emissions were measured from three types of TMR samples, which varied in the amount of water added (Table 9). Hourly ethanol and methanol emissions from corn silage and TMR samples were determined using flux-chambers (Chapter 3), with each trial lasting 14 hr.

Table 9. Details on total mixed ration (TMR) and corn silage samples used to represent feed lane emissions.

Trial sample	*Trial*	*Source*	*Amount prior water addition (kg)*	*Amount of water added (kg)*	*Effective % water*[1]
TMR + 0% water	13, 14, 15	TMR	2.0	0.0	7%
TMR + 5% water	16, 17	TMR	1.9	0.1	11.5%
TMR + 10% water	18, 19, 20	TMR	1.8	0.2	16.5%
Corn silage	21, 22	Corn silage	2.0	0.0	-

[1] Prior sampling, 7% water was already added to TMR during mixing.

Silage Characterization

Simulation of VOC emissions requires initial concentrations of the compounds within the silage (i.e., C_{sur} in eq. 3). Samples from conventional silage piles and silage bags, obtained using a silage core sampler, and samples of TMR and corn silage were collected for characterizing VOC concentrations. Samples were placed in separate sealed plastic bags, which were then immediately stored in a container with dry ice. Upon arrival at UC Davis, VOC concentrations in these samples were analyzed using gas chromatography (GC). Similar to Zhang et al. (2010), VOCs included in silage characterization were ethanol, methanol, acetic acid, propionic acid, iso-butyric acid, butyric acid, and valeric acid.

Simulation Settings

Parameters α and D_b, used in calculating j_{sur} (eq. 3) and j_{lyr} (eq. 4), respectively, are influenced by silage bulk density and moisture content (Hafner et al., 2012). In the absence of measurements, simulation settings for bulk density and moisture content were set as follows: (1) refinement through numerical modeling for conventional silage piles; (2) published or documented values for silage bags; and (3) estimated from volume and known mass for TMR samples. Values used are presented in Table 10. For conventional silage piles, refinement of bulk density and moisture content settings according to simulated emission profiles was acceptable as the new model worked well using the more comprehensive experimental data of Montes et al. (2010) (i.e., bunker silo silage sample) and Hafner et al. (2010) (i.e., loose silage sample), both of which included silage bulk density and moisture content measurements. But with concerns on low ethanol emissions simulated (as discussed below), this approach was not effective for silage bags; therefore, a dry bulk density of 190 kg/m^3, which is within published values, was used.

Table 10. Simulation settings used for dry bulk density and moisture content in model evaluation.

Silage set-up	*Parameters*	*Simulating setting*	*Published values*	
			Range	*Reference*
Silage bag	Dry bulk density (kg/m^3)	190	65 - 270	Muck and Holmes, 2006; Ohman et al., 2007
	Moisture content (%, wet-based)	50	40 - 70	Savoie and Jofriet, 2003
Conventional silage piles	Dry bulk density (kg/m^3)	240	160 - 320	Roach and Kammel, 2012; Silva-del-Rio, 2010
	Moisture content (%, wet-based)	60	60 - 70	Roach and Kammel, 2012
TMR	Dry bulk density (kg/m^3)	190	120 - 190	Buckmaster, 2005
	Moisture content (%, wet-based)	35	40 - 50	Buckmaster, 2005

As discussed above, h_m is a function of friction velocity. Although not measured in this project, effective air velocity inside the flux chambers was very low (Acevedo Perez, 2011); thus, friction velocity was set to 0 m/s. For the wind tunnel, equivalent average wind speed based on the 99 L/min setting was 0.04 m/s; assuming that friction velocity was 1/10th of the average wind speed, a 0.004 m/s setting was applied. Based on these settings, h_m for flux-chambers were

$1x10^{-3}$ m/s for methanol and $2x10^{-4}$ m/s for ethanol. For the wind tunnel, h_m was approximately $1.26x10^{-3}$ for methanol and $8.8x10^{-4}$ m/s for ethanol.

Model Evaluation Results

Below are figures and tables for ethanol and methanol emissions based on field measurements at the California farm and as simulated by the new process-based model for silage VOC emissions. To demonstrate the improvements made in VOC emission simulation using the new model, simulation results from the previous model are also shown. For both new and old models, corresponding ratios of simulated to measured emissions ($R_{s/m}$) were computed. The closer the $R_{s/m}$ to 1.0, the closer the simulated emission is to that measured. Statistical measures that can be used in comparing measured and simulated VOC emissions are also provided, and these included the mean absolute error (MAE), the root mean square error (RMSE), and the index of agreement (IA). Equations for these statistical measures are discussed by Willmott (1981) and Willmott et al. (2012). For IA, a value of 1.0 indicates 100% agreement between measured and simulated data whereas 0.0 indicates no agreement at all.

Conventional Silage Piles

Flux-chamber-based measured and simulated (for both new and old models) ethanol and methanol emissions are shown in Figure 22. With emission (e.g., h_m) and transport (e.g., k_{sg}) parameters derived from previous experimental data, the new process-based model performed well in simulating ethanol emissions (Figure 22). Based on overall values (Table 11), $R_{s/m}$ ranged from 0.62 to 1.49, with an average of 1.12 indicating relatively close agreement. The new model also was able to simulate the typical VOC emissions profiles for silage with high emissions during the first hours of exposure followed by a rapid decline for the remaining period (Montes et al., 2010; Hafner et al., 2010). Compared to the old model, the new model performed much better as the former simulated very high ethanol emissions for conventional silage piles. Using the old model, $R_{s/m}$ values were very high, ranging from 3.57 to 9.22, with an average of 6.36 suggesting that simulated ethanol emissions were 6x the measured values.

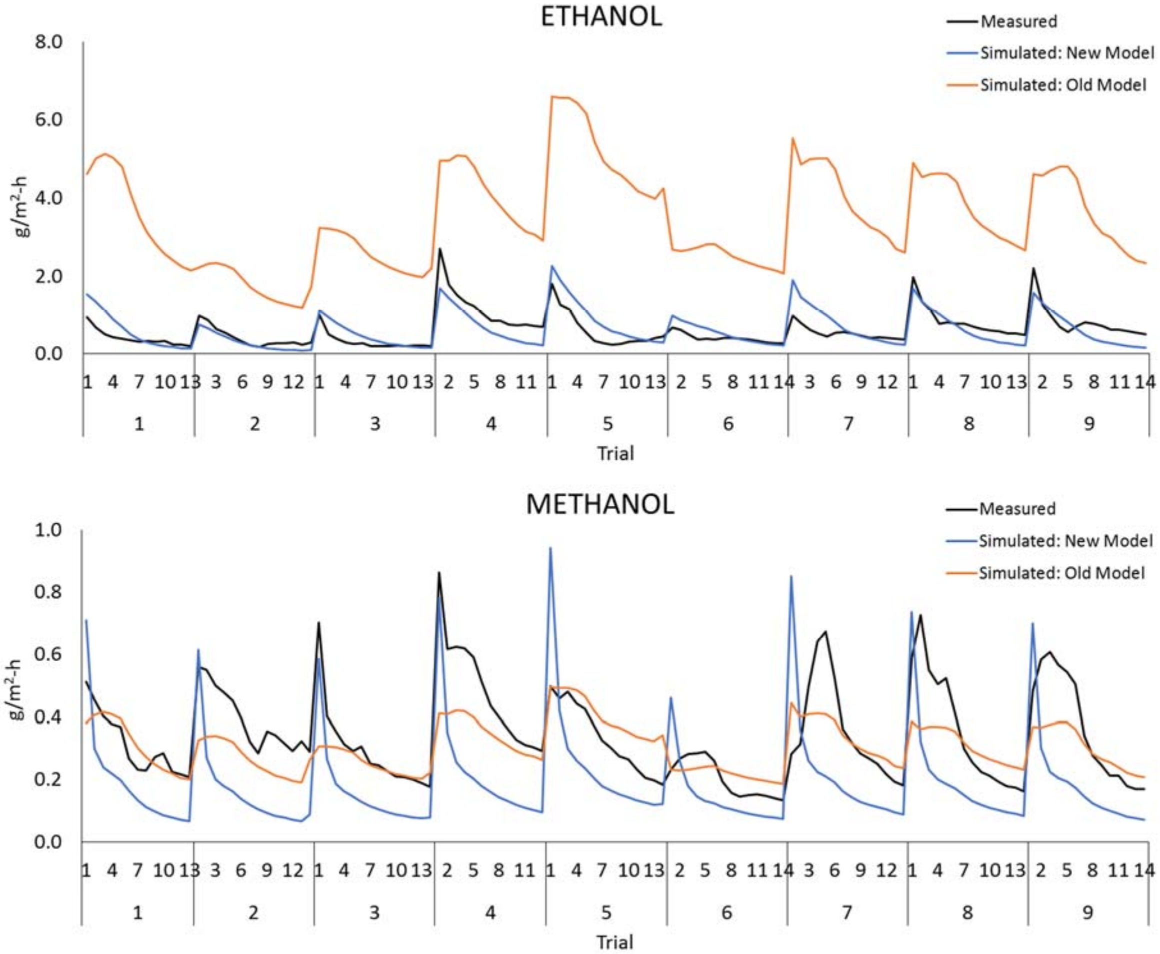

Figure 22. Comparison of simulated and flux-chamber-based emissions for conventional silage piles.

Compared to simulation of ethanol emission, however, a slightly lower model performance was observed for the new model when simulating methanol emissions from conventional silage piles. Except for being able to predict the high methanol emissions measured during the first hour of silage face exposure, the modeled emission profile was lower than that measured (Figure 22). Based on overall values (Table 12), $R_{s/m}$ when simulating methanol emissions was relatively low, with a range of 0.42 to 0.74 and an average of 0.57 (i.e., simulated was about 60% of that measured). This tendency of the model to underpredict methanol emissions is likely due to coefficients assumed in the simulation, specifically the diffusion-dispersion coefficient. Without experimental data, refinement of this parameter for methanol emissions was not possible. In contrast to its performance in simulating ethanol emissions, the old model did better in modeling methanol emissions, with $R_{s/m}$ ranging from 0.69 to 1.21 and an average of 0.91 (i.e., simulated was 91% of measured). Even though the old model seemed to perform much better in simulating methanol emissions from conventional silage profiles, these modeled methanol emissions were obtained with certain limitations and faults present in the model, which included: (1) use of an equation for K_H suggesting ethanol is more volatile than methanol; (2) an assumption that the layers (i.e., pools in the old model) behave independently, with no VOC transfer between any layers (Rotz et al., 2015b); (3) inability to simulate effects of silage dry bulk density and moisture content on VOC emissions (e.g., Figures A2.1 and A2.2); (4) inability to simulate the characteristic high VOC emissions during the first hour of exposure (Montes et al., 2010; Hafner et al., 2010); and (5) inability to simulate the rapid decline in emissions after the first hour of exposure (Montes et al., 2010; Hafner et al., 2010) resulting to generally higher emission profiles.

Table 11. Equivalent 12-h measured and simulated ethanol emissions for conventional silage piles (trials 1-9) and silage bags (trials 10-12) based on flux-chamber and wind tunnel measurements.[1,2]

Trial	*Flux-chamber*				*Wind tunnel*			
	Concentration (mg/L)	*Emission rate (g/m^2)*			*Concentration (mg/L)*	*Emission rate (g/m^2)*		
		Measured	*Simulated*			*Measured*	*Simulated*	
			New	*Old*			*New*	*Old*
1	253	4.7	6.9	44	182	4.4	6.0	28
2	136	4.9	3.4	21				
3	219	3.7	5.4	31				
4	330	13.8	8.6	49	194	15.8	6.4	29
5	436	7.2	10.7	62				
6	276	4.8	6.2	30				
7	389	6.3	9.1	48	336	10.7	9.6	36
8	340	9.9	8.1	45				
9	293	9.9	7.3	44				
10	146	10.6	2.3	19	123	16.6	2.3	14
11	158	11.9	2.7	20				
12	148	8.5	2.3	19				
Conventional silage piles (trials 1-9)		MAE	2.5	34		MAE	4.1	21
		RMSE	2.7	36		RMSE	5.6	22
		IA	0.65	0.14		IA	0.52	0.25
Silage bags (trials 10-12)		MAE	7.9	8.7		MAE	-	-
		RMSE	8.0	8.8		RMSE	-	-
		IA	0.23	0.23		IA	-	-

[1] MAE is the mean absolute error, RMSE is the root mean square error, and IA is the index of agreement.

[2] No MAE, RMSE, and IA computed for silage bags using wind tunnel measurements as one data point only.

Table 12. Equivalent 12-h measured and simulated methanol emissions for conventional silage piles (trials 1-9) and silage bags (trials 10-12) based on flux-chamber and wind tunnel measurements.[1,2]

Trial	*Flux-chamber*				*Wind tunnel*			
	Concentration (mg/L)	*Emission rate (g/m^2)*			*Concentration (mg/L)*	*Emission rate (g/m^2)*		
		Measured	*Simulated*			*Measured*	*Simulated*	
			New	*Old*			*New*	*Old*
1	26	3.7	2.3	3.7	27	5.8	2.3	3.4
2	24	4.7	2.0	3.2				
3	25	3.5	1.9	3.0				
4	33	5.8	2.7	4.2	24	10.2	2.0	3.1
5	40	4.0	3.0	4.9				
6	27	2.4	1.7	2.6				
7	38	4.3	2.6	4.0	40	10.6	2.7	3.8
8	32	4.3	2.3	3.7				
9	29	4.4	2.2	3.6				
10	10	1.2	0.7	1.1	10	3.3	0.7	1.0
11	10	1.6	0.8	1.1				
12	9	2.7	0.7	1.0				
Conventional silage piles (trials 1-9)		MAE	1.8	0.7		MAE	6.5	5.4
		RMSE	2.0	0.9		RMSE	6.8	5.8
		IA	0.42	0.67		IA	0.36	0.40
Silage bags (trials 10-12)		MAE	1.1	0.8		MAE	-	-
		RMSE	1.2	1.0		RMSE	-	-
		IA	0.43	0.45		IA	-	-

[1] MAE is the mean absolute error, RMSE is the root mean square error, and IA is the index of agreement.

[2] No MAE, RMSE, and IA computed for silage bags using wind tunnel measurements as one data point only.

With fewer data points, wind tunnel-based measured and simulated emissions are shown in Figure 23. Compared to flux-chamber measurements (Figure 22), ethanol and methanol emission profiles measured with the wind-tunnel did not consistently decrease through time with some high emissions measured several hours after silage face exposure (Figure 23). Still, based on overall values (Table 11), the new model performed reasonably and similarly in simulating ethanol emissions as measured by the wind tunnel, with $R_{s/m}$ ranging from 0.40 to 1.35 and an average of 0.88, whereas the old model predicted very high ethanol emissions resulting to $R_{s/m}$ ranging from 1.85 to 6.39 and an average of 3.87. As with flux-chambers, the new model underpredicted the methanol emissions as measured by the wind tunnel, with $R_{s/m}$ (0.2 to 0.4) lower than those computed for flux-chambers. As mentioned above, this underprediction of methanol emissions might be due to the relationship used for approximating the diffusion-dispersion coefficient for methanol. Although the old model did well in predicting methanol emissions measured by flux-chambers, it did not do as well in simulating those measured by the wind tunnel based ($R_{s/m}$ of 0.31 to 0.59).

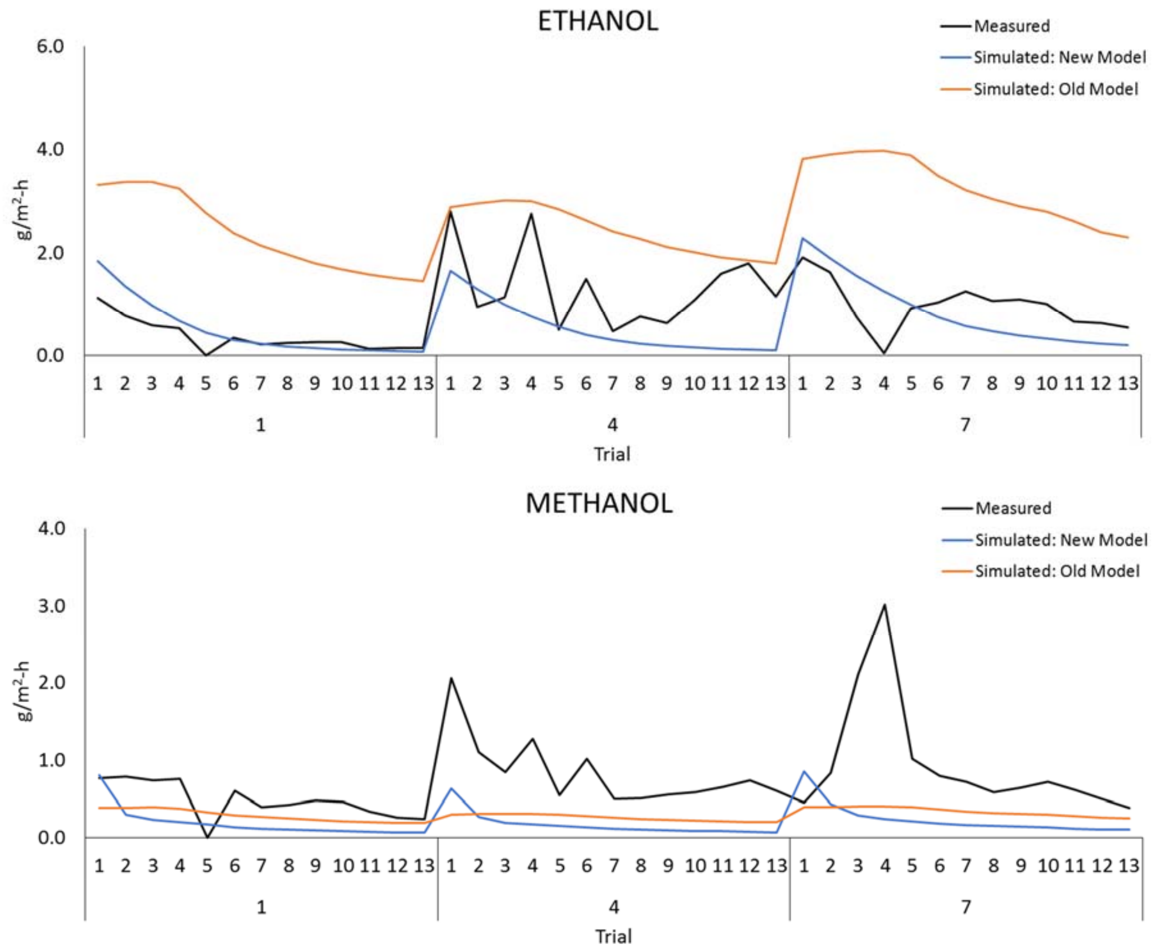

Figure 23. Comparison of simulated and wind tunnel-based emissions for conventional silage piles.

Silage Bags

The new model did not do well in representing ethanol emissions from silage bags through time. For both flux-chamber and wind-tunnel trials (Figures 24 and 25, respectively), although the model did simulate high ethanol emissions during the first hour of exposure, the predicted ethanol emission profile for the next hours was very low. As shown in Figures 24 and 25, after six hours of exposure, ethanol emissions predicted by the model were negligible whereas measured emissions were still above 0.5 g/m^2-h. Based on accumulated loss over time (Table 11), simulated ethanol emissions were just 22% to 28% and 14% of those measured with flux-chambers and the wind tunnel, respectively. Similar findings apply when simulating methanol emissions with the new model where simulated emissions are just 27% to 61% and 22% of measured values for flux-chambers and the wind tunnel (Table 12), respectively.

On the other hand, the old model was inconsistent when simulating emissions from silage bags, similar to its performance for conventional silage piles. For ethanol emissions, simulated profiles were much greater than flux-chamber measurements (Figure 24); but compared to wind tunnel measurements, the simulated profile was comparable to that measured (Figure 25). For methanol emissions, the old model did well in simulating 2 out of 3 trials using flux-chambers (Figure 31); but for wind tunnel measurement, the old model predicted a very low emission profile comparable to that simulated by the new model (Figure 25).

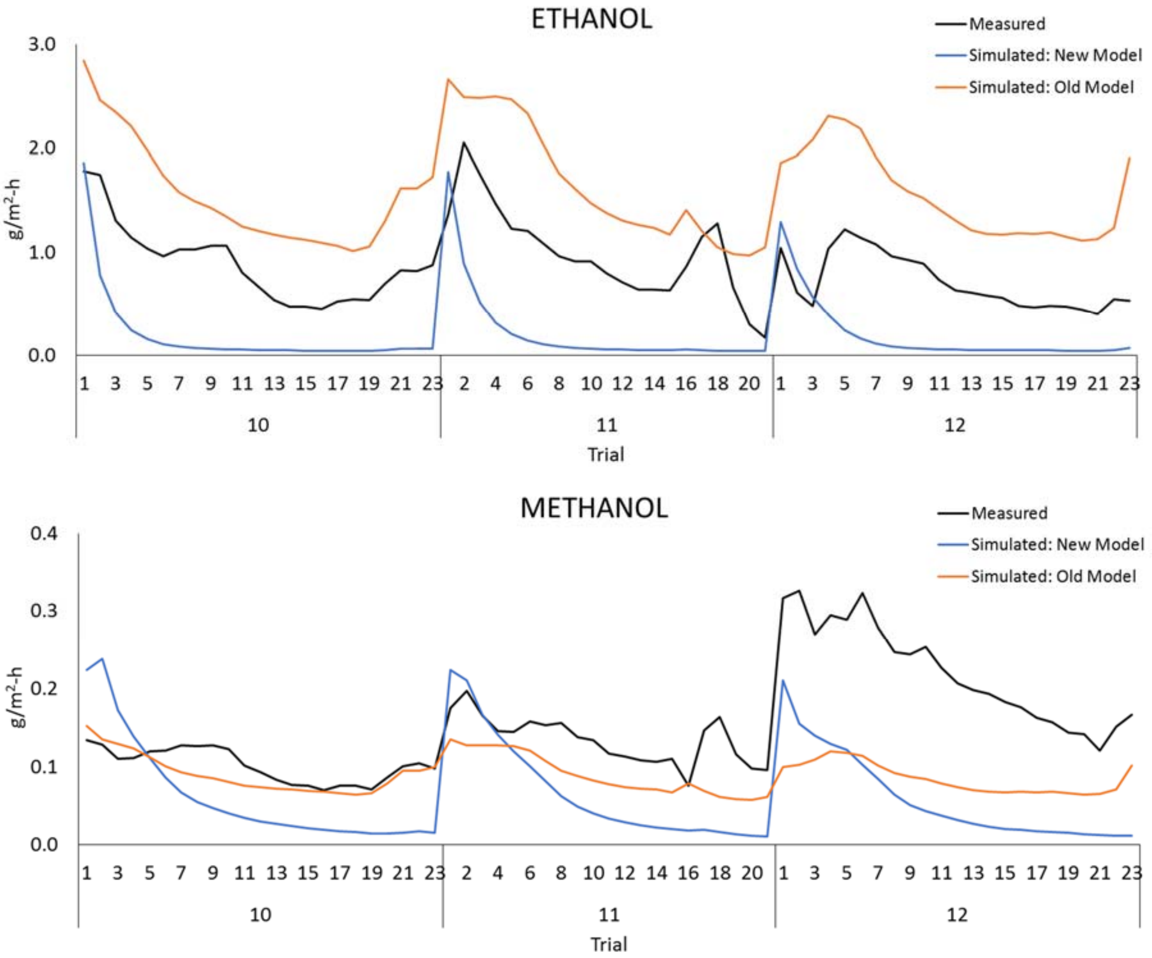

Figure 24. Comparison of simulated and flux chamber measured emissions from silage bags.

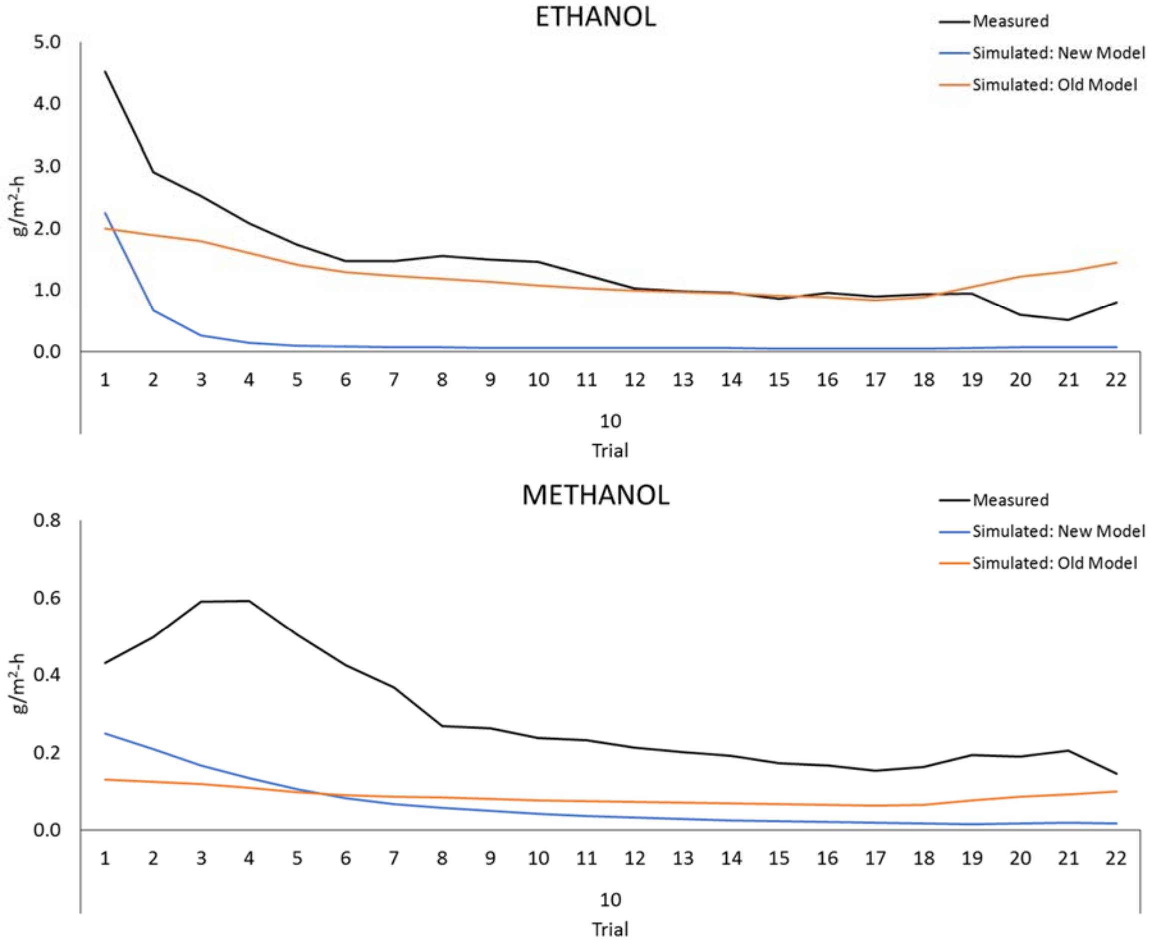

Figure 25. Comparison of simulated and wind tunnel measured emissions from silage bags.

Focusing on the new model, the lower emission profiles simulated for silage bags could be explained largely by the loss of ethanol (and methanol) at the surface layer. This behavior was verified through numerical modeling using fine spatial and temporal resolution, in which there was no need to assume or specify depth for the surface layer. Compared to conventional silage piles, silage bags had lower initial amounts of ethanol (and methanol) at the surface layer, and in the simulation, this contributed to loss of ethanol readily available for volatilization within the first few hours of exposure. Based on average initial silage concentrations, both ethanol and methanol concentrations for silage bags (151 and 10 mg/L, respectively) were less than half of corresponding concentrations for conventional silage piles (297 and 30 mg/L, respectively).

With lower initial alcohol concentrations in the silage, the higher emission profiles measured for silage bags, therefore, must be attributed to other conditions that can potentially increase volatilization. In the simulation, volatilization could be increased by one of the following: (1) decreasing the dry bulk density (e.g., from 190 to 70 kg/m^3), (2) decreasing the moisture content (e.g., from 50% to 30%), and (3) increasing diffusion-dispersion rates within the silage. Among the three, it was the last that led to emission profiles closer to those measured. Higher diffusion-dispersion coefficients allowed the new model to simulate higher transfer rates of ethanol and methanol from the second layer to the surface layer; this was also verified through numerical modeling with fine resolution, in which a faster movement of ethanol and methanol mass within the whole silage profile was modeled. But without comprehensive measured data (e.g., bulk density, moisture content, etc.), diffusion-dispersion coefficients were not refined. Also, it must be emphasized that the diffusion-dispersion coefficient relationship for ethanol implemented in the process-based model worked well with the experimental data by Montes et al. (2010) for packed silage (i.e., minimally disturbed bunker silo sample) and Hafner et al. (2010) for loose silage (i.e., with dry bulk density of around 130 kg/m^3).

Feed lanes (TMR Samples)

In simulating TMR samples representing feed lying in feed lanes, a dry bulk density of 190 kg/m^3 (Table 10) was estimated from known mass and approximate volume of TMR samples measured. In simulating corn silage samples, a lower dry bulk density (120 kg/m^3) was used. For both TMR and corn silage samples, measured and simulated ethanol and methanol emissions are plotted in Figure 26, with overall values summarized in Table 13. Unlike simulation of silage storages, no consistent trend was observed when simulating ethanol emissions from both TMR and corn silage samples using the new model. The new model did well in predicting ethanol emissions for a couple of TMR samples, namely trials 16 (+ 5% water) and 18 (+ 10% water) with $R_{s/m}$ of 0.78 and 0.74, respectively, and also for a corn silage sample (trial 21) with $R_{s/m}$ of 1.24. For trials 14 (TMR), 19 (TMR + 10% water), and 22 (corn silage), the new model was still able to simulate ethanol emissions reasonably, with predicted values within a factor of 2 of measured ($R_{s/m}$ of 0.53 to 0.56). For other remaining TMR samples (trials 13, 15, 17 and 20), $R_{s/m}$ were low, ranging from 0.22 to 0.41. There could be substantial uncertainty in measured ethanol emissions for trials 13, 15, and 22, where the amount of ethanol emitted appeared to exceed the initial ethanol content of the samples (see Figure A2.5 in the Appendix Supplementary Information section). The old model, on the other hand, tended to overpredict ethanol emissions (Figure 26), with $R_{s/m} > 1.5$ for 6 out of 10 trials.

Unlike the performance in simulating methanol emissions from silage storages, the new model overpredicted methanol emissions from TMR (trials 13 to 20) and corn silage samples (trials 21 to 22) (Figure 26). For all TMR samples, the cumulative amount of methanol emitted almost equaled the initial amount of methanol within the first 4 to 5 hours of measurement (Figure S4). Based on overall values (Table 13), $R_{s/m}$ for the new model were lowest for TMR without water addition (1.1 to 1.5) and highest for TMR with 10% water addition (2.4 to 3.5). In contrast, $R_{s/m}$ for corn silage samples were very low, with values of 0.09 and 0.23. These very low $R_{s/m}$ values, however, can be attributed to uncertainty in the measured emissions as total amounts of methanol emitted greatly exceeded the corresponding initial methanol contained in the samples (Figure A2.5). Similarly, the old model did not perform well in simulating methanol emissions from TMR and corn silage samples, with $R_{s/m}$ values (0.14 to 3.18) comparable to those for the new model (0.09 to 3.34).

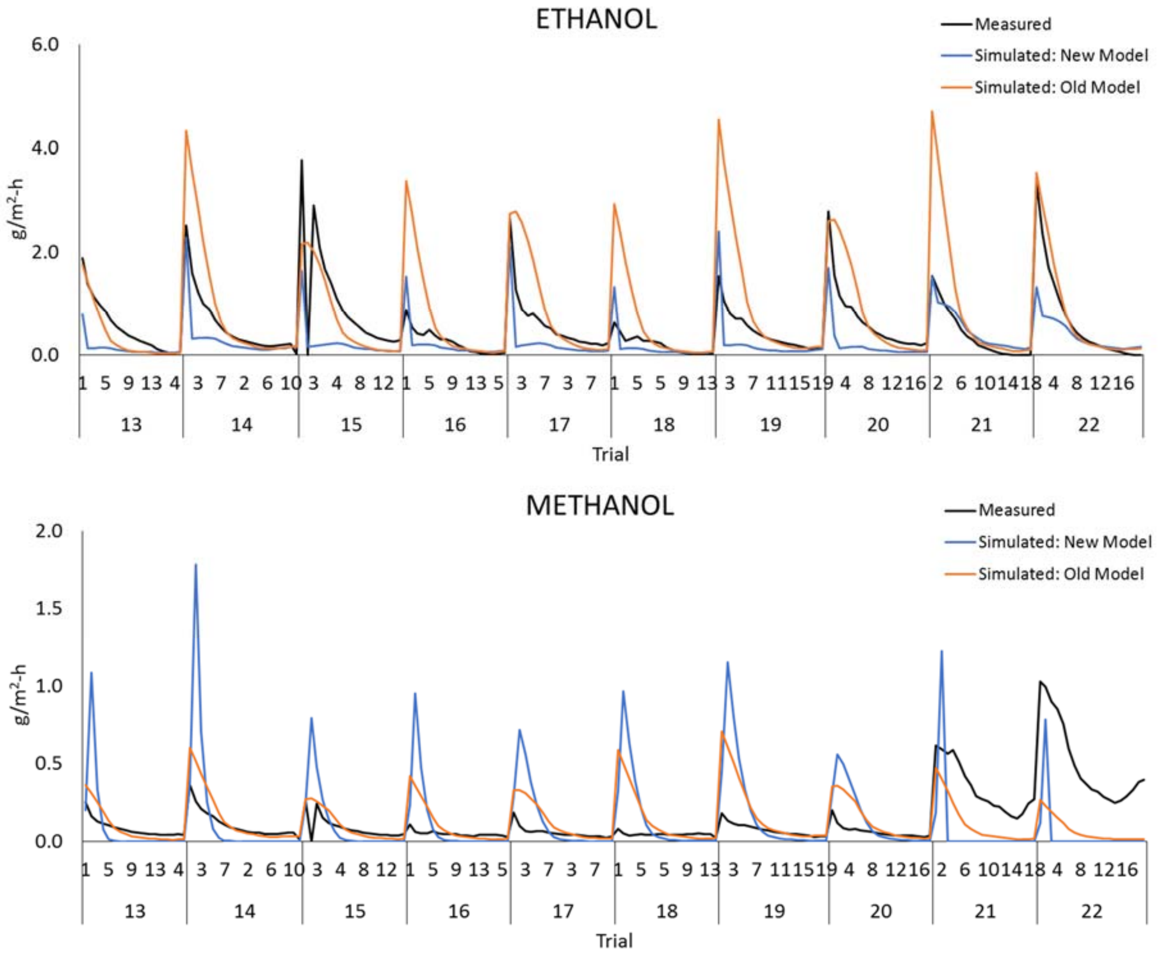

Figure 26. Comparison of simulated and flux chamber measured emissions for TMR and loose corn silage samples.

Similar to silage bags, the new model was able to predict the high ethanol emissions measured during the first hour but predicted a considerably lower emission profile for the succeeding hours (Figure 26). As explained for silage bags, the diffusion-dispersion coefficient relationship used may be causing the model to simulate low ethanol transfer rates from the second layer to the surface layer.

For both TMR and corn silage samples, the high methanol emission was predicted by the new model not for the first hour but for the second. For the first hour, $R_{s/m}$ were as follows: (1) 0.80 to 1.0 for TMR without water additions, (2) 1.5 to 2.1 for TMR + 5% water, (3) 1.5 to 4.0 for TMR + 10% water, and (4) 0.1 to 0.3 for corn silage samples. For the second hours, $R_{s/m}$ increased significantly: (1) ~ 7.0 for TMR without water additions, (2) 7 to 15 for TMR + 5% water, (3) 4.7 to 19.0 for TMR + 10% water, and (4) 0.8 to 2.1 for corn silage samples. To have the simulated profiles agree with measured, these findings suggest the need to lower the diffusion-dispersion coefficients used to predict methanol emission from TMR samples, which is opposite that needed for silage storages.

Table 13. Measured and simulated 12-h accumulated emissions of ethanol and methanol from TMR and corn silage samples.[1]

Trial	*Trial Sample*	*Ethanol*				*Methanol*			
		Concentration (mg/L)	*Emission rate (g/m^2)*			*Concentration (mg/L)*	*Emission rate (g/m^2)*		
			Measured	*Simulated*			*Measured*	*Simulated*	
				New	*Old*			*New*	*Old*
13	TMR + 0% water	62	6.4	1.4	4.4	16	1.0	1.1	1.1
14	TMR + 0% water	177	6.8	3.6	11.2	30	1.3	1.9	1.8
15	TMR + 0% water	127	11.9	2.7	8.8	18	1.1	1.3	1.2
16	TMR + 5% water	119	3.0	2.3	8.4	18	0.6	1.3	1.3
17	TMR + 5% water	165	7.3	3.0	11.2	22	0.7	1.6	1.5
18	TMR + 10% water	103	2.3	1.7	7.3	25	0.5	1.9	1.8
19	TMR + 10% water	186	5.4	2.8	12.3	35	0.9	2.4	2.2
20	TMR + 10% water	155	8.1	2.4	10.6	24	0.7	1.7	1.6
21	Corn silage	166	4.7	5.8	11.8	20	4.1	0.9	1.4
22	Corn silage	145	8.2	4.5	9.6	13	6.0	0.6	0.8
	All data		MAE	3.6	4.2		MAE	1.5	1.4
			RMSE	4.4	4.6		RMSE	2.2	2.0
			IA	0.44	0.38		IA	0.08	0.13

[1] MAE is the mean absolute error, RMSE is the root mean square error, and IA is the index of agreement.

Discussion on the Performance of the New Process-based Model

The new process-based model for silage VOC emissions performed well in simulating ethanol emissions for conventional silage piles. Using the refined settings for silage bulk density and moisture content, hourly ethanol emissions predicted were within range of and followed the trends of measured ethanol emissions. Simulation of methanol emissions for conventional silage piles suggests the need for experimental data to refine the emission and transport coefficients for different VOCs to be used in the new model. As presented, lower methanol emissions were predicted for conventional silage piles when using general equations (e.g., Mackay and Yeun, 1983). In our farm models, there are four different VOC groups simulated for silage sources: alcohols (represented by ethanol), acids (acetic acid), esters (ethyl acetate), and aldehydes (acetaldehydes). Among the four representative VOCs, only ethanol has relationships for these coefficients derived from experimental silage data.

Figure 27 shows the comparison of silage bags and conventional silage piles in terms of ethanol emission rate (i.e., mass of ethanol emitted per unit area of exposed silage face) and total mass of ethanol emitted based on measurements and simulation using the new model. Results for the old model are also included to illustrate the large improvement in VOC emission simulation using the new model. Note that trial 2 for a conventional silage pile was treated separately for demonstration purposes as it had an initial ethanol concentration (136 mg/L) half of that for other conventional silage piles (average of 317 mg/L) but within range of those for silage bags (average of 151 mg/L). Even if conventional silage piles (excluding trial 2) had the highest initial ethanol concentrations, it was silage bags that had the highest measured amounts of ethanol emitted per unit area of exposed silage face (Figure 27a). In addition, comparing measured emissions for silage bags and trial 2 of conventional silage piles showed that changing silage storage from conventional silage piles to silage bags doubled the amount of ethanol emitted per unit area (Figure 27a). These findings just show the high VOC emission rates (i.e., on an area basis) associated with low bulk density settings. With larger areas of exposed silage face, however, conventional silage piles had much greater total emissions than silage bags as shown in Figure 27b. Using areas of 13 m^2 and 140 m^2 for silage bags and conventional silage piles, total masses of ethanol emitted based on measurements were 134 g for silage bags and 684 (trial 2) to 1,051 g from conventional silage piles.

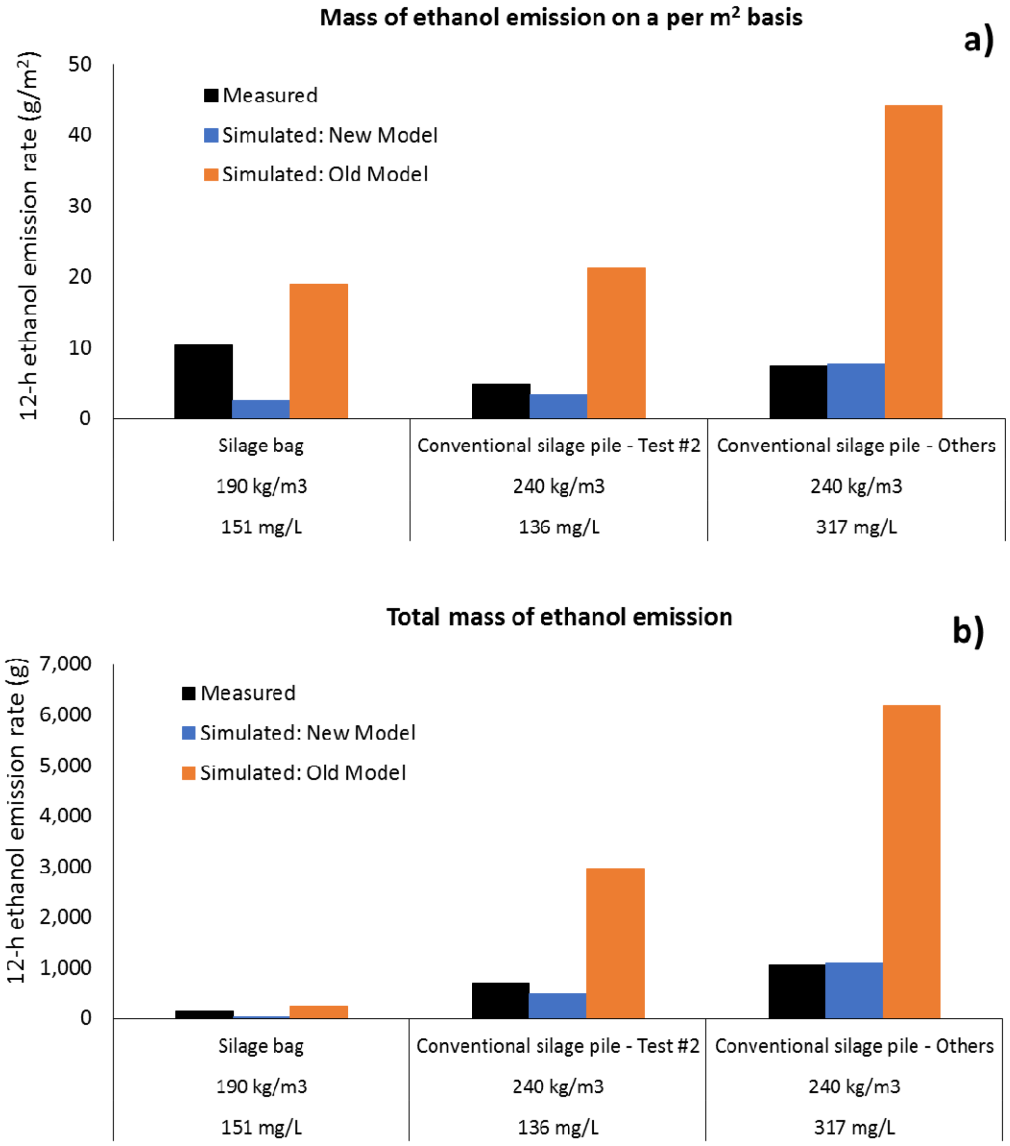

Figure 27. Comparison of simulated and flux-chamber measured 12-h ethanol emissions for TMR and loose corn silage samples: a) mass emitted on a per m^2 basis of exposed silage face; b) total mass emitted.

For silage bags and TMR samples, both of which had lower bulk densities than conventional silage piles, the new model predicted lower ethanol emissions on an area basis. In the new model, dry bulk density affects the calculation of the effective surface mass transfer coefficient (α in eq. 3), effective diffusion mass transfer coefficient (D_b in eq. 4), adjustment of diffusion-dispersion coefficient (k_{sg}) to represent diffusion in a porous media (i.e., Millington-Quirk model), and the amount of VOC in the surface layer readily available for volatilization. With the 240 kg/m^3 setting as reference, simulating the conventional silage piles at different bulk densities with the new model resulted in the following (maximum) percent changes in ethanol emissions: 3% increase at 190 kg/m^3, 7% decrease at 290 kg/m^3, and 18% decrease at 350 kg/m^3. At lower dry bulk densities (< 190 kg/m^3), a decrease rather than an increase in ethanol emissions were simulated. Even by adjusting the depth of the surface layer with respect to dry bulk density (Table 10), a very low dry bulk density setting would eventually have limited the amount of ethanol readily available for volatilization in the simulation.

If dry bulk densities assumed for silage bags and TMR samples were close to actual conditions and emissions measured were reliable, results suggest a need to refine emission and transport coefficients (e.g., k_{sg}) not only as a function of wind speed and friction velocity but also dry bulk density. Refinement was not performed at this time as dry bulk densities for conventional silage piles and silage bags were not measured. It is also important to have more measurements to verify the effects of dry bulk density and/or storage type on VOC emissions. Using measured emissions, percentage losses of initial ethanol and methanol present in the first 1 m of silage were 0.45% and 2.5% for conventional silage piles and 3% and 6% for silage bags, respectively. These indicate that changing the storage type from conventional silage piles to silage bags (or decreasing dry bulk density) resulted to a 7x increase in measured ethanol emissions per unit of exposed surface area but only a 2.5x increase in measured methanol emissions. This was quite unexpected as methanol is more volatile than ethanol. In addition, comparing conventional silage piles and silage bags in terms of measured initial concentrations and measured 12-h emission rates (flux-chambers) resulted to contrasting trends between ethanol and methanol (Tables 11 and 12). Silage bags, which had lower initial methanol concentrations (average of 10 mg/L), had lower 12-h methanol emission rates on an area basis (1.8 g/m^2) than conventional silage piles (30 mg/L, 4.1 g/m^2). In contrast, even with lower initial ethanol concentrations (151 mg/L), silage bags had higher 12-h ethanol emission rates (10 g/m^2) than conventional silage piles (297 mg/L, 7.2 g/m^2).

There could be two possible scenarios to explain why the new model overpredicted methanol emissions from TMR samples, which was in contrast to simulations of conventional silage piles and silage bags. First, given that the new model overpredicted methanol emissions, water addition could have lowered methanol emissions from TMR samples as some VOCs may have high affinity to a liquid phase leading to lower volatilization (which is not simulated in the model); but then again, this might not be the case as the new model actually underpredicted ethanol emissions. Second, with TMR samples having a very loose structure after mixing and methanol having high volatility (i.e., twice that of ethanol), some of the methanol might have been lost during sample collection and set-up prior to emission measurement. Considering the findings for conventional silage piles and silage bags, the second scenario would likely explain the higher methanol emissions predicted by the new model.

Application in Whole Farm Analyses

The new silage VOC emission model is incorporated as a component of IFSM (Rotz et al., 2015b) for simulating VOC emissions from silage storages, such as conventional piles and silage bags, following feed removal and from feed lanes during feeding. Integrated in IFSM, the new model can be used to evaluate the effects of silage storage and feeding management on the overall performance, economics and environmental impacts of farm systems. As performed in this model application, the new model was used to assess and compare VOC emissions as influenced by different storage types, packing density, animal housing facilities, etc. Despite the uncertainty remaining in model predictions, it still provides a valuable tool for comparing management options. Although we cannot be certain of the absolute amounts of emissions predicted, the relative differences created through management and environmental changes should reflect the impact of mitigation strategies. To illustrate the use of the model, several silage management options were simulated on a representative dairy farm in Central California.

Whole Farm Model

The IFSM simulates crop production, feed use, and the return of manure nutrients back to the land for many years of daily weather on a crop, dairy, or beef farm (Rotz et al., 2015b). Daily growth and development of crops are predicted based upon soil water and N availability, ambient temperature, and solar radiation. Simulated tillage, planting, harvest, storage, and feeding operations predict resource use, timeliness of operations, crop losses, and nutritive quality of feeds. Feed allocation and animal responses are related to the nutrient contents of available feeds and the nutrient requirements of the animal groups making up the herd. The quantity and nutrient contents of the manure produced are a function of the feeds consumed and herd characteristics.

Nutrient flows are tracked to predict losses to the environment and potential accumulation in the soil (Rotz et al., 2015b). Losses include ammonia (NH_3) volatilization, denitrification and leaching losses of N, and erosion of sediment and runoff of sediment-bound and dissolved N and P across the farm boundaries. Carbon dioxide, CH_4, and N_2O emissions are tracked from crop, animal, and manure sources and sinks to predict net greenhouse gas emission in CO_2 equivalent units. Whole-farm mass balances of N, P, K, and C are determined as the sum of nutrient imports in feed, fertilizer, deposition, and fixation minus the nutrient exports in milk, excess feed, animals, manure, and losses leaving the operation. A cradle-to-farm gate life cycle assessment is done to determine annual carbon, energy, water, and reactive N footprints of the farm products produced.

Simulated performance is used to determine production costs, incomes, and economic return for each year of weather. A whole-farm budget includes fixed and variable production costs (Rotz et al., 2015b). All important production costs are subtracted from the total income received for animal and excess feed sales to determine a net return to management. By comparing simulation results, differences among production systems can be determined, including annual resource use, production efficiency, environmental impacts, production costs, and farm profit. The distribution of annual values can be used to evaluate the risk or variance due to the variation in daily and annual weather patterns.

The new silage VOC component provides the ability to evaluate management effects on VOC emissions along with other aspects of the farm. To represent total VOC emission, we consider four groups of VOCs which have the most potential to contribute to poor air quality: acids, alcohols, esters, and aldehydes (Hafner et al., 2013). On farms, VOC emission from silage is determined by the production of VOCs in silage and the fraction of each compound that is volatilized. VOC production can vary greatly among silages, and the sources of this variability are not yet known (Hafner et al., 2013). Therefore, VOC production is set as an initial concentration based on typical values for different types of silage. From these fixed initial concentrations, we simulate VOC emissions as described above. Emission losses are predicted and the remaining VOC mass is tracked as silage moves through three stages: storage removal (when silage is exposed on the open surface following daily or more frequent feed removal), feed mixing, and feeding in a feed lane or bunk. Emissions during initial filling, fermentation and storage phases of silage management are not modeled. Emissions during these phases have not been measured and they are assumed to be small and unimportant compared to those from the silage face and feeding of the silage. VOC emission during storage removal and mixing reduces the concentration of VOCs present in the remaining stages. Calculated emissions from each group of compounds are aggregated after normalizing emissions based on the ozone formation potential of each group. Normalized ozone formation potential is determined as the predicted VOC emission of that group times the Equal Benefit Incremental Reactivity (kg O3 per kg VOC) of that compound group (Howard et al., 2015).

For completeness, VOC emissions are also predicted from manure sources in the housing facility, during storage and following field application (Rotz et al., 2015b). A similar approach as that used for silage is used to estimate manure emissions where an initial concentration is assumed and losses are predicted using theoretical relationships of mass transfer. Total VOCs tracked are divided into 5 groups (C2 and C3 acids, C4 and larger acids, alcohols, aromatic acids and aromatics). Compounds used to represent each of the groups are acetic acid, butyric acid, ethanol, phenyl-acetic and indole, respectively. This portion of the model has not been evaluated with farm data so the accuracy of these estimates are unknown. We include a measure of these predictions in our simulations to indicate how changes in silage emissions affect whole farm emissions. In general, reactive VOC emissions from manure are relatively small compared to that from silage. Our whole farm estimated emissions do not include enteric emissions from the animals other than methane. There are likely other compounds emitted by the animals, but little data exist to support a model of this source. This source is also expected to be relatively small compared to silage and manure sources.

Farm Description

To illustrate the impacts of silage management, a representative dairy farm was simulated in central California. The farm represented a well-managed dairy production system for this region. The farm included 2,000 Holstein cows and 1,650 replacement heifers on 300 ha of clay loam soil. Crops produced were corn silage followed by oat silage in a double crop system. Irrigation was used as needed with up to 60 cm applied to corn and up to 20 cm applied to the winter oat crop. Corn silage harvest was initiated around September 1 and oat silage was harvested in the spring beginning around April 20. Corn and oat silages were preserved in covered silage piles.

Annual milk production was 11,000 kg/cow corrected to 4% fat and 3.3% protein. All animals were fed total mixed rations. Farm produced silage was supplemented with purchased alfalfa hay, corn grain, and high protein feed mixes to meet energy, protein and mineral requirements. All animals were housed in free stall barns with access to open lots. Manure was flushed from free stall floors daily and handled as a liquid slurry. Manure from the lots was handled dry and exported from the farm to maintain a phosphorus balance for the cropland. Liquid manure was stored in a lined earthen basin for up to 6 months and applied to cropland with 70% of the manure applied to the corn crop. Nitrogen fertilizer was applied to corn at a rate of 100 kg/ha. All other crop nutrient needs were met through manure application. The farm was simulated over 25 years of historical weather for Sacramento (1981 to 2005).

Silage Management Options

Simulation results for various silage management options are shown in Table 14. For the base farm with silage stored in conventional piles, about 4,000 kg of reactive VOCs were emitted each year with over 30,000 kg emitted during feeding. Most of the feeding loss occurred from the feed lane with a relatively small emission during the mixing of the total mixed ration. The main driver for this relatively large loss during feeding is the large surface area exposed. The exposed surface area of the silage face is about 140 m^2. When the feed is laid in front of the cattle, the exposed area is about 0.5 m^2 per cow with a little less area for younger animals. For the simulated farm, the exposed surface area of feed in the feed lane was about 1,200 m^2, over 8 times that of the silage face. With similar emission rates per unit of exposed area, much more emission occurs from the feed lane. An additional 8,000 kg of reactive VOC was predicted to be emitted from manure sources, which was about 25% of that emitted from silage.

Table 14. Effect of various silage storage and feeding practices on the potential ozone forming VOC emissions[1] from a representative California dairy farm[2].

		Silage face	*Feeding*[3]	*Total silage loss*		*Total farm*[4]	
		kg	*kg*	*kg*	*% change*[5]	*kg*	*% change*[5]
Storage type	Conventional pile	4,053	30,734	34,787		42,973	
	Bunker	4,474	30,841	35,315	1.5	43,491	1.2
	Bag	427	32,222	32,649	-6.1	40,806	-5.0
Silage unloader	Bucket	4,053	30,734	34,787		42,973	
	Defacer	3,088	30,986	34,974	-2.0	42,260	-1.7
Pack density	Light tractor	4,472	30,663	35,135		43,319	0.8
	Heavy tractor	4,053	30,734	34,787	-1.0	42,973	
Feeding site	Dry lot corral	4,056	49,298	53,354		61,936	44.1
	Free stall barn	4,053	30,734	34,787	-53	42,973	
	Enclosed barn	4,053	31,125	35,178	-52	42,855	-0.3
Location	Central CA	4,053	30,734	34,787		42,973	
	Southern ID	2,844	21,580	24,424	-30.0	31,584	-26.5

[1] Total VOC emissions are converted to their potential to form atmospheric ozone based upon their reactivity.

[2] 2000 cows plus 1650 replacement heifers on 3000 ha of double cropped corn and small grain harvested, stored and feed as silage.

[3] Loss occurring during feed mixing and silage lying in the feed lane.

[4] Total farm includes estimated losses from manure during housing, storage and field application.

[5] Percent change is computed as 100 times the difference between the emission from the alternative option and the base option divided by the base option emission. The base option for each are the conventional pile, bucket unloader, light tractor, dry lot corral and central California, respectively.

The storage type used can have a major effect on VOC emissions (Table 14). A bunker silo can be used with side walls allowing a greater depth and smaller width along with some increase in packed density. This change, however, had little effect on emissions. Use of silage bags greatly reduced the loss from the silage face due to the relatively small exposed surface area. With less loss at the silage face, greater loss occurred during feeding, and overall there was a 7% decrease in reactive VOC emissions from silage and about a 5% decrease from the whole farm.

Technology referred to as a silage defacer, provides a smoother and denser face on the silage surface. Simulation of this option provided a 24% decrease in loss from the face of the silage pile. The increased concentration in the silage fed caused a small 1% increase in emissions from the feed lane. Over all sources, there was only a 2% decrease from silage and less than a 2% decrease from the whole farm (Table 14). Although this defacing technology can provide substantial reductions from the silage face, this simulation indicates relatively low benefit from a whole farm perspective.

The size of the tractor used to pack the silage affects the density of the packed silage. Our simulation indicates that this difference in density has little effect on VOC emissions (Table 14). Our present model assumes that the initial concentrations of VOC compounds in the silage are similar regardless of density. This may not be the case in reality. Better packing should improve silage fermentation, which may reduce the concentrations of some compounds and increase the concentrations of others. If the production of the most volatile and reactive compounds such as alcohols is reduced, this may provide more benefit than the current model illustrates. The effect of silage density on VOC production is not well understood, but is likely relatively small.

The cow housing (i.e. feeding location) may have the greatest impact on silage VOC emissions (Table 12). Our simulations indicate that feeding cows in an open feed lane on an open dry lot can greatly increase reactive VOC emissions compared to an open, naturally ventilated (i.e. roofed but w/o side walls) free stall barn or an enclosed free stall barn that is mechanically ventilated (not used in CA but in the Midwest and Eastern US). The cause of this great difference is the velocity of air moving over the silage surface. When cows are fed inside a structure, air movement is reduced and our model shows a high sensitivity to air speed over the feed. To our knowledge, on-farm measurements have not been made to support or disprove this prediction for emissions across housing/feeding systems. Such measurements are needed before recommendations on mitigation strategies can be made. These simulated data indicate that changes in the feed bunk design to limit air flow over the feed could perhaps provide the greatest benefit in reducing VOC emissions from California dairy farms and this may be achieved with little added cost to the producer.

A final set of simulations illustrates the effect that climate can have on reactive VOC emissions. By simulating the same dairy farm in the climate of southern Idaho, emissions were reduced by 30% (Table 14). This effect is influenced primarily by lower ambient temperatures where the average annual temperature in Idaho was 5°C less than that in the SJV. Wind speed also averaged about 15% less in Idaho, which contributed to the reduction in emissions.

Conclusions

Using measurements from commercial California dairy farms collected through the present project, it was determined that the former silage VOC emission component of our whole farm simulation models, namely IFSM and DairyGEM, performed poorly in predicting ethanol and methanol emissions from different silage sources measured under field conditions, particularly those for conventional silage piles in which simulated ethanol emissions were 4 to 9 times the measured data. The tendency to overpredict ethanol emissions and the inconsistency associated with simulating methanol emissions was attributed to the nature of the original simple three-pool model. Rather than simulating the different processes (i.e., surface emission and mass transport) leading to emission of VOCs from silage, the previous model just approximated the fraction of VOC lost from each pool with respect to time. As a result, the old model was not able to simulate effects of silage bulk density and moisture content on VOC emissions, and was not capable of predicting the characteristic trends of VOC emissions.

Through the present grant, these inadequacies in simulating silage VOC emissions were addressed by developing a new process-based model based upon theoretical relationships of mass transfer and surface emission. Surface emission and mass transfer of VOCs within silage were simulated through numerical modeling. Data from our previous laboratory experiments were used to refine expressions for coefficients for surface mass transfer and gaseous phase diffusion-dispersion for ethanol emissions. Critical for incorporation into our whole farm simulation models, simulation layers in the new process-based model were made functions of friction velocity and silage source dry bulk density to significantly shorten the simulation time required (i.e., from several hours to a few seconds). Simulating emissions from the surface and mass transfer of VOC groups within the silage, the new model worked relatively well in predicting ethanol emissions measured from corn silage on California dairies. Profiles characteristic to silage ethanol emissions are now simulated, with high emissions during the first hours of exposure followed by a decline in the succeeding hours. For methanol, however, the new model underpredicted the measured emissions. Hence, more work is needed to determine the cause of and to reduce the discrepancy when simulating emissions of methanol and, possibly, other VOCs.

The new silage VOC emission model was incorporated as a component of a whole farm simulation model where it can be used to evaluate management effects on VOC emissions along with other aspects of farm performance, environmental impact and economics. Simulations of a representative dairy farm in California indicate that most of the reactive VOC emissions occur from feed lying in feed lanes during feeding as opposed to the exposed face of silage piles and/or bags. This implies that mitigation efforts on reducing emissions during feeding rather than those from the exposed face of the silage pile will be most effective.

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Appendix

A1. Emission comparisons between Conventional Silage Pile vs. Silage Bag per Area

The emissions between the conventional silage pile and the silage bag were compared to provide differences of VOC and NOx emissions of two commonly used silage storage systems. Both silage storage systems commonly use extraction via front-end loader with perpendicular defacing action, a practice used in the present study.

Figures A1.1-A1.7 show means of gas emissions of the two major storage forms, namely the conventional silage pile vs. a silage bag for the area of coverage by the flux chamber (m^2). More meaningful are Figures 8-14 in the main text of this report, that show means of gas emissions for conventional silage pile vs. a silage bag but this time corrected for the total exposed silage face (rather than per area coverage of the flux chamber). True comparisons between storage types should be conducted in the latter manner, because the silage bag vs conventional silage pile have exposure areas that differ by an order of magnitude. Figures A1.1-A1.7 present measurements between the silage bag and the conventional silage pile. The silage bag produced greater methane, nitric oxide, nitrous oxide, ammonia, and ethanol emissions when compared by surface area of the flux chamber. Conversely, the conventional silage pile vs. silage bag produced more methanol and nitrogen dioxide (Figures A1.1-A1.7). However, it must be reiterated, that these measurements in Figures A1.1-A1.7 depict only the emissions from the area of the flux chamber (i.e. only sampling the area they covered). For completeness, the raw data from the conventional silage pile and the silage bag are provided, however, more important than the emissions per measured m^2, are the emissions per silage pile face exposed to the atmosphere.

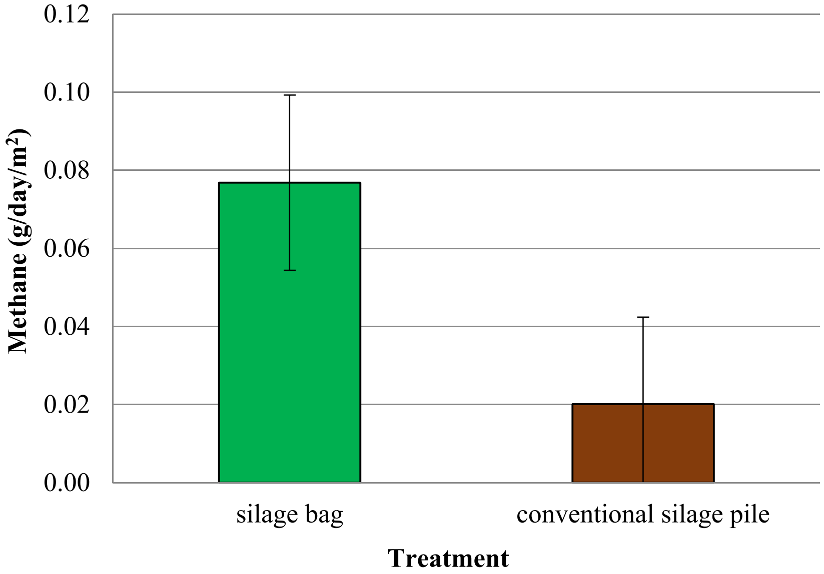

Figure A1.1. Means of silage storage types on methane emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

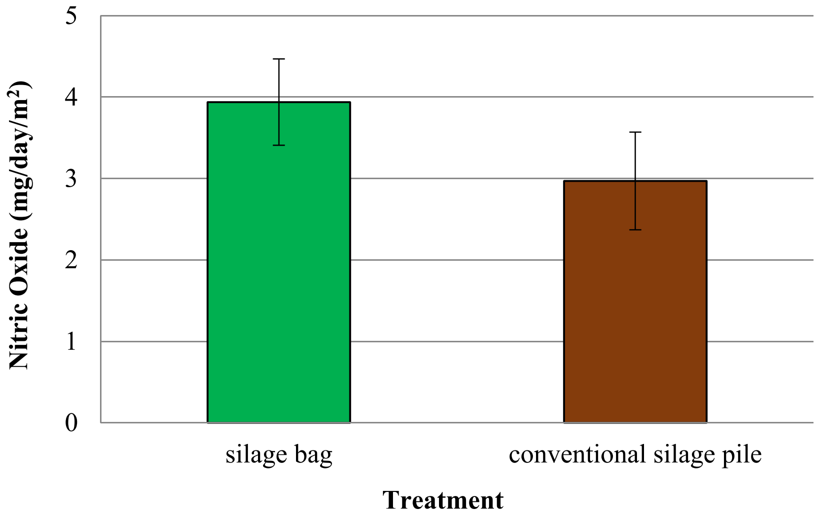

Figure A1.2. Means of silage storage types on nitric oxide emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

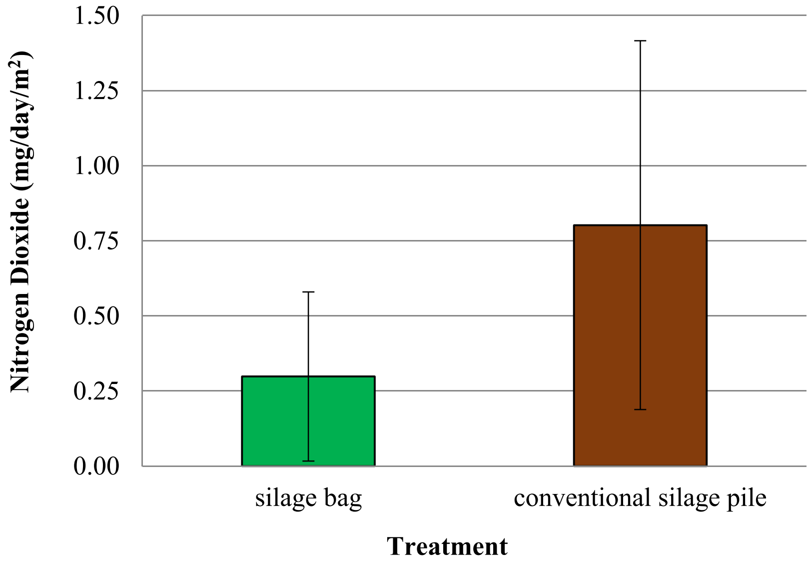

Figure A1.3. Means of silage storage types on nitrogen dioxide emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

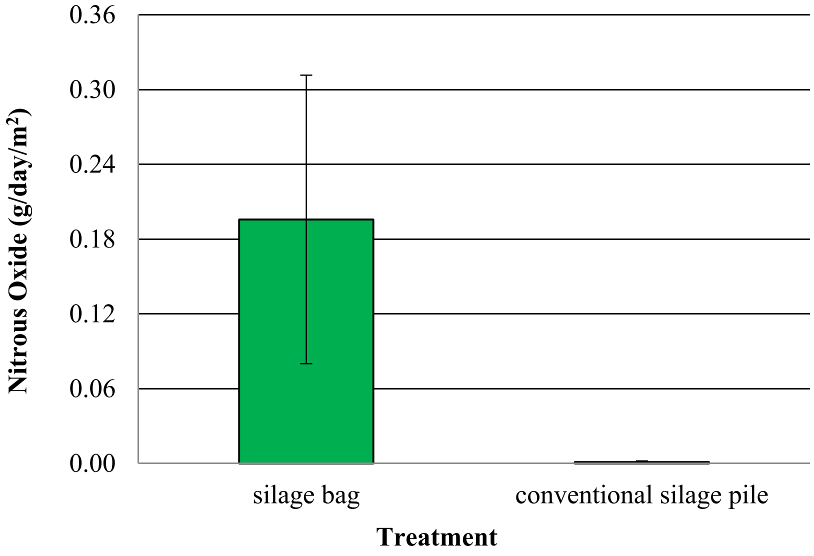

Figure A1.4. Means of silage storage types on nitrous oxide emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

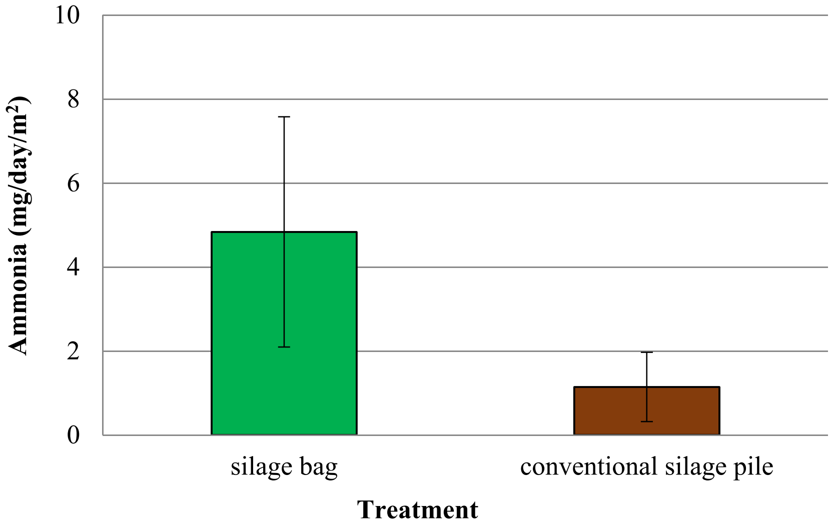

Figure A1.5. Means of silage storage types on ammonia emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

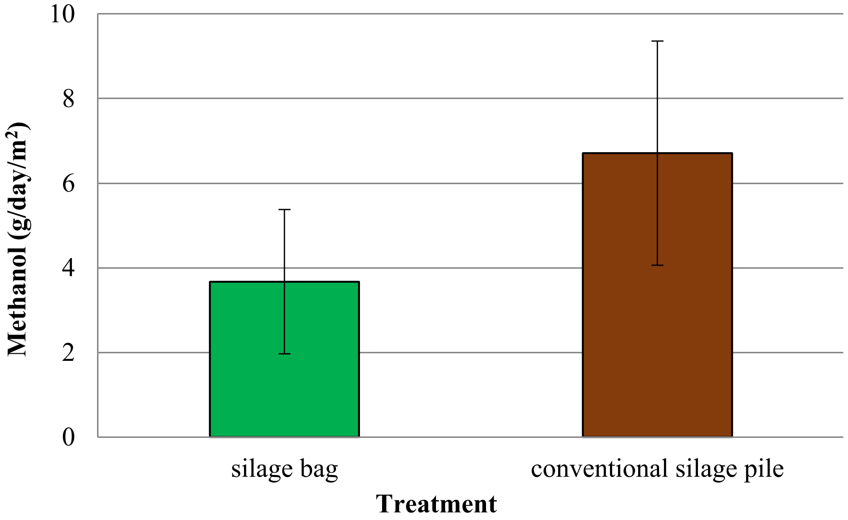

Figure A1.6. Means of silage storage types on methanol emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

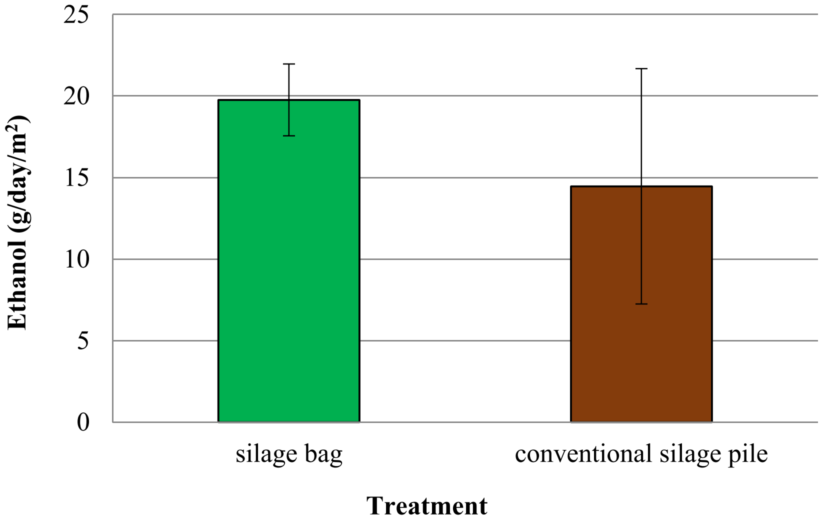

Figure A1.7. Means of silage storage types on ethanol emissions (each of these treatments were measured on three different days and the bars indicate the standard deviation).

Table A1.1 summarizes the results of Figure A1.1-A1.7 comparing the gas emissions per area from conventional silage pile vs. silage bag.

Table A1.1. Comparison of gas emissions per area between different silage storage

	Silage storage	
Gas emissions	Silage bag	Conventional silage pile
Methane (g/day/m^2)	0.08 ± 0.02	0.02 ± 0.02
Nitric Oxide (mg/day/m^2)	3.94 ± 0.53	2.97 ± 0.60
Nitrogen Dioxide (mg/day/m^2)	0.30 ± 0.28	0.80 ± 0.61
Nitrous Oxide (mg/day/m^2)	0.20 ± 0.12	0.001 ± 0.001
Ammonia (mg/day/m^2)	4.84 ± 2.74	1.14 ± 0.82
Methanol (g/day/m^2)	3.67 ± 1.71	6.71 ± 2.65
Ethanol (g/day/m^2)	19.76 ± 2.20	14.46 ± 7.21
TOFP[1] (O_3 g/day/m^2)	31.04	25.33

[1] TOFP: Total Ozone Forming Potential of Methane, Methanol, and Ethanol

A2. Supplementary Information for Chapter 4.

Note: Figures A2.1 and A2.2 are simulation results for ethanol and methanol emissions from the conventional silage piles using the former VOC emission model (i.e., the model incorporated in IFSM ver. 4.2 and DairyGEM ver. 3.2). Similar profiles were obtained for silage bags (profiles not shown).

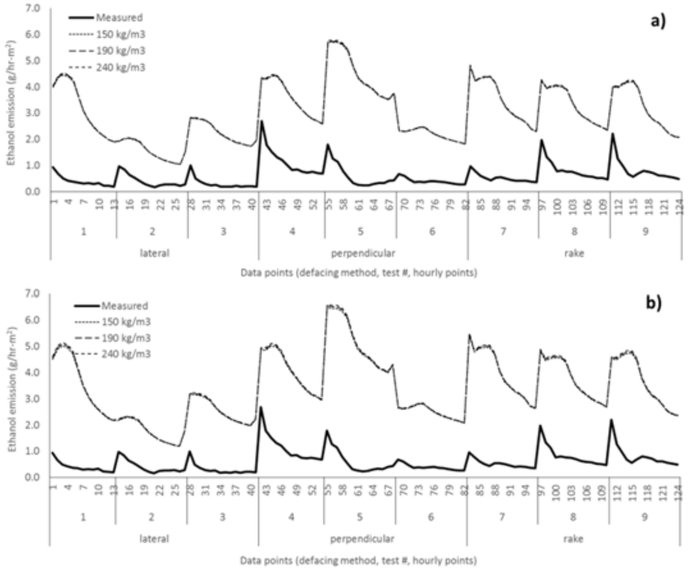

Figure A2.1. Measured and simulated ethanol emissions for the conventional silage piles using the former VOC emission model. For simulation, figures presented are based on various dry bulk densities and moisture contents of a) 70% and b) 60%.

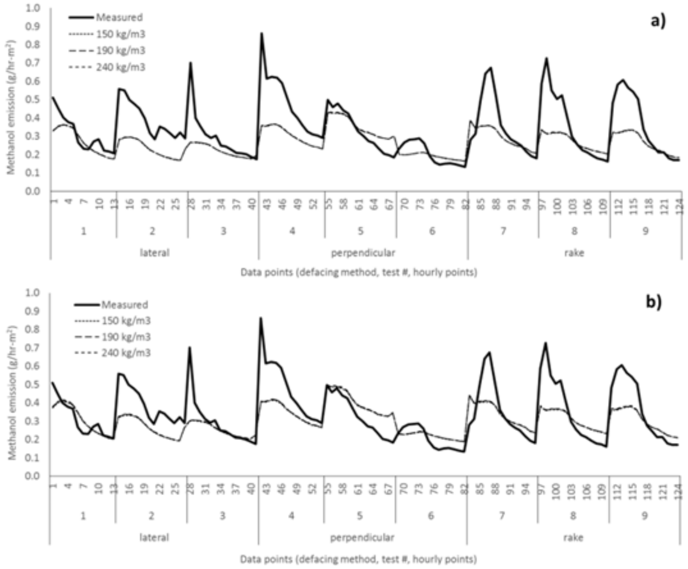

Figure A2.2. Measured and simulated methanol emissions for the conventional silage piles using the former VOC emission model. For simulation, figures presented are based on various dry bulk densities and moisture contents of a) 70% and b) 60%.

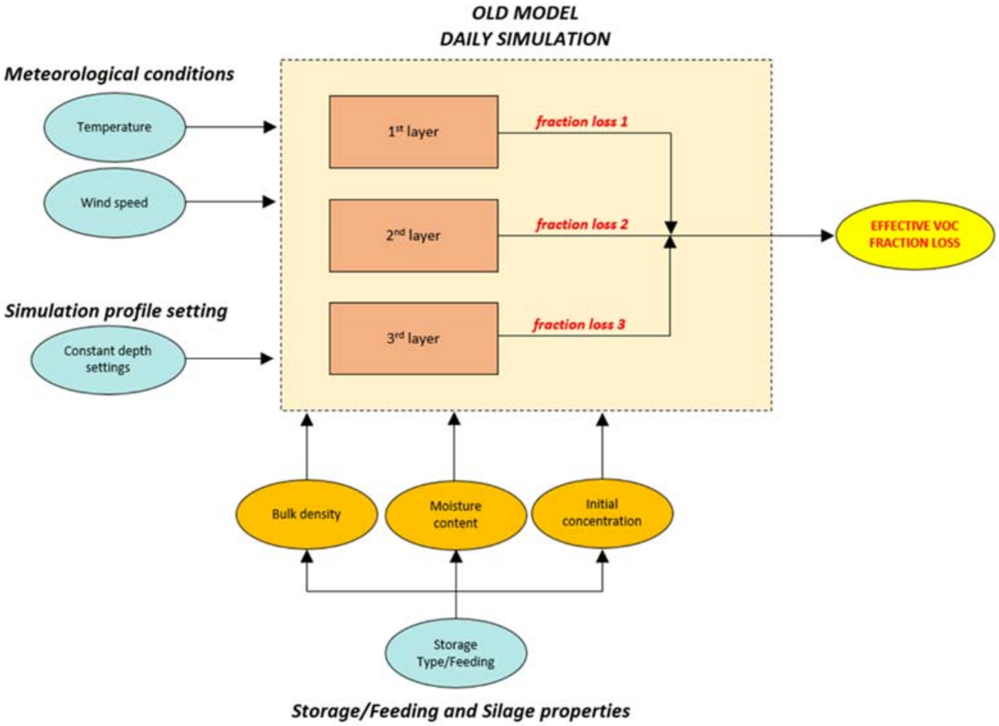

Figure A2.3. Schematic representation of the former VOC emission model for silage sources implemented in the Integrated Farm System Model (IFSM).

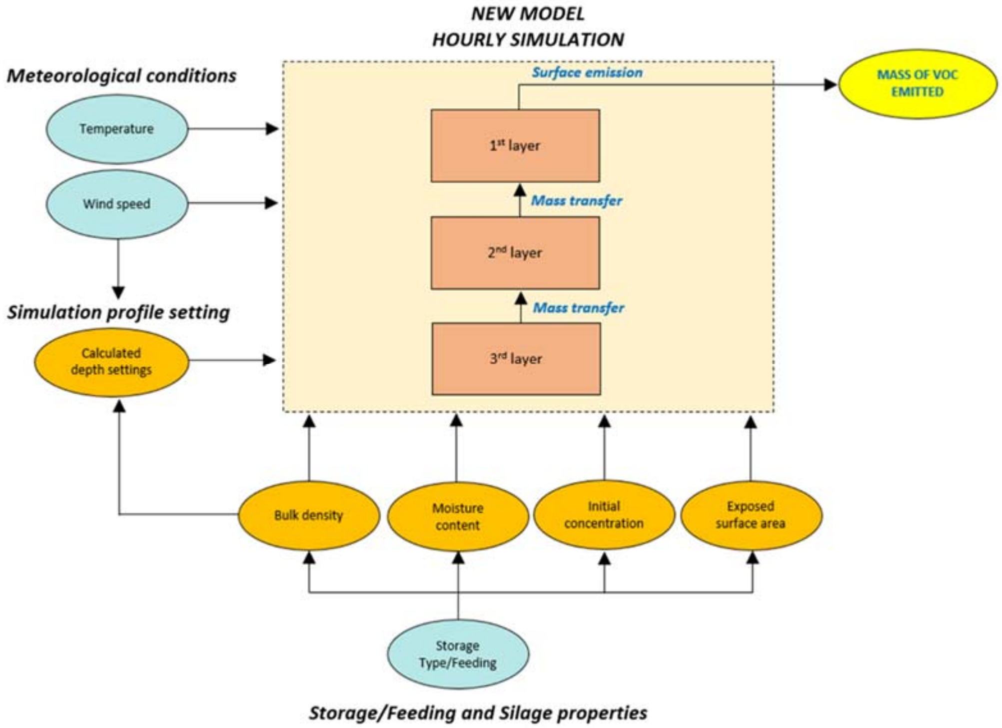

Figure A2.4. Schematic representation of the revised VOC emission model for silage sources as implemented in the Integrated Farm System Model (IFSM).

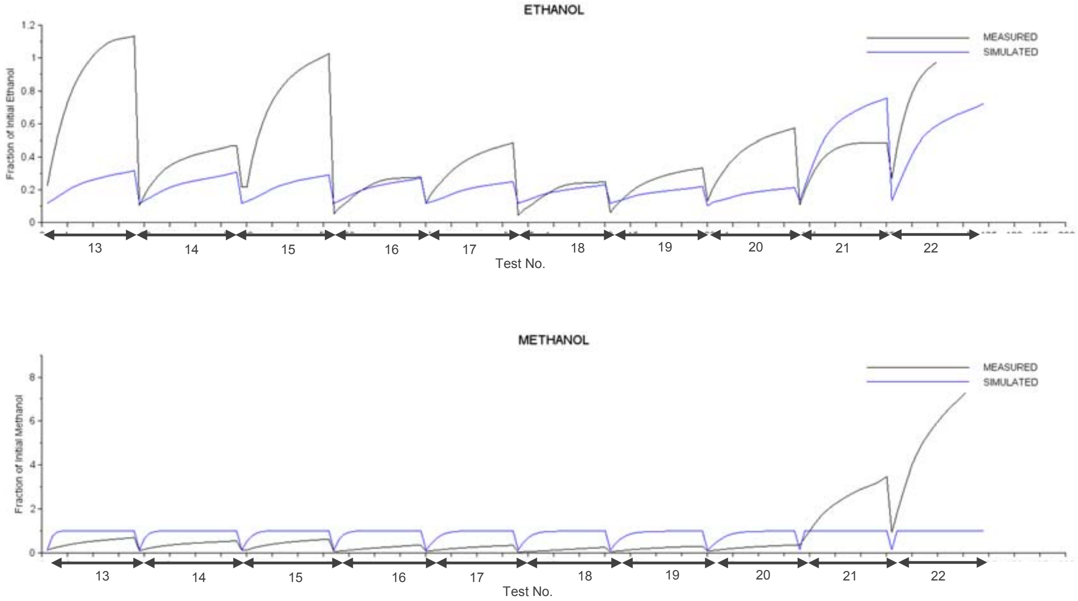

Figure A2.5 Comparison of simulated and flux-chamber-based emissions for TMR and loose corn silage samples normalized with respect to initial ethanol and methanol contents.

A3. San Joaquin Valley Air Pollution Control District Rule 4570

The following section describes the current feed related rule elements for SJVAPCD Rule 4570:

As a result, we caution the use of additives as a mitigation measure for silage as is currently listed in Rule 4570. Listed below are the various mitigation strategies specifically for animal feed, outlined by Rule 4570.

Rule 4570 “The purpose of this rule is to limit emissions of volatile organic compounds (VOC) from Confined Animal Facilities (CAF).

- Phase I Mitigation Measures: Owners/operators of large CAFs shall comply with the following Phase I Mitigation Measures in Section 5.5 until compliance with all applicable Phase II Mitigation Measures in Section 5.6 is demonstrated in accordance with the compliance schedule in Section 8.0.
- 5.5.1 Dairy CAF: Owners/operators of a large Dairy CAF shall comply with the Phase I requirements in Table 3.1:
  - Table 3.1 – Large Dairy CAF Phase I Mitigation Measure Requirements
    - A. Owners/operators shall incorporate at least four (4) of the following feed mitigation measures:
      - Class One Mitigation Measures
        - 1. a. Feed according to National Research Council (NRC) guidelines.
        - 2. a. Feed animals high moisture corn or steam-flaked corn and not feed animals dry rolled corn.
        - 3. a. At least once every fourteen (14) days remove feed from the area where animals stand to eat feed.
        - 4. a. At least once every fourteen (14) days remove spilled feed from the area where equipment travels to place feed in the feed bunk.
        - 5. a. Remove uneaten wet feed from feed bunks within twenty-four (24) hours of a rain event.
        - 6. a. Feed or dispose of rations within forty-eight (48) hours of grinding and mixing rations.
        - 7. a. Store grain in a weatherproof storage structure from October through May.
        - 8. a. Implement an alternative mitigation measure(s), not listed above.
    - B. Owners/operators shall incorporate at least one (1) of the following feed mitigation measures:
      - Class One Mitigation Measures
          - 1. a. Cover the horizontal surface of silage piles, except for the area where feed is being removed from the pile.

    - 2. a. Collect leachate from the silage piles and send it to a waste treatment system such as a lagoon at least once every twenty-four (24) hours.
    - 3. a. Implement an alternative mitigation measure(s), not listed above.
  - Class Two Mitigation Measures
    - 4. a. Enclose silage in a bag and vent to a VOC control device with a combined VOC capture and VOC control efficiency of at least 80%, or b. Enclose silage in a weatherproof structure and vent to a VOC control device with a combined VOC capture and VOC control efficiency of at least 80%, or c. Eliminate silage from animal diet.
- 5.6 Phase II Mitigation Measures: Owners/operators of CAFs subject to the regulatory threshold in Table 2 shall comply with all applicable Phase II Mitigation Measures in accordance with the compliance schedule in Section 8.0.
  - 5.6.1 Dairy CAF: An owner/operator of a medium or large Dairy CAF shall comply with the Phase II mitigation measures in Table 4.1.
- Table 4.1 – Dairy CAF Phase II Mitigation Measure Requirements
  - A. Feed: An owner/operator of a dairy CAF shall implement mitigation measures 1, 2, 3, and 4 and at least one (1) additional mitigation measure:
  - 1. Feed according to National Research Council (NRC) guidelines.
  - 2. Push feed so that it is within three (3) feet of feed lane fence within two hours of putting out the feed or use a feed trough or other feeding structure designed to maintain feed within reach of the cows.
  - 3. Begin feeding total mixed rations within two (2) hours of grinding and mixing rations.
  - 4. Store grain in a weatherproof storage structure or under a weatherproof covering from October through May.
  - 5. Feed steam-flaked, dry rolled, cracked or ground corn or other steam-flaked, dry rolled, cracked or ground cereal grains.
  - 6. Remove uneaten wet feed from feed bunks within twenty-four (24) hours after the end of a rain event.
  - 7. For total mixed rations that contain at least 30% by weight of silage, feed animals total mixed rations that contain at least 45% moisture.
  - 8. Implement an alternative mitigation measure(s), not listed above.
- B. Silage: An owner/operator of a dairy CAF that feeds silage shall implement at least one (1) of the following silage mitigation measures:
  - 1. Operators selecting this option must choose mitigation measure 1a plus one (1) from mitigation measures 1b, 1c, 1d plus two (2) from mitigation measures 1e, 1f, 1g:
  - a. Cover the surface of silage piles, except for the area where feed is being removed from the pile, with a plastic tarp that is at least five (5) mils thick (0.005 inches), multiple plastic tarps with a cumulative thickness of at least 5 mils (0.005 inches), or an oxygen barrier film covered with a UV resistant material, within seventy-two (72) hours of last delivery of material to the pile.

- b. Build silage piles such that the average bulk density of silage piles is at least 44 lb/cu ft for corn silage and 40 lb/cu ft for other silage types, as measured in accordance with Section 7.11; or
- c. When creating a silage pile, adjust filling parameters to assure a calculated average bulk density of at least 44 lb/cu ft for corn silage and at least 40 lb/cu ft for other silage types, using a spreadsheet approved by the District; or
- d. Incorporate all of the following practices when creating silage piles:
  - i. Harvest silage crop at ≥65% moisture for corn; and ≥60% moisture for alfalfa/ grass and other silage crops; and
  - ii. Incorporate the following parameters for Theoretical Length of Chop (TLC) and roller opening, as applicable, for the crop being harvested. Crop Harvested TLC (inches) Roller Opening (mm) Corn with no processing ≤ 1/2 in N/A Processed Corn
  - iii. Manage silage material delivery such that no more than six (6) inches of material are un-compacted on top of the pile.
- Choose two of the following:
  - e. Manage exposed silage (select one of the following):
    - i. Manage silage piles such that only one silage pile has an uncovered face and the uncovered face has a total exposed surface area of less than 2,150 square feet; or
    - ii. Manage multiple uncovered silage piles such that the total exposed surface area of all uncovered silage piles is less than 4,300 square feet.
- f. Maintain silage working face (select one of the following):
  - i. Use a shaver/facer to remove silage from the silage pile; or
  - ii. Maintain a smooth vertical surface on the working face of the silage pile.
- g. Silage Additives (select one of the following):
  - i. Inoculate silage with homolactic lactic acid bacteria in accordance with manufacturer recommendations to achieve a concentration of at least 100,000 colony forming units per gram of wet forage; or
  - ii. Apply propionic acid, benzoic acid, sorbic acid, sodium benzoate, or potassium sorbate at a rate specified by the manufacturer to reduce yeast counts when forming silage pile; or
  - iii. Apply other additives at specified rates that have been demonstrated to reduce alcohol concentrations in silage and/or VOC emissions from silage and have been approved by the District and EPA.
- 2. Utilize a sealed feed storage system (e.g., Silage bag) for silage.
- 3. Implement an alternative mitigation measure(s), not listed above.

(SJVAPCD, 2010)