

IMPACTS OF DAIRIES AND SILAGE ON AIR QUALITY

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ABSTRACT

Ground-level ozone formation continues to be a critical problem in the United States. The problem is especially severe in California, generally, and Central California's San Joaquin Valley (SJV), specifically. Dairies are one of the major sources of volatile organic compounds (VOCs) in SJV and have recently attracted considerable attention from the regulatory agencies. A number of recently conducted studies have reported actual emissions data from different dairy sources. However, there is currently limited data available for feed storage and silage piles, which are potentially significant contributors to ozone formation. The impact of different VOCs on ozone formation varies significantly from one species to another. Comprehensive measurements of VOC emissions are required to fully characterize and include all the important contributors to atmospheric reactivity. Therefore, the identification of emitted VOCs is needed to properly assess the wide spectrum of chemicals involved in ozone formation. This research study aims to identify and quantify the VOCs emitted from various silages and other feed sources. We have conducted experiments in an environmental chamber using large representative samples under controlled conditions. Over eighty VOCs were identified and quantified from corn, alfalfa, and cereal silages, total mixed rations, almond shells, and almond hulls using gas chromatography-mass spectrometry (GC/MS). Emissions of aldehyde compounds and acetone were measured using high performance liquid chromatography (HPLC). The results revealed high fluxes of alcohols and other oxygenated species. Lower, but perhaps comparably significant, concentrations of highly reactive alkenes and aldehydes were also detected. Additional quantitation and monitoring of these emissions are essential for assessment of and response to the specific needs of the regional air quality in the SJV.

Keywords: Volatile organic compounds (VOCs), ozone precursors, silage emissions, Gas Chromatography/Mass Spectrometry (GC/MS), High Performance Liquid Chromatography (HPLC)

INTRODUCTION

Tropospheric ozone is one of the most important pollutants throughout the United States. Currently, higher ozone levels are found not only in densely populated areas and areas

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with intense agricultural operations, but also in remote areas. The United States Climate Change Science Program and the Subcommittee on Global Change Research have recently reported that over the past 50 years the ozone at the land surface has risen in rural areas of the United States, and is forecast to continue to increase during the next 50 years (U.S. Climate Change Science Program, 2008).

The Central California's San Joaquin Valley (SJV) has long suffered from some of the worst air pollution in United States, in general, and high ozone levels in particular. Ground level ozone formation is caused by the gas-phase reaction of emitted VOCs and oxides of nitrogen (NO_x) in the presence of sunlight. The United States Environmental Protection Agency (EPA) has identified the SJV as a "severe non-attainment" area based on the federal 8-hour ozone standard. In March of 2008 the EPA adopted a new 8-hour ozone standard of 0.075 ppm (US EPA, 2008). In order to attain this new standard for agriculturally intensive regions, the reduction of agricultural emissions of VOCs and NO_x is essential.

Considerable effort at ozone reduction has been attempted in the past few decades by reducing the total mass of VOC emissions (US EPA, 2008). However, impacts of various VOCs on ozone formation differ significantly from one species to another. This makes the determination of individual VOCs crucial for the assessment of ozone reduction strategies. In particular, non-traditional VOC control strategies take into account the pronounced differences in "reactivities" of VOCs (Carter et al., 1995), and therefore further provide the means for additional ozone reduction, which could supplement mass-based control approaches. Additionally, VOC reductions have been more effective in reducing ozone in dense urban areas where, due to higher NO_x levels, VOCs are the limiting factor in ozone formation. Away from dense urban areas, NO_x are limiting, and the natural background of VOCs (from soils, grasses and trees) can make anthropogenic VOCs less dominant. Based on current models of the SJV air basin, even complete elimination of all sources of all types of anthropogenic VOCs would not achieve attainment of the ozone standard; in fact, it would only produce modest improvement. NO_x reductions are paramount but, nevertheless, an increase in VOCs, especially the more reactive ones, would necessitate even greater NO_x reductions.

Although the vast majority of ozone precursors' sources are well characterized, and their control has proven effective at reducing urban ozone (ARB, 2005, Kumar and Viden, 2007, EPA, 2008), data on dairy emissions remain sparse. Dairies are believed to be one of the largest sources of VOCs and their high concentration in the SJV is of particular concern (CARB, 2006). To make matters worse, the combination of extensive and intensive agriculture, stagnant air and low wind speeds coupled with high summer air temperatures, high summer levels of solar irradiation and cloudless skies provide the optimal conditions for ozone formation in the SJV. Therefore, evaluation and understanding of emission sources, speciation of a wide range of dairy- and agricultural-related compounds and assessment of their reactivities are critical.

Several research efforts have been undertaken in the past few years to better quantify emissions from dairies and agricultural sources. Seventy different VOCs including p-

cresol, 2-butanone, ethyl acetate, α -pinene, and Δ^3 -carene were identified on eight dairy farms in Sweden by Sonesson et al. (2001). Measurements to identify VOCs with a focus on odorants such as amines, sulfides, phenols, and volatile fatty acids (VFAs), were conducted from livestock facilities (McGinn et al., 2003; Rabaud et al., 2003). Hobbs et al (2004) measured emissions from dairy cattle manure in the UK using the sorbent trap-Gas Chromatography/Mass Spectrometry (GC/MS) technique and identified approximately 20 compounds in which acetic acid and dimethyl sulfide are dominant.

A total of 113 compounds were identified at the Washington State University Knott Dairy Farm (Filipy et al, 2006) using GC/MS, sorbent tubes, and cryogenic traps techniques. The wide range of VOCs included alcohols in which ethanol was dominant, aldehydes, ketones, esters, ethers, sulfides, carbonyls, aromatics, and other hydrocarbons. VOC emissions from dairy cows and their waste at various stages of the lactation cycle were measured with a proton-transfer-reaction mass spectrometer (PTR-MS) using a facility at the University of California, Davis (Shaw et al., 2007). The measurements of alcohols, VFAs, phenols, and methane (CH₄) emitted from non-lactating and lactating dairy cows and their manure under controlled conditions were reported by Sun et al. (2008).

Ngwabie et al. (2008) reported chemical ionization mass spectrometry and photo-acoustic spectroscopy measurements of mixing ratios of VOCs over a two week measurement period in a large cowshed in Mariensee, Germany. Numerous VOCs were detected with alcohols (ethanol, methanol, C₃–C₈ alcohols) being dominant, followed by acetic acid and acetaldehyde, and included ketones, amines, sulfides, aromatic compounds, and VFAs. These results indicated that animal husbandry VOC emissions are dominated by oxygenated compounds.

Alanis et al (2008) quantified emissions of six VFAs from non-enteric sources at a small dairy located on the campus of California State University Fresno. Both animal feed and animal waste were found to be major sources of VFAs, with acetic acid contributing 70–90% of emissions from the sources tested. Measured total acid fluxes during the spring (with an average temperature of 20° C) were 1.8 ± 0.01 , 1.06 ± 0.08 , $(1.3 \pm 0.5) \times 10^{-2}$, $(1.7 \pm 0.2) \times 10^{-2}$ and $(1.2 \pm 0.5) \times 10^{-2}$ gm⁻² h⁻¹ from silage, total mixed rations, flushing lane, open lot and lagoon sources, respectively with silage being the highest contributor. These data indicated high fluxes of VFAs from dairy facilities.

Recently reported studies provided improved information regarding VOC emissions from dairy facilities in general and animal waste in particular. However, while fermented cattle feed (silage) could arguably be one of the largest, and perhaps the largest, sources of dairy-related VOCs, currently there is no experimental data available on the identification and characterization of VOC emissions from silage and other feed sources. We have utilized a combination of GC/MS and high performance liquid chromatography (HPLC) with specific objectives to: (1) identify gaseous compounds emitted from different types of silage and other feed sources in order to better understand their contribution to ozone formation; (2) quantify emitted VOCs concentration and compare different silage types

across the dairy; (3) measure concentration of aldehydes and ketones emitted from silages.

Here, we report the first detailed speciation profile from representative (large volume) samples of silage and other feed obtained under controlled conditions. Large sample volume is important because even within the same silage pile the nature of the sample and therefore the emitted VOC concentrations may vary considerably. Furthermore, while field measurements are crucial for identification and characterization of dairy-related VOCs, differences in dairy management styles, effects of metrological conditions and climate, and other factors could result in differences in the experimental results obtained by different research groups. In addition, interpretation of the emissions sources may be confounded by compounds from other nearby sources such as diesel-fueled vehicles used at the dairies amongst others. Reported experiments were conducted under controlled conditions, which further allow comparison of different types of typical dairy silage, and other feed sources and eliminate the influence of ambient conditions.

MATERIALS AND METHODS

Feed Samples Collection

Silage and other feed samples were collected from commercial dairy located approximately 20 miles northwest from campus of University of California at Davis. This is a typical large size Californian dairy, representative of most western dairy operations. In this relatively new and modern facility, approximately 3000 cows are housed in freestall naturally ventilated barns with open walls. Silage piles are used as forage in dairy rations; placed aside and near other feed storage structures. The layout of these structures allows forming a feeding center.

The feed (total mixed ration-TMR) is a mixture of various components formulated to provide the optimum amount of energy and nutrition to the animals at the dairy. Silage is the largest component of the TMR. Typically, there are few different forage piles located at the dairy. Except for the vertical open-face, silage piles are covered with black plastic sheet and sealed along the sides. Tires are used for holding plastic tightly against the top surface of the pile. This helps to prevent silage spoilage, due to air exposure, and reduces emissions (Fig.1).

Typically, 6-12 inches of forage are removed from the face of the pile daily leaving this open part of the pile exposed to ambient air. All forage samples (corn, alfalfa, and cereal silages) within the dairy were collected early in the morning, right after a new portion of silage was removed. High moisture ground corn pile was not covered and samples were also collected immediately after new portion was removed for the TMR preparation. Other piles of feedstuff (almond hulls and almond shells) were covered for sun and rain protection (roof only, no walls structure) and their samples were collected in a similar manner.

Various feed components are loaded into a large truck where they are mechanically mixed and delivered to the animals. This operation normally takes place twice each day. The TMR samples were collected as soon as it was delivered to the animals. Large plastic

bags (doubled to avoid emissions leakage) were tightly closed and immediately transported to campus.

Experimental procedures

Experiments were conducted in an Environmental Chamber (4.4m x 2.8m x 10.5m) at the Department of Animal Sciences, University of California at Davis. This facility is widely used for research projects with dairy cows and other animal groups and described in greater detail by Shaw et al (2007) and Sun et al (2008). Prior to initial silage experiments, the facility was thoroughly cleaned and continuously flushed with the ambient (inlet) air for a week. Background and inlet air samples were collected throughout all experiments.

Approximately 40-70 kg of silage or other feed sample were placed in large round shape bin (diameter 1.92 m) located in the center of the chamber and spread to a depth of approximately 30 cm. Chamber door was closed and sealed. All major experiments were conducted in duplicates.

Air samples collection and their analyses

Multiple air samples from the chamber outlet port were collected using 6 L SUMMA[®] passivated stainless steel canisters from two manufactures: TO-Cans from Restek (110 Benner Circle, Bellefonte, PA) and Model S6L-G AeroSphere sampling canisters from LabCommerce Inc. (San Jose, CA). Chamber residence time was approximately 6 minutes, so canister samples were collected 10 min later after feed sample was exposed in the chamber. Canister sampling could be performed in two modes: either grab or time integrated sampling (up to 24 hours). The results of preliminary tests conducted with small size silage samples at the lab bench under isolation flux chamber (Mitloehner et al. 2009, in preparation) showed that VOCs (primarily alcohols) were releasing immediately once the sample was exposed to the air and significantly decreased with time. Based on these results, grab samples were collected with canisters to enable the capture of emitted VOCs at their highest concentrations. A single head Teflon coated aluminum pump (Model M161-GT-AA1, Air Dimensions Incorporated, FL) was used to pressurize canisters while sample collection so that the sampled canister can be analyzed directly by analytical system to avoid any dilution (pressurizing with nitrogen in the laboratory) prior the analysis. Sampling procedures, canisters cleaning and preparation were performed according recommendations of EPA method TO-15 for the determination of toxic organic compounds through analysis of ambient air samples collected in specially-prepared canisters which are further analyzed by GC/MS (US EPA, TO-15 method) and the Laboratory Standard Operating procedures for ambient air analysis used by the California Air Resources Board (CARB, SOP MLD 059).

The analytical system was set up according to recommendations of US EPA TO-14 and US EPA TO-15 methods. Canister samples were analyzed using the GC/MS system consisting of a Varian CP-3800 Gas Chromatograph and Varian Saturn 2200 Ion Trap Mass Spectrometer (Varian, Inc., Palo Alto, CA) with built-in high performance sample concentrators (Lotus Consulting, Long Beach, CA). A GC equipped with Cryogenic/Adsorbent Concentration System, handles concentration of the sample and

introduction of the concentrated sample onto the gas chromatographic column. Samples were loaded through a 16-position automated valve and trapped onto a low-volume adsorbent carbo-trap system (consisting of Carbopack B, Carbotrap C, and Carboxen 569) at 50°C with a mass flow controller setting the sample size. Then the sample was trapped on a cryogenic trap at -180 °C. The cryo-focus trap was rapidly heated up to 200 °C to inject the sample onto a DB-624 fused silica capillary column with dimensions 60 m x 0.32 mm x 1.8 µm and helium as a carrier gas. The GC oven temperature program was as follows: initially, temperature 200°C was maintained for 14.5 min (during sample injection and pre-concentration); then was ramped at 100°Cmin⁻¹ to -30°C (sample was injected onto the column) with a holding time 5 min; then was ramped at 5 °Cmin⁻¹ to a final temperature of 220 °C. This temperature was held for 3.65 min resulting in a total run time of 75 min.

The mass spectrometer was operated in electron impact ionization mode at 70 eV and signals were collected using m/z 25-220 AMU (atomic mass unit). Compounds were identified using the National Institute of Standards and Technology (NIST) library. To improve reliability of identification of some of the compounds, additional tests with the individual compounds were performed in order to confirm their retention time.

The GC/MS system was calibrated using a TO-15 calibration mix of 62 components (Scott Specialty Gases, Plumsteadville, PA). The contents of this mix were transferred into the canister dedicated for standards and further diluted down to 10 ppb. For other compounds, which were not present in the calibration mix, quantification assumptions were made using known standards of different molecules of the same class of compounds. The system linearity was verified for most of compounds present in the calibration mix by using four calibration points. The absolute accuracy of the concentration measurement for most of compounds was estimated to be ±10%.

An additional standard consisting of acetaldehyde, methanol, ethanol, isoprene, acetone, dimethyl sulfide, and phenol (Apel-Riemer Environmental, Inc., Broomfield, CO) was also used for the GC/MS calibration.

Determination of carbonyl compounds and HPLC analysis

Sampling and analytical methodology for the determination of carbonyls was based on the TO-11A US EPA method (1999). Carbonyl compound emissions from each type of feed sample were collected using cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) (Waters Corp.) at the sampling rate of around 600 ml/min. Samples were collected for about 180-230 minutes depending on experimental set up. Sample cartridges and field blanks were capped and placed in polypropylene bags immediately after sampling and stored under refrigeration prior to analysis.

During sampling, carbonyl compounds react with the DNPH to form derivatives that are called hydrazones (CARB, SOP MLD 022, 2001). These compounds' derivatives were extracted from the DNPH cartridges by gravity feed with 5 ml of acetonitrile (HPLC grade-99.9%, Chromasolv, Sigma-Aldrich) in a plastic syringe reservoir. Sample extract was collected in a 16 ml vial. A field blank cartridge was also extracted in the same

manner as samples. The eluate was analyzed by isocratic reverse phase HPLC (Agilent, Model HP1100, Palo Alto, CA) equipped with an ultraviolet absorption detector operated at 360 nm. Restek Ultra C18 column with the dimensions of 250mm x 4.6mm was used for compound separation. Acetonitrile and water in the ratio of 70:30 at a flow rate of 1ml/min was used as mobile phase.

Calibration solution containing 15 carbonyl compounds in acetonitrile at 15µg/ml was purchased from Supelco (Belfonte, PA). HPLC calibration was done with the standard calibration solution after diluting it to 0.015 µg/ml, 0.15µg/ml, and 1.5 µg/ml. A solvent blank was analyzed prior to any standard and sample analysis to make sure the HPLC and solvent are contamination-free and do not have any carbonyl compounds above the detection limit.

Head space technique and second GC/MS

In addition to experiments conducted in an environmental chamber, a headspace approach was performed to qualify emissions from feed samples. In these experiments, a one liter glass bottle (carboy) was flushed with nitrogen for 30 min, then 25 grams of tested silage sample was placed and the carboy was immediately closed and tightly sealed with the help of large septa serving as an air tight top.

Upon reaching equilibrium, a head space sample was analyzed on a GC/MS system (different than that used for the canisters samples analysis) by direct injection. Gas Chromatography (Agilent 6890A, Palo Alto, CA) separations were performed using a capillary column ZB-624 (Phenomenex, Torrance, CA) with dimensions 30m × 0.25mm × 1.4µm and helium as a carrier gas. GC oven temperature was programmed as follows: initial oven temperature was set to 35°C for five minutes, and then ramped by 8°Cmin⁻¹ to 220°C for a hold time of 5 minutes. Second ramp was 10°Cmin⁻¹ to 240°C with the hold time of 2 minutes. Injector temperature was set at 200°C. Mass Spectrometry measurements were performed on Agilent MS 5973N instrument. Electron ionization conditions were as follows: ion energy - 70eV, scan range from 30 to 300 AMU, tune reference compound was perfluorotributylamine.

Calibration mixture consisting of 7 compounds were made and used to generate a headspace in ppm level in similar one liter bottle. After 30 min, 200 µl of the head space was injected directly onto the column.

RESULTS AND DISCUSSION

Headspace analyses results

Prior to the measurements in an Environmental Chamber, a series of laboratory experiments using a headspace technique was conducted to determine which VOCs might be normally emitted from silage at elevated concentrations. Fresh silage sample was used in each experiment and at least three analyses were conducted using the GC-MS#2 system.

A total of 24 compounds were identified and quantified from silage and TMR emissions. These included 6 alcohols, 5 VFAs, and 13 carboxylic acids esters. Alcohol emissions from all silages and TMR were the dominant VOCs, with ethanol concentrations being the highest among all emitted alcohol compounds. The highest concentrations of ethanol and propanol were detected from corn silage. Significant concentration of 2-butanol was also detected from corn silage. In addition, low concentration of isopentyl alcohol was measured from corn and cereal silages. Emission fluxes of hexanol were detected from all silage samples at relatively small concentrations and not quantified. Corn silage was found to emit the highest concentration of alcohols.

Volatile fatty acids were identified as the second most abundant group of compounds emitted from silages and TMR, with acetic acid having the highest concentration within VFA emissions. High concentration of acetic acid observed in our experiments could be correlated to its presence (up to several percent by mass) in silage (Danner et al., 2003, Kung and Shaver, 2001). Propionic, isobutyric, butyric, and isovaleric acid emissions were also detected and quantified from the alfalfa silage and TMR. These findings are consistent with recently reported data on the evaluation of non-enteric emission fluxes of VFAs from five different locations including silage and TMR (Alanis et al., 2008). The highest fluxes of VFAs were observed from silage, with TMR producing lower emissions. Similar to our results, the emissions of acetic acid were found to be higher (1-2 orders of magnitude depending on the source) from all selected sources among all measured VFAs (Alanis et al. (2008). Further, in our chamber experiments, the VFA emissions from alfalfa silage and TMR were also measured (data not reported here) using sorbent tubes method described in details by Sun et al. (2008). In these experiments we have detected fluxes of acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic, and heptanoic acids. It is important to underline that despite the relatively high concentrations of emitted VFAs from dairy silages found in this report and study conducted by Alanis et al. (2008), these compounds are known to have insignificant effect on ozone formation (Carter, 1994).

A wide variety of carboxylic acids esters have been identified and quantified in addition to alcohols and VFAs emitted from silages and TMR. The emitted propyl acetate, propyl propionate, as well as ethyl, propyl, and butyl esters of butyric acid had the highest concentrations for corn silage. The highest concentration of ethyl acetate was detected from cereal silage. The composition and concentrations of identified emitted esters varied significantly among tested silage and TMR samples. Corn silage was found to emit the widest range and highest concentrations (except for ethyl acetate) of carboxylic acids esters.

Emission of only several VFAs and propyl propionate was detected from dry food components (almond hulls and almond shells), with their concentrations being below the quantification limit.

Based on preliminary flux chamber experiments (Mitloehner et al. 2009, in preparation), the alcohols (methanol and ethanol) were expected to be the dominant compounds emitted from silage. In headspace experiments, this was only the case for ethanol.

Methanol was difficult to retain on the GC column and it had eluted too fast (GC/MS#2 system). Similarly, no methanol data are reported in the experiments which utilized the GC/MS#1 system described in section 2.3.1. This was due to the fact that the adsorbent pre-concentration system of the GC/MS#1 was originally designed to be hydrophobic in order to reject water. These major system features preclude analyzing the most polar alcohol.

It is known that methanol is not only one of the most abundant oxygenated volatile organic compounds in the atmosphere (Brunner et al., 2007), but also plays a significant role in atmospheric chemistry as it influences the concentrations of various oxidants. Formaldehyde, ozone and peroxy radical concentrations are enhanced while OH radical levels are decreased through the atmospheric reactions of methanol. It was estimated (Jacob et al., 2005, Brunner et al., 2007) that only 11–20% of the methanol in the atmosphere is of anthropogenic and atmospheric origin, while the major part (80–89%) is of biogenic origin. In addition to several investigators, who reported methanol emissions as part of the plant metabolism (Brunner et al., 2007), several authors determined methanol fluxes emitted from agricultural crops, including an alfalfa field (Warneke et al., 2002). In addition, senescing, cutting, and drying of plant leaves are known to be sources of methanol (de Gouw et al., 1999; Warneke et al.). Thus, future experiments on the methanol emissions quantification from dairy feed sources appear to be important for the assessment of the air quality strategies.

Canisters analyses results

Following the determination of a suite of compounds emitted from silages through the headspace method, further detailed identification and quantification of VOC emissions from assorted feed samples were conducted using GS/MS analyses of canister samples collected in the environmental chamber. In environmental chamber experiments, four canisters for each tested feed source were collected and analyzed. Since low emissions were expected from dry almond hulls and shells, only two canisters were collected for analysis of VOC emissions from these samples. For each experiment, duplicate analysis of every second canister was conducted as well.

The results show that the majority of VOCs identified in the environmental chamber experiments were oxygenated compounds with alcohols being the major contributors. Total concentration of alcohols was found to vary in the range of 500-600 ppb from the TMR, alfalfa silage, and high moisture ground corn to approximately 1.7 and 2 ppm from corn and cereal silages respectively. Among alcohols, ethanol was the most abundant throughout measurements of all silages and TMR. Besides ethanol, significant concentrations of propanol and other isomers of C3-C4 alcohols were also detected with the highest concentration emitted from corn silage. Ethanol is expected to be a dominant VOC compound since it is produced by yeast fermentation of the plant material as part of ensiling process. The combined alcohols (excluding methanol) accounted for over 80% of the total VOCs emissions measured by the canisters analyses, with the ethanol concentration alone exceeding 70% and 90% of total alcohols emissions for silages, TMR and high moisture ground corn, respectively. The ethanol emissions from cereal silage were determined to be the highest, followed by emissions from corn and alfalfa silages.

However, the variability in emissions of alcohols in general and ethanol emissions in particular could vary significantly due to number of factors. In general, silages made from grass and winter grown cereals with lower carbohydrate content are expected to produce less ethanol than corn and grain silages. Furthermore, silage preparation methods, different additives, management style, climate, and ambient conditions could contribute to the variability in emissions.

In addition, the density of silage piles could also play an important role. The plant material during silage production is compressed to the point where no oxygen is present and anaerobic conditions are established that promote the growth of autochthonous lactic acid bacteria (Neureiter et al., 2005). The microbial conversion of free soluble carbohydrates into lactic acid and the resulting decrease in pH prevents the growth of undesirable microorganisms. In case of incomplete compression, the amount of oxygen could be sufficient for yeast and ferment carbohydrates to ethanol. This could be an indication of poor quality of silage.

Therefore, our experiments have demonstrated that levels of alcohol emissions from different silage types vary significantly and determine total VOC emissions.

Since silage is typically the largest component of TMR, significant but lower ethanol fluxes were detected from TMR. Alcohols are very volatile and rapidly vaporize during preparation and distribution of TMR. While the alcohols and other VOC emissions are lower from the TMR compared with silage, the feed (TMR) typically spread over a much larger area than the silage pile face. Thus, because of the larger surface area the potential for emissions from TMR could be greater than from silage.

However, composition of TMR significantly varies across dairies depending on climate and geographical location, its herd size, and management practices. Boguhn et al. (2006) studied the effect of TMR composition on fermentation and efficiency of ruminal microbial crude protein synthesis *in vitro*. Researchers used 16 total TMRs that varied in ingredient composition and nutrient content (Boguhn et al., 2006), which is an appropriate illustration of the TMR composition variability. Corn and/or grass silage were main ingredients in all TMR while others components widely varied. Some dairies use additives, vitamins, and liquid components in their TMR. In case liquid components are present, the higher moisture content in TMR compared to silage may also explain lower alcohol emissions when soluble alcohols are being trapped. Both major alcohols (methanol and ethanol) are well known to have low reactivity (Maximum Incremental Reactivity-MIR) (Carter et al., 1995b) and are not expected to significantly impact the formation of ground level ozone (Howard et al., 2007).

The wide variety of carboxylic acids esters were found emitted from all silages except dry feed sources (almond hulls and shells) with propyl acetate and propyl propionate being the most abundant. In addition, a relatively high concentration of ethyl propionate was detected from TMR samples. As illustrated in Fig. 6, the total emissions of carboxylic acids esters varied significantly across assorted silages. As reported by Figueiredo et al. (2007), due to the fermentation the esters were found to be the most

represented class of compounds in red clover silage. In respect to their atmospheric reactivities, contribution of carboxylic acids esters into ozone formation is not significant. Thus, it was established that methyl acetate is approximately 1/3 to 1/2 as reactive as ethane, which has MIR of 0.3 and has been used by the EPA to define the borderline between reactive and negligibly reactive for VOC exemption purposes (Carter et al., 1996). Similarly, the atmospheric ozone impact of t-butyl acetate was also concluded to be lower than that of ethane (Carter et al., 1998).

In environmental chamber experiments emissions of highly reactive alkene compounds were found from all feed samples with the C4 alkenes such as 2-butene and methylpropene possessing the highest concentration from corn silage. Other identified alkene compounds emitted from all silages and TMR included pentadiene, 1,4-hexadiene, and an alkyne compound (2-methyl-3-hexyne). These compounds, even at lower concentrations, could contribute significantly to ozone formation (Carter, 1994).

The vegetation/biogenic emissions are typically more reactive than the VOC emissions from automobiles and can have higher ozone-forming potential (Carter, 1994). The minor constituents among identified VOCs included monoterpenes. Thus, limonene was detected at low concentration in wheat silage and high moisture ground corn, while cineole (limonene oxide) was present in wheat and alfalfa silages. Some dairies use citrus pulp either on a regular base or occasionally as a component of their TMR. While it was not a case with the dairy which was a source of feed samples for our studies, the potential presence of limonene at higher concentrations elsewhere could be attributed to the addition of citrus pulp as a nutrient supplement. Alpha-pinene was detected in all tested samples including almond hulls and almond shells. The variations in concentrations of the compounds group included alkenes, alkynes, dienes, and monoterpenes from different feed sources ranged from 8 ppb (high moisture ground corn) to 80 ppb (corn silage). The emitted aliphatic alkanes were detected at concentrations as low as approximately 1 ppb and their concentrations were found to be the highest in high moisture ground corn. On both GC-MS's, effort was made to detect isoprene, a highly reactive biogenic diene. It co-eluted with the large ethanol peak, but by substituting a column with different polarity on GC-MS#2, headspace samples were re-prepared and re-analyzed to confirm that isoprene concentrations were below the quantitation limit.

The highest aldehydes emissions in descending order were detected from cereal silage and TMR. Concentrations of emitted ketone compounds, which were found to be significantly lower than aldehydes, varied in the range of 2-12 ppb with the highest concentrations from high moisture ground corn.

A wide range of aromatic compounds, which could significantly contribute into ozone formation, were identified at low concentration levels (Table 2). Among others these included toluene, styrene, xylenes, ethylbenzene, and chlorobenzene. Emissions of aromatic compounds were found to be the highest from TMR followed by the wheat silage. Note, that a number of halogen hydrocarbons, which were identified from all sources and detected at low (ppt) concentration most likely correspond to the ambient air

background. Similarly, trace concentrations of acetonitrile are probably due to the ambient air background as well.

Other compounds may be present in feed samples at trace levels, which were not detected in this study, particularly ones, which could be present in samples from different dairies.

Carbonyl compounds analyses results

Concentrations of carbonyl compounds emitted from feed were also determined by using DNPH cartridges. This method provides significantly more accurate measurements for carbonyl compounds than any technique requiring sample storage (including canisters). Ten aldehydes (including formaldehyde) and acetone from various feed sources were quantified in this project. While formaldehyde quantification is important because it is a major promoter in the formation of photochemical ozone, its quantification is also complicated. For instance, formaldehyde cannot be quantified with the PTR-MS due to its low proton affinity (Shaw et al. 2007).

Acetaldehyde was found to be the most abundant in all cases with contribution from 55 to 60% of total aldehyde compounds emissions from corn and alfalfa silages to 85-90% from TMR and cereal silage. Emissions of propionaldehyde, butyraldehyde, and isovaleraldehyde at relatively high concentrations were also identified and quantified. Additionally, emissions of C6 aldehydes were detected with all analytical methods described above.

The presence of these compounds is consistent with results from the proton-transfer chemical-ionization mass spectrometry measurements from cutting and drying of plant material during crop harvest (De Gouw et al. 2000). Thus, for clover, alfalfa, and corn, leaf wounding and in particular drying were shown to lead to strongly enhanced emissions of a series of C6-aldehydes, alcohols, and esters derived from (*Z*)-3-hexenal. Furthermore, enhanced emissions of methanol, acetaldehyde, acetone, and butanone from the forage crops clover and alfalfa were also reported (De Gouw, 2000). Warneke (2000) utilized a novel combination of disjunct eddy covariance and PTR-MS for selected VOCs flux measurements from an alfalfa field, which were conducted before, during, and after cutting. Over the course of one day, a significant methanol flux was observed from undisturbed alfalfa. A smaller release of hexenals, acetaldehyde, and acetone was reported as well. After the alfalfa was cut, the emissions of methanol, acetaldehyde, acetone, and hexenals were significantly enhanced and remained high for three days during which the alfalfa was drying.

Steiner et al., (2008) indicated that in central California 30–50% of the modeled urban VOC reactivity is due to aldehydes and other oxygenated species. In rural vegetated regions, biogenic and aldehyde reactivity dominates. Emitted reactive hydrocarbons may undergo photochemical oxidation in the atmosphere, producing formaldehyde and other carbonyls. The ketones have potential to react with the hydroxyl radical to form aldehydes and peroxyacetyl nitrate (PAN) precursors if sufficient NO₂ is present. Acetone can undergo photooxidation to form formaldehyde, carbon dioxide and PAN (Seinfeld and Pandis, 1998).

However, emissions of aldehydes and other oxygenated VOC are currently poorly quantified from all of these sources. Oxygenated compounds in the SJV are currently estimated to be low. Thus carbonyl compounds, including low molecular weight aldehyde and ketones, are receiving increased attention from the regulatory agencies. This indicates that more attention should be focused on the accuracy of the existent models as well as on the measurements of both primary emissions of oxygenated VOC and secondary production of oxygenates (in particular formaldehyde and other aldehydes) (Steiner et al., 2008).

CONCLUSIONS

This research has demonstrated the diversity of VOCs emitted from various types of silages and other feed sources. The measurements indicated that open-face silage piles are likely a significant source of VOCs in California dairies. The bulk of emitted compounds identified here are oxygenated VOCs in which alcohols are dominant, and known to have a small impact on ozone formation. However, emissions of alkenes, alkynes, diene compounds, and aldehydes from silage, which were identified and quantified here, could make a significant contribution to ozone formation. The atmospheric implications of these findings may include effects on the local air quality in agricultural areas. Comprehensive measurements of fluxes of a suite of oxygenated VOC emitted from assorted dairy feed sources are needed to assess their importance in regional chemistry.

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