San Joaquin Valley
Unified Air Pollution Control District

San Joaquin Valley
Air Pollution Control District

Air Pollution Control Officer's Revision of the Dairy VOC Emission Factors

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Note: The revised dairy VOC emission factors that are set forth in this document are based on the best scientific data that were available. As with other emission factors, the dairy VOC emission factors will be periodically updated if new scientific information indicates that revisions may be necessary.

Introduction

This report provides the bases for the District's revision to the District's Volatile Organic Compound (VOC) emission factors for dairies, which were previously established on August 1, 2005 in the report, entitled "*Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies*"[1]. The emission factors set forth in this document will be used for permitting dairies in the San Joaquin Valley.

This document lists some of the previous studies that were analyzed to develop the previous dairy VOC emission factors and reviews the more recent studies that were not available to the District during the previous process. It includes a summary of the analyses performed by the District that resulted in the determination of the District's Dairy VOC emission factors, as well as general recommendations for further research necessary to continue to improve our understanding of VOC emissions from dairy operations.

Accurate dairy emission factors are required for the proper implementation of applicable air quality regulations and also for the evaluation of appropriate technologies and practices to reduce emissions. Dairy VOC emission factors are needed to implement the requirements of State law. Under State law (SB 700, Florez 2003) agricultural operations, including dairies, that have emissions greater than ½ of any of the major source thresholds are required to obtain air district permits. In order to determine which operations exceed this level of emissions, accurate VOC emission factors are needed. Emission factors for the specific processes at dairies are also needed to evaluate and revise Best Available Retrofit Control Technology (BARCT) for existing dairies as required under the District's attainment plan and to evaluate and establish Best Available Control Technology (BACT) for new and expanding dairies to comply with the requirements of New and modified Source Review (NSR). The magnitude of the emission factor will be one of the several factors that are considered when establishing the final BARCT and BACT requirements. The District, through a public process, will also fully examine the technological feasibility, availability, and cost of possible control measures that may be required.

San Joaquin Valley Air District staff members have gained a great deal of experience in the evaluation of emissions from agricultural sources through collaborative efforts with other institutions, agencies, and interested stakeholders. Technical methodologies for determining agricultural emissions that were compiled and developed by Valley Air District engineers and specialists are currently being used by air quality agencies throughout California to establish permitting requirements for agricultural sources, determine the applicability of requirements under Title V of the Federal Clean Air Act, and

[1] San Joaquin Valley Air Pollution Control District (APCO), August 1, 2005. Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies

develop air quality attainment plans. Additionally, members of the Valley Air District have been thoroughly involved with recent and ongoing collaborative scientific research efforts to evaluate emissions from agricultural sources. This is particularly true of the agricultural emissions research efforts that have been ongoing in California. The extent of Valley Air District involvement in agricultural research efforts includes providing recommendations on the allocation of funds; evaluating test methods and protocols to quantify emissions from agricultural sources; identifying important areas in which further research is needed; evaluating and commenting on study proposals; working with other parties to lead research projects; and interpretation of the data obtained. These research efforts require coordination between air quality agencies, research institutions, independent researchers, and agriculture. The Valley Air District plays an important role in these essential coordination efforts through the San Joaquin Valleywide Air Pollution Study Agency (Study Agency) and the Study Agency's Agricultural Air Quality Research Committee (AgTech).

The revised Dairy VOC emission factors proposed in this report is based on a detailed review of the available science. There has been significant additional scientific research conducted since the development of the previous emission factor in the report by the APCO, dated August 1, 2005. These additional studies have been conducted with greater focus on processes and compounds of interest and were also designed to be more reflective of conditions found at California dairies. The District has compared some of these recent studies with the studies that were used to develop the previous emission factor. As would be the case with emission factors for other sources, the District's dairy emission factors will be revised to reflect the latest scientific information that is currently available.

In revising the dairy emission factors, the District continued to adhere to the sound guiding principles which were used to establish the District's original dairy emission factor. Continued adherence to these principles ensures that the revised dairy emission factors are supported by best available science.

In evaluating the latest research studies, studies performed on California dairies and in conditions representative of California conditions were always given preference. The revised dairy emission factors are entirely based on results from studies of California researchers at California dairies. The District's previous emission factor was also predominantly based on California research. However, because at the time there was not adequate California research to quantify emissions of volatile fatty acids (VFAs), studies from outside of California (Hobbs et al and Koziel et al) were previously used to calculate emissions of these compounds from dairy manure. In establishing the revised dairy emission factor, these studies have been replaced with more recent studies on enteric VFA emissions from dairy cattle conducted by Dr. Frank Mitloehner from UC Davis and studies on total VOC emissions from various dairy processes conducted by Dr. Charles Schmidt, a private consultant based in California. This report also uses California emission studies to quantify emissions from dairy feed, an important emissions source for which there was previously insufficient research.

The District's Dairy Emission Factors are summarized in the tables below.

The District continues to support continued and ongoing research at California dairies to further refine and supplement these emission factors.

Summary of Dairy Emission Factors

Dairies Subject to Phase I of District Rule 4570 (≥ 1,000 milk cows)

Per Cow Dairy VOC Emission Factors	
Process or Constituent	**Emissions (lb/hd-yr)**
1. Enteric Emissions from Cows	4.1
2. Milking Parlor(s)	0.03
3. Freestall Barns	1.8
4. Corrals/Pens	6.6
5. Liquid Manure Handling (Lagoons, Storage Ponds, Basins)	1.3
6. Liquid Manure Land Application	1.4
7. Solid Manure Land Application	0.33
8. Separated Solids Piles	0.06
9. Solid Manure Storage	0.15
Total not including Feed	**15.8**

Dairies not Implementing Phase I of District Rule 4570 (< 1,000 milk cows)

Uncontrolled Per Cow Dairy VOC Emission Factors	
Process or Constituent	**Emissions (lb/hd-yr)**
1. Enteric Emissions from Cows	4.3
2. Milking Parlor(s)	0.04
3. Freestall Barns	1.9
4. Corrals/Pens	10.0
5. Liquid Manure Handling (Lagoons, Storage Ponds, Basins)	1.5
6. Liquid Manure Land Application	1.6
7. Solid Manure Land Application	0.39
8. Separated Solids Piles	0.06
9. Solid Manure Storage	0.16
Total not including Feed	**20.0**

VOC Emissions from Dairy Feed Sources

Silage Pile VOC Emissions Flux*	
10. Silage Piles	**Emissions Flux (lb/ft^2-day)**
1. Corn Silage	1.02E-02
2. Alfalfa Silage	5.15E-03
3. Wheat silage	1.29E-02

*Assuming silage piles are completely covered except for the "face" from where feed can be removed

Average Total Mixed Ration (TMR) VOC Emissions Flux	
11. Average TMR	**Emissions Flux (lb/ft^2-day)**
TMR	3.85E-03

Background

The San Joaquin Valley Air Basin has an inland Mediterranean climate characterized by hot, dry summers and cool, foggy winters. The San Joaquin Valley is surrounded by mountains on the east, west, and south sides. This creates stagnant air patterns that trap pollution, particularly in the south of the San Joaquin Valley. Additionally, the sunshine and hot weather, which are prevalent in the summer, lead to the formation of ozone (photochemical smog). Because of the San Joaquin Valley's geographic and meteorological conditions, it is extremely sensitive to increases in emissions and experiences some of the worst air quality in the nation.

The San Joaquin Valley Air Basin was previously classified as a serious non-attainment area for the health-based, Federal eight-hour ozone standard. However, EPA recently reclassified the air basin as an extreme non-attainment area for the eight-hour ozone standard because of the inability to reach attainment of the standard by the earlier serious and severe classification attainment dates using currently available technologies. The air basin is also classified as a non-attainment area for the Federal PM-2.5 (ultra-fine particulate matter) standard.

Purpose of the San Joaquin Valley Air Pollution Control District

The San Joaquin Valley Air District is a public health agency whose mission is to improve the health and quality of life for all Valley residents through efficient, effective and entrepreneurial air quality management strategies. To protect the health of Valley residents, the District works toward achieving attainment with health-based ambient air quality standards as required under State and Federal law. To achieve this goal, the District develops and adopts air quality attainment plans that include control measures aimed at further reducing emissions from a broad range of sources, including agriculture.

As mandated by Federal Law, the San Joaquin Valley Air District adopted its 2007 ozone attainment plan to demonstrate how the Valley would reach attainment with the Federal eight-hour ozone standard. In developing the ozone attainment plan every feasible measure to reduce emissions of ozone precursors (VOC and NOx) was explored. However, even though the District will be requiring every practical VOC and NOx control, and will be relying on the state and federal governments to significantly reduce emissions from mobile sources of pollution, the San Joaquin Valley will still need the development and adoption of future, not-yet-developed, clean air technologies to reach attainment by the 2023 deadline. Achieving the goal of attainment with air quality standards will require continued contributions from all industries, businesses, and individuals in the San Joaquin Valley.

Permitting Requirements

A critical tool that the air districts use to limit increases in emissions of air pollutants and to assure compliance with air quality regulations is the issuance of conditional construction and operating permits to commercial and industrial sources of air pollution. Since the 1970s, the San Joaquin Valley Air Pollution Control District and its predecessors have issued tens of thousands of conditional permits that are being used to assure compliance with air pollution control requirements throughout the Valley. District permits address the requirements of federal standards, state regulations, and District rules that specifically apply to a source of air pollution. New and modified sources of air pollution are also subject to the more protective requirements of “New Source Review”, which are determined on a case-by-case basis and are also included in the permit. Permit holders, District Inspectors, and others use these District permits, rather than directly reference the complex and voluminous underlying regulations, to verify compliance with applicable air quality requirements.

Removal of the Agricultural Exemption from Permitting

Under California state law, agricultural sources of air pollution, including dairies, were previously exempt from air district permitting requirements and new source review emissions limitations. This exemption was removed effective January 1, 2004, when Senate Bill 700 (Florez) amended the California Health and Safety Code to eliminate the longstanding permit exemption for agricultural operations that grow crops or raise animals. With the elimination of the agricultural permit exemption, San Joaquin Valley dairies also became subject to “New Source Review” requirements, including the requirement to apply Best Available Control Technology (BACT) to new and expanding operations.

San Joaquin Valley Dairies and Air Quality

Dairies are significant sources of smog-forming Volatile Organic Compounds (VOCs) and fine particulate matter in the San Joaquin Valley. Volatile Organic Compounds are emitted directly from the Valley’s approximately 2.5 million dairy cows[2], from the fermentation and decomposition of cattle feed, and from the decomposition of the manure generated each day from dairy cows in the San Joaquin Valley. Dairies are among the largest sources of VOCs in the Valley, and these smog-forming VOC emissions can have an adverse impact on efforts to achieve attainment with health-based air quality standards.

VOC Emission Factors for Dairies

When agricultural sources in California first became subject to air district permitting requirements on January 1, 2004, there was very little data available

[2] USDA, National Agricultural Statistics Service. 2007 Census of Agriculture – County Data, Table 11 – Cows and heifers that had calved

that could be used to quantify Volatile Organic Compounds (VOC) emissions from confined animal facilities, such as dairies. To calculate VOC emissions from dairies, EPA and the California Air Resources Board (ARB) used a VOC emission factor of 12.8 lb/head-year based on the very limited information that was available. Subsequently, California air districts, including the San Joaquin Valley Air Pollution Control District, adopted this VOC emission factor for dairy permitting and emissions inventory purposes. However, the basis for the 12.8 lb/head-year VOC emission factor was an older study performed in the 1930s that only measured methane emissions from dairy cows in environmental chamber tests. Volatile Organic Compounds emissions were not directly determined in the tests but were estimated using an assumed ratio of VOCs to total organic gasses with the methane emission measurement values used as total organic gas emissions. Additionally, the 1930 chamber tests did not represent the majority of dairy processes. Because of the age of the original study and the many assumptions that were needed to derive the dairy VOC emission factor, there was a great deal of uncertainty as to whether the 12.8 lb/head-year emission factor accurately reflected VOC emissions from dairy cows and dairy processes and was scientifically defensible.

As such, the District revised the dairy emission factor in its report entitled, "*Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies*"[1] which was released on August 1, 2005 and resulted in the District's previous dairy VOC emission factor of 19.3 lb/head-yr. This is the emission factor that the District used for permitting dairy operations in the San Joaquin Valley. This emission factor was based on a thorough review of the scientific research available and represents a significant improvement compared to the previous value of 12.8 lb/head-year. However, the emission factor report identified several dairy processes and compounds for which additional research was needed to accurately quantify emissions. This second revision is brought about because of an accumulation of significant additional scientific research on the majority of sources of emission at a dairy, specifically at those sources where no data were available during the initial revision.

Deferral of Permit Requirements for Some Smaller Operations

Under SB 700, permitting requirements were deferred for smaller agricultural operations with emissions less than one-half of the major source thresholds. Based on the original dairy VOC emission factor of 12.8 lb/head-year, existing dairies with 1,954 cows[3] were estimated to have VOC emissions equal to or greater than one-half of the District major source threshold, and were required to apply for District permits by June 30, 2004. Dairies with less than 1,954 cows were determined to have emissions less than one-half of the major source

[3] The 1,954 number is an estimated threshold assuming all cows on the dairy emit VOCs at the same rate as milk cows, which is not the case. The actual threshold (generally above 1,954) must be determined on a case-by-case basis and varies with the number of milk cows, dry cows, heifers, and calves on the dairy.

threshold; therefore, District permitting for these smaller dairy operations was not initially required. However, on August 1, 2005 the District revised the Dairy VOC emission factor from 12.8 lb/head-year to 19.3 lb/head-year using the best available science. As a result of the revised emission factor, dairies with more than 1,190 milk cow (or an equivalent mix including support stock) became subject to District permits after August 1, 2005.

Additionally, under the provisions of SB 700, an air district may permit smaller sources by making the following findings in a public hearing:

> 1) A permit is necessary to impose or enforce reductions in emissions of air pollutants that the district shows causes or contributes to a violation of a state or federal ambient air quality standard.
>
> 2) The requirement for a source or category of sources to obtain a permit would not impose a burden on those sources that is significantly more burdensome than permits required for other similar sources of air pollution.

The District did, in fact, make these findings during its adoption of District Rule 4570 – Confined Animal Facilities (CAF). The District determined that to ensure enforceability of the VOC mitigation measures required by state law and the District's attainment plans, agricultural facilities subject to the rule required District permits. As determined by the California Air Resources Board (ARB), a dairy with 1,000 milk cows or more is defined as a large CAF. Therefore, any dairy with 1,000 or more milk cows became subject to District permits.

It should be noted that agricultural sources of air pollution do not become subject to District permitting, "New Source Review" (NSR), or Best Available Control Technology (BACT) requirements until the emissions from these sources exceed one-half of the major source threshold values, which was previously 12.5 tons (25,000 lbs) of NOx or VOC, but was recently reduced to 5 tons (10,000 lbs) of NOx or VOC after EPA approved the re-designation of the San Joaquin Valley as an Extreme Nonattainment area for the Federal 8 hour ozone standard. For non-agricultural source categories, District permits and BACT are generally required at the far lower emissions rate of anything greater than 2 lb/day. For numerous years, permits and significant air pollution controls have been required for much smaller sources of emissions such as print shops, autobody shops, gasoline stations, and dry cleaners.

Authority to Construct Permitting Requirements for Dairies Constructed or Modified after 1/1/2004

As well as requiring operating permits for existing dairies, SB 700 also required dairies with emissions greater than one-half the major source thresholds that were constructed or modified on or after 1/1/2004 to obtain Authority to Construct permits from the District prior to commencing construction. These new and modified dairies, like all other new and modified sources of air pollution, are subject to the requirements of the District's New and Modified Stationary Source Review Rule (District Rule 2201), including the requirement to apply BACT, and may potentially be required to offset emission increases once protocols are in place to allow agricultural sources to bank Emission Reduction Credits from qualified emission reductions.

Large CAF Rule for Existing Dairies

In addition to the Air District permitting requirements described above that resulted from the elimination of the agricultural exemption, Section 40724.6 of the Health and Safety Code required the California Air Resources Board (ARB) to develop a definition for the source category of "large" Confined Animal Facilities (CAF) that would be subject to VOC control requirements. In developing the large CAF definition, ARB was required to review relevant scientific information, including potential air quality impacts, the effects that confined animal facilities may have on the attainment and maintenance of air quality standards, and applicable livestock emission factors. This section of the Health and Safety Code also required the District to adopt a rule establishing VOC control requirements for large CAFs, including dairies.

On June 23, 2005, at the conclusion of a public hearing, ARB adopted Resolution 05-35, which established the definition of large Confined Animal Facilities. The definition adopted by ARB specifies that dairies with 1,000 or more milk cows that are in a region designated as a federal ozone nonattainment area as of January 1, 2004 are large CAFs and that dairies in all other areas with 2,000 or more milk cows are large CAFs. Because of the San Joaquin Valley Air Basin's status as a federal ozone nonattainment area, dairies in the Valley with 1,000 or more milk cows are large CAFs. On June 15 2006, the District adopted Rule 4570 – Confined Animal Facilities to require existing large CAFs to begin to implement VOC control requirements that are suitable to each particular operation. District Rule 4570 included various options and management practices that could be used to achieve the required emission reductions from different sources at confined animal facilities, such as feed storage and handling, animal housing, manure handling and storage, and lagoons. The District issued Authority to Construct permits to over 600 confined animal facilities, including over 500 dairies, to implement various mitigation measures and practices to reduce VOC emissions from these facilities.

The District recently amended the existing version of Rule 4570 to achieve further reductions from existing confined animal facilities in order to attain compliance with applicable health-based ambient air quality standards. The amendments resulted in lowering the applicable threshold and requiring Phase II mitigation measures. The Phase II mitigation measures include additional practices to reduce VOC emissions from feed sources at dairies, which are now known to be a significant source of VOC emissions. During the District's process to amend Rule 4570 it was critical to use the most accurate emissions information available. The use of the revised dairy emission factors from this document allowed for a more accurate assessment of sources that contribute to emissions at a dairy and allowed these emission sources to be targeted for cost-effective emission control strategies. Implementation of the recently adopted Phase II mitigation measures of District Rule 4570 is expected to result in significant reductions of smog-forming VOCs in the San Joaquin Valley that will be in addition to the VOC reductions that have already been achieved by the implementation of Phase I of District Rule 4570.

Important Findings from Latest Dairy Emissions Research

Recent dairy emission research studies performed under the direction of California air quality agencies and stakeholders have significantly increased knowledge of dairy emissions and also shed some light on potential strategies to reduce these emissions. Recently completed California dairy emission studies of note include:

- A study at UC Davis, led by Dr. Frank Mitloehner, entitled "*Volatile Fatty Acids, Amine, Phenol, and Alcohol Emissions from Dairy Cows and Fresh Waste*".[4] This study measured emissions of alcohols, volatile fatty acids, and amines directly from lactating and dry cows and also from their fresh manure. This study provides valuable information on enteric emissions from cattle as well as emissions from freshly excreted manure.
  - The original study led by Dr. Mitloehner (May 2006) was found to have incorrect data due to the lack of an ammonia filter in the INNOVA measurement device. The lack of an ammonia filter resulted in significant interference when measuring alcohols; therefore, readings of ammonia emissions were incorrectly reported as alcohol emissions. In order to obtain accurate data; Dr. Mitloehner repeated the study with the proper filters in place. The study was completed in October 2009.[5] At the request of District staff, Dr. MItloehner provided the resulting preliminary data, minimal but sufficient, to the District so that emissions could be estimated using this data.
- Two studies conducted by Dr. Charles Schmidt and Thomas Card (Dairy emissions using flux chambers, 2006 - Phase III[6] and 2009 - Phase IV[7]),

[4] Mitloehner, F. Trabue, S. Koziel, J.A. (2006) Volatile Fatty Acids, Amine, Phenol, and Alcohol Emissions from Dairy Cows and Fresh Waste (May 31, 2006). Final Report to California Air Resource Board (ARB)
[5] Mitloehner, Frank, 2009. Revision of May 2006 Study- Alcohol Emissions from Dairy Cows and Fresh Waste from Environmental Chambers (data set only)
[6] Schmidt, C. Card, T. (2006) Dairy Air Emissions Report: Summary of Dairy Emission Estimation Procedures (May 2006). Final Report to California Air Resource Board (ARB)
[7] Schmidt, C. Card, T. (2009) 2008 Dairy Emissions Study: Summary of Dairy Emission Factors and Emission Estimation Procedures. August 2009. Final Report to San Joaquin Valley Air Pollution Control District

which measured various emission compounds along with total VOCs from dairy manure and feed. The emission measurements were taken from silage piles, bunker feed (Total Mixed Ration (TMR)), lagoons, manure piles, corrals, flush lanes, solid manure application and liquid manure application. This information will be used to develop estimates of annual emissions from important sources such as corrals, silage piles, and total mixed ration.

- A series of studies in which flux chambers were used to evaluate VOC emissions from sources at six dairies in the San Joaquin Valley; the field sampling program was led by Dr. Charles Krauter of CSU Fresno and the corresponding analytical program was headed by Dr. Donald Blake at UC Irvine.[8] The emission measurements were taken from many sources at the dairy including the corrals, flush lanes, lagoons, feed storage areas, and Total Mixed Ration (TMR). Seasonal and diurnal data were also taken for certain sources during the flux chamber studies.
- An ARB research project led by Dr. Ruihong Zhang of UC Davis in which a team of researchers identified and quantified significant VOC compounds emitted from thin layers of loose silage, cows and manure in environmental chambers, and dairy manure storage for the purpose of developing VOC emissions models to quantify emissions from dairy processes.[9] Flux chambers were used to measure emissions from samples of loose silage. The emissions were evaluated using Proton Transfer Reaction Mass Spectroscopy (PTRMS) and an INNOVA photo-acoustic analyzer to measure alcohols. A wind-tunnel was used to evaluate the effect of wind speed on VOC emissions from silage and the information gathered was used to create a preliminary model to estimate ethanol emissions from thin layers of loose silage given the initial ethanol concentration. A preliminary model was also generated to estimate acetic acid emissions from manure storage depending on the characteristics of the manure in storage (i.e. acetic acid concentration, pH, temperature, solids content, etc.). This ARB project was supported by UC Davis, UC Berkley, and USDA Agricultural Research Service (ARS). A large number of researchers contributed to the project including: Dr. Ruihong Zhang, Dr. Frank Mitloehner, Dr. Hamed El-Mashad, Dr. Irina Malkina, Dr. Huawei Sun, Dr. Peter Green, Dr. Baoning Zhu, Dr. Yongjing Zhao, Ms. Veronica Arteaga, Mr. Kameron Chun, Ms. Sara Place, and Ms. Yuee Pan, Dr. Allen Goldstein, Dr. Daniel Matross, Dr. Sasha Hafner, Dr. Felipe Montes, and Dr. C. Alan Rotz. This project greatly increased the available data regarding the speciation of VOC compounds emitted from sources at dairy operations and provides a strong foundation for the continued

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[8] Krauter, C. Blake, D. (2009) Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions in the San Joaquin Valley (May 01, 2009). Final Report for California Air Resource Board (ARB)

[9] Zhang, Ruihong. (2010) Process-Based Farm Emission Model for Estimating Volatile Organic Compound Emissions from California Dairies. May 2010. Final Report for California Air Resource Board (ARB)

development of emission models to estimate VOC emission models from dairies and is expected to become a useful tool for identifying and evaluating measures that have the potential to reduce emissions from important sources at dairy operations.

Important findings of the latest dairy research studies include:

- Manure storage ponds and lagoons, which were previously thought to be one of the largest sources of VOC emissions at dairies (approximately 8.1 lb/head-year of the District's previous dairy VOC emission factor of 19.3 lb/head-year was attributed to lagoons and volatile fatty acids from wet processes), now appear to emit a comparatively small fraction of the overall dairy VOC emissions;
- Feed at dairies is a significant source of VOC emissions. The exposed faces of silage piles that are used to store and preserve silage to be fed to the cattle and the total mixed ration placed in lanes for cattle consumption emit significant amounts of VOCs, particularly alcohols.
- Emissions of alcohols (primarily ethanol) from feed, fresh manure, and directly from cows appear to comprise a significant fraction of dairy VOC emissions;
- Manure deposited in open corrals appears to be an important source of VOC emissions on some dairies;
- Emissions of volatile fatty acids (VFAs) from non-feed sources, which comprised 15.5 lb/head-year (over 80%) of the District's previous dairy VOC emission factor of 19.3 lb/head-year, are not as significant as previously estimated;
- The practice of flushing freestall barns more frequently has the potential to reduce VOC emissions from cow housing areas.
- Several of the compounds that have been identified as important components of dairy emissions, such as alcohols and volatile fatty acids, are highly soluble in aqueous solutions. This property may be important when developing potential mitigation strategies.
- Land application of solid and liquid dairy manure appears to contribute a relatively small amount to total VOC emissions at dairy.
- Seasonal variation in emissions may be an important factor to consider when developing annual emission estimates. The seasonal variation in emission rates was observed to be more pronounced with ammonia emissions than VOC emissions.

This additional research, which has been completed since the August 1, 2005 revision to the dairy emission factors, will be evaluated to update the dairy VOC emission factors that are used to permit dairies in the San Joaquin Valley.

The Purpose of this Revision to the Dairy VOC Emission Factors

The District is charged with the responsibility of adopting emission factors for various sources of air pollution in order to establish accurate emissions inventories for the San Joaquin Valley air basin and to develop rules and standards to efficiently allocate resources to reduce emissions in the most cost-effective way. For sources, such as agriculture, that have only recently become subject to air quality regulations, there can be a lack of consensus as to the emission factors that are most suitable. In these cases the District must use its expert judgment to evaluate the scientific information available to establish an appropriate emission factors. This District did exactly this during the previous revision to the dairy VOC emission factor. However, as stated earlier, dairy emissions research that better reflects the conditions at California dairies has recently been completed. These studies have greatly improved our knowledge of the emissions of compounds, such as alcohols and volatile fatty acids. These studies have also given us valuable, new information on emissions from important sources, such as dairy feed and land application, which had not previously been measured. The District has determined that the new information on dairy emissions that is contained in the latest studies must be included in the District’s dairy VOC emission factors in order to accurately quantify emissions and assess potential mitigation strategies that may be required by BACT and the revised version of District Rule 4570. As with the previous revision to the dairy VOC emission factor, the contents of this report went through a public process in which comments on the proposed emission factor were addressed.

Guiding Principles Used by the APCO for Determining Appropriate Emission Factors

Dairies are fairly complex emissions sources that emit several types of VOCs from the different dairy processes. Because of this, it is difficult to design and carry out a single research effort that would measure all of the VOCs emitted. Therefore, in order to determine appropriate dairy emission factors, the District reviewed several different studies in the previous revision to the dairy VOC emission factor. This current revision will reevaluate the dairy VOC emission factor in light of the recently completed California dairy emissions studies. The results of these studies will be used to augment or replace values in the previous dairy emission factor for categories of dairy processes or compounds emitted for which better emissions research is now available.

The following principles were utilized to evaluate studies and select appropriate data for revision of the dairy emission factor:

1. Emissions data from research studies provided by scientists, information of dairy emissions research, and data from available scientific literature were used to determine the emission factor.
2. The methods used to collect the data were reviewed. Data were considered invalid if any of the following problems are found, unless an appropriate way to correct the data is available:
    a) Indications that samples may have been contaminated.

b) Evidence that sample collection procedures may have resulted in the potential for significant loss of analyte.
c) Evidence that sample storage procedures may have resulted in the potential for significant loss of analyte.
d) Sample loss determined to have occurred in the analytical process (e.g. low laboratory spike recovery due to matrix effects)
e) Indications of mis-calibration or excessive calibration drift.
f) Appropriate laboratory protocols were not followed.
g) Other uncorrectable errors were identified.

3. When VOC data for a process or compound is available from more than one source, the following steps are to be followed to select the best available data for use in developing an emission factor:

   a) Valid data from recent tests performed at California dairies was given preference over data from other sources. The District will carefully consider specific process conditions (such as meteorological conditions, season, manure moisture content, available information on feed, etc.) in evaluating the transferability of out-of-state data.
   b) Data representing a specific constituent or process are to be given preference over data that represents a broad range of constituents or processes.
   c) Where test results from more than one source are deemed equivalent, an average emission factor is to be determined.

4. Non-quantitative or anecdotal evidence of emissions such as compound concentrations measured near dairies or feedlots that could not be related to process parameters, or the presence of varying levels of odors near dairy processes, will not be used to determine emission factors.

5. When no valid source of quantitative VOC data that could be linked to dairy processes is found, no emission factor is to be determined, and the constituent or process emission factor is to be reported as “NA” or not available and further research is to be recommended.

6. When evidence indicates that significant quantities of VOC compounds are emitted, but the emissions cannot be quantified based on available data, the constituent or process emission factor is to be reported as “TBD, >0”, meaning To Be Determined, but known to be greater than zero, and further research is to be recommended.

Analysis

Category 1: Enteric Emissions

Basis of Previous VOC Emission Factor

Basis of the Previous Dairy VOC Emission Factor – Enteric Emissions		
Process or Constituent	**Emission Factors (lb/hd-yr)**	**Basis for Previous Emission Factors**
Previous Category 1: Emissions from Cows and Feed in Environmental Chamber		
Emissions from Cows and Feed	1.4	Emissions from Cows and Feed in Environmental Chamber with analysis by PTR/MS (Mitloehner, 2005)[10]
From Previous Category 5: VFA Emissions from Cows and Feed in Environmental Chamber		
Enteric VFA Emissions	8.3	Measurement of airborne volatile fatty acids emitted from dairy cows and their manure using sorbent tubes with GC/MS analysis (Estimated based on preliminary unpublished data from Trabue, Koziel, & Mitloehner, 2005)

VOC emissions from cows, feed, and fresh manure were measured in environmental chambers by Dr. Mitloehner and other researchers using Proton Transfer Reaction Mass Spectroscopy (PTRMS). VOC emissions were estimated to be 1.6 lb/head-year. Because other VOC tests by Dr. Mitloehner using EPA Method TO-15 had shown that emissions from fresh manure in the test chamber represented approximately 10% of emissions, the value for enteric and feed emissions without the excreta was calculated to be to 1.4 lb/head-year.

Enteric Volatile Fatty Acid (VFA) emissions in the District's previous dairy emission factor were estimated based on preliminary unpublished information from an environmental chamber study conducted by Dr. Mitloehner, Dr. Steven Trabue and Dr. Jack Koziel. The purpose of the study was to determine the relative concentration of VFA components. The VFA samples were collected from the environmental chamber using sorbent tubes. Preliminary data indicated high levels of VFAs in the exhaust from the environmental chamber but the inlet concentrations of VFAs were not measured and there was a high amount of variation in the concentration data. Further analysis of the data and the subsequent performance of similar studies have measured enteric VFA emissions that are significantly less than the estimate used in the District's

[10] Study conducted in 2005, but published in 2007: *Shaw, S.L. Mitloehner, F.M. Jackson, W.A. DePeters, E. Holzinger, R., Fadel, J. Robinson, P. and Goldstein, A.H. "Volatile Organic Compound Emissions from Dairy Cows and Their Waste as Measured by Proton Transfer-Reaction Mass Spectrometry", Environmental Science and Technology. VOL. 41, NO. 4, 2007, 1310-1316*

previous dairy emission factor. This may be related to the lack of VFA inlet data. It also may be possible that the type of feed that was used during the preliminary chamber studies may have influenced VFA measurements since it is now known that silage-based feed is a significant source of VOC emissions. It is not known what type of feed was used during the preliminary measurements but the subsequent environmental chamber studies used grain-based feed.

Recent VOC Emissions Studies

Recent Studies – Enteric Emissions		
Recent Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Emissions from Cows and Feed in Environmental Chambers with analysis by TDS/GC-MS, NIOSH 2010, alcohols by INNOVA photoacoustic analyzers (Mitloehner, 2006)[4]	**Milk Cows** VFAs: 0.015 Phenols/Cresols: 0.08	The alcohol measurements were performed using INNOVA photoacoustic analyzers with no ammonia filters. It was later shown that ammonia present in the mixture of gases being measured results in inferences that cause measured alcohol concentrations to be greater than the true values.
Alcohol Emissions from Cows and Feed in Environmental Chambers by INNOVA photoacoustic analyzers with ammonia filters (unpublished data Mitloehner, 2009)[7]	**Milk Cows** Ethanol: 2.6 Methanol: 0.03	Unpublished Data for Period before Manure Accumulates in the Environmental Chamber

Evaluation

The California research that is currently available to quantify enteric emissions from dairy cows is from a series of studies conducted at UC Davis led by Dr. Mitloehner, including a recent study that has not yet been published. Dairy cows were placed in controlled environmental chambers and various methodologies were used to quantify VOC emissions from cows and the manure deposited in the chambers.

In the first environmental chamber study conducted in 2005 (published in 2007), Proton-Transfer-Reaction Mass Spectrometry (PTRMS) was used to quantify emissions from dairy cattle and fresh manure. PTRMS detected a number of oxygenated compounds and some volatile fatty acids. However, ethanol emissions were not quantified in this study because the measurement process converts much of the ethanol to ethane, which has a low proton affinity, and is, therefore, undetectable by PTRMS. Several other studies have shown that large quantities of ethanol are emitted from the various processes at dairies; therefore, the inability to measure ethanol is a significant weakness in the PTRMS data. However, the PTRMS measurements were used to quantify emissions for the

August 2005 revision to the dairy emission factor because it was the best information available at the time.

In the second environmental chamber study completed in 2006, INNOVA photoacoustic analyzers were used to quantify ethanol and methanol emissions from dairy cattle and fresh manure and emissions of VFAs and phenolic compounds were sampled using a modified sorbent tube method and quantified using thermal desorption and gas chromatography (EPA TO-17). The instrumentation was calibrated to measure the following VFAs: acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic, and heptanoic acids and was calibrated to measure the following phenol and cresol compounds: phenol, 2-methylphenol, 2-ethylphenol, 3-methylphenol, 4-methylphenol, indole, and 3-methylindole. The results of this study indicated very high emissions of alcohols from cows and their fresh manure. However, subsequent research by Dr. Mitloehner has confirmed that when using the INNOVA analyzer without an ammonia filter, significant interference occurs when measuring alcohols. Because the INNOVA analyzer in this study did not include an ammonia filter, ammonia present in the chamber was incorrectly identified as alcohols. Therefore, the alcohol measurements from this study are not reliable. The study results showed very low levels of VFAs and phenol and cresol compounds. The only VFAs that were detected in measurable quantities were acetic, propionic, and butyric acid. Acetic acid was the only VFA that was consistently above the Limit of Quantification and the only VFA found to measurably contribute to enteric VOC emissions from milk cows but this contribution was very small. The VFA emissions measured in this study were lower than the acetic acid values measured in the earlier study using PTRMS.

The third environmental chamber study was completed by Dr. Mitloehner in late 2009. The experimental setup was as described in the California EPA, ARB project led by Dr. Zhang (May 2010), Section 6.0 - Measurement and Modeling of Volatile Organic Compound Emissions from Free Stall and Corral Housing. However, the information used to estimate enteric emissions from cows is based on unpublished data from the study for the period when cows are initially introduced into the environmental chamber and manure had not begun to accumulate. This unpublished data was provided by Dr. Mitloehner. This study is intended to replace the alcohol data from the previous 2006 study. In this study INNOVA photoacoustic analyzers with ammonia filters were used to quantify ethanol and methanol emissions from dairy cattle and fresh manure. The alcohol measurements from this study are considered to be much more reliable than the measurements from the earlier study, in which INNOVA analyzers without ammonia filters were used. This study resulted in significantly lower alcohol emissions. Enteric ethanol emissions from milk cows were significantly lower and enteric methanol emissions from milk cows were nearly zero. The methanol emissions measured in this study were lower than the value measured in the earlier study using PTRMS.

Conclusion

The APCO has chosen to continue to use the 1.4 lb/head-yr from PTRMS to quantify emissions of methanol, acetic acid, and other compounds in this category due to the conservative nature of the PTRMS measurement and sample loss. The storage and transport loss was less likely than with the sorbent tube method used to measure VFAs in the second chamber study. Additionally, 0.08 lb/head-year will be added to represent the measured value for enteric emissions of phenols and cresols from the second chamber study and 2.6 lb/head-year will be added to account for the ethanol emissions measured in the third chamber study. Therefore, enteric VOC emissions from milk cows are determined to be 4.1 lb/head-year.

Category 2: Milking Parlor (manure emissions)

California VOC Emissions Studies

Milking Parlor (manure emissions)		
Process or Constituent	**Emission Factor (lb/hd-yr)**	**Basis for Previous Emission Factor**
VOCs from Milking parlors	VOCs by TO-15: 0.02 lb/hd-yr Amines: 0.01 lb/hd-yr	Flux chambers with analysis by EPA TO-15, & EPA TO-11 (Schmidt, 2004)[11]

Dr. Charles Schmidt and Thomas Card measured VOC emissions from a dairy milking parlor at one Merced County dairy using flux chambers in conjunction with EPA method TO-15 and EPA method TO-11. The emission measurements were performed in 2004. The TO-15 measurements resulted in a total VOC measurement of 0.02 lb/head-year and amines were found to contribute an additional 0.01 lb/head-year. Therefore, total VOCs from the milking parlor were 0.03 lb/head-year based on this study.

Evaluation

The VOC emissions measured from the milking parlor were found to be very low. This is likely the result of the high solubility of the VOCs that would be emitted. Milking parlors are constantly flushed with fresh water so these compounds are likely to remain in solution in the water rather than being emitted to the atmosphere.

[11] Schmidt, C.E. April 2005. Results of the Dairy Emissions Evaluation Using Flux Chambers Merced Dairy- Summer Testing Event. Final Report to the Central California Ozone Study (CCOS) group

Conclusion

The only California data available to calculate non-enteric VOC emissions from milking parlors are from Schmidt and Card's 2004 study; therefore, the APCO proposes an emission factor of 0.03 lb/head-year for milking parlors. Because of the high solubility of VOCs emitted at dairies and the relatively small surface area of milking parlors, this source does not contribute significantly to total VOC emissions at a dairy.

Category 3: Freestall Barns (manure emissions)

Recent VOC Emissions Studies

Recent Studies – Freestall Barns (bedding and flush lanes)		
Recent Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of barns (flush lanes and stalls) with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 - Phase III)[6]	**1.8 lb/hd-yr** Average pre-flushed flush lane flux of 131 μg/m^2-min (Dairy 1: 158 μg/m^2-min; Dairy 2: 104 μg/m^2-min) Average bedding solids flux of 246 μg/m^2-min	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3
Flux chamber sampling of ROG from flush lanes with analysis by GC/MS (Krauter, 2009)[7]	Average flush lane flux of 187 μg/m^2-min (pre-flush/scrape: 353 μg/m^2-min; post-flush/scrape: 21 μg/m^2-min) Average flush lane flux excluding outlier: 111 - 131 μg/m^2-min (pre-flush/scrape: 200 - 241 μg/m^2-min; post-flush/scrape: 21 μg/m^2-min)	Analysis and speciation by GC/MS 1st average includes single outlier with higher ROG primarily due to refrigerant CFC-12, which was removed from second average flux value

Evaluation

The recent California research that is currently available to quantify emissions from dairy freestall barns is from two studies conducted at dairies in the San Joaquin Valley.

The first study was performed in 2005 (report completed in 2006) by Dr. Charles Schmidt and Thomas Card and used flux chambers to quantify emissions at two dairies located in Merced County and Kings County. Flux chambers were used to collect samples and SCAQMD Method 25.3 was used to quantify total VOC flux. Several other methods were also used to quantify emissions during this study, including EPA TO-11, EPA TO-13, EPA TO-8, BAAQMD 29, EPA TO-14, and EPA TO-15. SCAQMD Method 25.3, which quantifies total carbon atoms from VOCs excluding methane and ethane, consistently resulted in higher mass values of VOC as methane than the sum of the other methods when the total carbon measured by these methods was also converted to methane. The measured flux values and the surface areas of specific processes at the dairies were used to determine the emissions rate. The emissions rates were then divided by the number of cows at the dairies to arrive at the emission factors for the dairies. VOC emissions measured from the flush lanes prior to flushing were low and the emissions flux was similar at both dairies. The original study report calculated an emission factor based on the total head at the dairies. The measured flux and process surface areas for only the milk cow areas and estimated number of milk cows at the dairies in 2005 were used to calculate the VOC emission factors based only on milk cows. The resulting VOC emission factors were 0.8 lb/head-year for the flush lanes and 1.0 lb/head-year for the stall bedding, for a total of 1.8 lb/head-year from the freestall barns.

A recently completed study, in which the field sampling program was led by Dr. Charles Krauter with sample analysis headed by Dr. Donald Blake, measured VOC flux from six dairies in the San Joaquin Valley using flux chambers. Flux chambers were used to collect samples and GC/MS was used to quantify VOC flux. Sampling occurred during the winter, early summer, and fall. The report did not provide the surface areas of specific processes at the dairy, which are needed to calculate the total mass emissions rates. However, the average flux values from this study can be compared to the flux values obtained in the Schmidt and Card study. This study measured higher average VOC flux values for the flush lanes prior to flush/scrape than Dr. Schmidt’s 2005 study, but also measured very low VOC flux from the lanes after flushing/scraping. Therefore, the overall averages were similar. There was one flux measurement at Dairy A that had several times the flux value of the next highest measurement, primarily due to the refrigerant CFC-12, which was not found in more than trace amounts in the other samples. When this measurement is removed, the overall average for VOC flux from the flush lanes is nearly the same as Dr. Schmidt’s 2005 dairy study. Although the study report did not provide sufficient information to calculate an emission factor for the individual dairies sampled, the study did contain an example of emissions that could be expected from a fictitious dairy based on the information gathered in the study. The fictitious dairy in the report had a VOC emission factor of 1.0 lb/head-year for the flush lanes, which is very close to the value of 0.8 lb/head-year from the Dr. Schmidt’s 2005 dairy study.

Conclusion

The APCO has determined that the total VOC measurements from Schmidt and Card’s 2005 study provide the best available data to quantify VOC emissions from dairy freestall barns. Dr. Schmidt's 2005 dairy study measured total VOC emissions from both flush lanes and stalls in the freestall barns and provided the information needed to calculate specific emission factors for these processes. The study by Krauter and Blake resulted in similar average VOC flux from the freestall flush lanes. If the one potentially anomalous measurement is removed from the Krauter and Blake study, the average VOC flux from the freestall is equivalent or less than the average flux determined in the Schmidt and Card study using a different analytical method. Both studies indicated that VOC emissions from flush lanes are low because of the high solubility of many of the compounds. The flush lane VOC emission factor from the data in the Schmidt and Card study and the VOC emission factor for the fictitious dairy described in the report for the Krauter and Blake study are nearly the same. Therefore, both studies clearly support each other. However, it is more defensible to base the emission factor on the data from Dr. Schmidt's study because the surface areas used to calculate the emission factor in this report were based on the processes observed at the dairies studied rather than approximations based on a fictitious dairy. Therefore, the APCO proposes an emission factor of 1.8 lb/head-year for non-enteric emissions from freestall barns.

Category 4: Exercise Pens and Corrals (manure emissions)

Recent VOC Emissions Studies

Recent Studies – Exercise Pens and Corrals (manure emissions)		
New Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of corrals/ pens with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 - Phase III)[6]	Turnout Average: **8.3 lb/hd-yr** (Average flux of 243 μg/m^2-min) Seasonally Adjusted Turnout Average based on 2008 Study: **6.8 lb/hd-yr** (Average flux of 195 μg/m^2-min)	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3
Flux chamber sampling of corrals/ pens during summer and winter seasons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009 – Phase IV)[7]	Seasonally Adjusted Turnout Average: **6.5 lb/hd-yr** (Average flux of 207 μg/m^2-min)	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3
Flux chamber sampling of ROG from open lots with analysis by GC/MS (Krauter, 2009)[8]	Average flux of 173 μg/m^2-min from open lots	Analysis and speciation by GC/MS

Evaluation

The recent California research that is available to quantify emissions from corrals and exercise pens at dairies is from three studies conducted at dairies in the San Joaquin Valley.

As mentioned above, Dr. Schmidt and Card performed a study in 2005 using flux chambers and SCAQMD Method 25.3 to quantify emissions at two dairies located in Merced County and Kings County. Dr. Schmidt and T. Card performed a follow-up study in 2008 using flux chambers and SCAQMD Method 25.3 to quantify emissions at the same two dairies. However, the first study measured emissions only during the summer season while the 2008 study collected some samples during the winter season to characterize seasonal effects on the VOC emissions rates. The study results showed that winter VOC emissions rates from the corrals were lower than the summer rates. This information was used to adjust the summer data from the 2005 and 2008 studies to arrive at an annual average considering seasonal variability. The original study reports calculated emission factors based on total head at the dairies. The measured flux and process surface areas for only the milk cow areas and estimated number of milk cows at the dairies in 2005 and the reported number of milk cows at the dairies in 2008 were used to calculate the VOC emission factor based only on milk cows. This resulted in an annual VOC emission factor of 6.6 lb/head-year for the exercise pens and corrals.

The Krauter and Blake study also measured VOC flux from six dairies in the San Joaquin Valley using flux chambers to collect samples. GC/MS was used to quantify VOC flux. Sampling occurred during the winter, early summer, and fall. The average flux values from this study can be compared to the flux values obtained in Dr. Schmidt's study. This study resulted in average VOC flux values for the corrals that were similar but slightly less than the seasonal-adjusted averages from Dr. Schmidt's 2005 and 2008 dairy studies. The study report states that emissions from the corrals were found to vary with surface temperature and season. Like the Schmidt and Card dairy studies, emissions from the corrals were found to be higher in the summer than the winter. As previously mentioned, the report contained an example of emissions that could be expected from a fictitious dairy based on the information gathered in the study. The fictitious dairy in the report had a VOC emission factor of 3.2 lb/head-year for the corrals/pens, which is approximately half the annual average value from Dr. Schmidt's dairy study.

Conclusion

The APCO has determined that the total VOC measurements from Dr. Schmidt's 2005 and 2008 studies provide the best available data to quantify VOC emissions from corrals and exercise pens at dairies. The study by Krauter and Blake resulted in similar average VOC flux rates from corrals but the study estimated a lower overall emissions rate for the fictitious dairy presented in the report. It appears that the dairy VOC compound profile used for the GC/MS captured a large portion of the mass of VOC emissions from corrals since the average flux measurements were similar to Dr. Schmidt's study. Based on this, it appears that the corral area needed for the fictitious dairy was possibly underestimated, thereby resulting in lower VOC emissions. As stated above, it is more appropriate to base the emission factor on the actual data from Dr. Schmidt's study because the surface areas used to calculate the emission factor in this report were based on the processes observed at the dairies studied rather than approximations based on a fictitious dairy. Therefore, the APCO proposes an emission factor of 6.6 lb/head-year for the corrals and exercise pens.

Category 5: Lagoons, Storage Ponds, and Settling Basins

Basis of Previous VOC Emission Factor

Basis of the Previous Dairy VOC Emission Factor		
Process or Constituent	**Emission Factors (lb/hd-yr)**	**Basis for Previous Emission Factors**
Previous Category 4: VOCs from lagoons and storage ponds		
VOCs (except VFAs and Amines) from settling basins, lagoons, and storage ponds	1.0	Flux chambers with analysis by EPA TO-15, & EPA TO-11 (Schmidt, 2004)[11] Concentration analysis by EPA TO-15 and Emissions Modeling by ISCST3 (Krauter, 2005)[12]
From Previous Category 5: VFAs from Wet Processes		
VFAs from wet processes (settling basins, lagoons, storage ponds, etc.)	7.14	Estimated based on laboratory manure slurry study and a correlation between ammonia and VOC emissions from manure (Hobbs, P.J. Webb, J. Mottram, T.T. Grant, B. and Misselbrook. T.M. 2004)

Dr. Schmidt and Card measured VOC emissions from a dairy lagoon at one Merced County dairy using flux chambers in conjunction with EPA method TO-15 and EPA method TO-11. In a study led by Dr. Krauter VOC emissions from lagoons and storage ponds at two San Joaquin Valley dairies were estimated using TO-15 measurements of upwind and downwind concentrations in conjunction with inverse dispersion modeling techniques.

[12] Krauter Presentation to DPAG on March 8, 2005 at the San Joaquin Valley Air Pollution Control District Central Office, Fresno, CA - Concentration analysis by EPA TO-15 and Emissions by Inverse Dispersion Modeling using ISCST3

At the time of the previous revision to the District's dairy VOC emission factor, no California studies were available to estimate VFA emissions from wet processes, such as lagoons. Therefore, VFA emissions from wet processes were estimated based on the Hobbs et al study, in which VFA emissions were measured from manure slurry in a laboratory. The lb/head-year VFA emission factor was calculated based on a correlation between ammonia emissions and VOC emissions from manure and assuming that 60% of the manure on a typical San Joaquin Valley dairy is handled in a wet process.

Recent VOC Emissions Studies

Recent Studies – Lagoons, Storage Ponds, and Settling Basins		
New Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of lagoons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 - Phase III)[6]	1.3	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3

Evaluation

Dr. Schmidt's 2005 study used flux chambers to collect samples at two dairies located in Merced County and Kings County and SCAQMD Method 25.3 was used to quantify total VOC flux. The original study reports calculated emission factors based on total head at the dairies. The measured flux, process surface areas, and estimated number of milk cows at the dairies in 2005 were used to calculate an emission factor based only on milk cows. This resulted in an annual VOC emission factor of 1.3 lb/head-year for the liquid manure handling system.

Conclusion

The District has determined that the VOC measurements taken in the study led by Dr. Krauter in 2005 and the total VOC measurements from Dr. Schmidt's 2005 study provide the best available data to quantify VOC emissions from dairy lagoons, storage ponds, and settling basins. Each of these studies resulted in a VOC emission factor of 1.3 lb/head-year. Therefore, the APCO proposes an emission factor of 1.3 lb/head-year for the lagoons, storage ponds, and settling basins. Dr. Schmidt's earlier 2004 study reported lower emissions but only focused on a very limited number of compounds. SCAQMD Method 25.3, which was used in Dr. Schmidt's later studies, is able to measure total VOCs and captures a greater proportion of the VOCs emitted at dairies, including volatile fatty acids and amines. Recent studies that are available have indicated that VOC emissions from lagoons were relatively low; therefore, VFA emissions from this source are not as significant as previously thought.

Category 6: Liquid Manure Land Application

Recent VOC Emissions Studies

Recent Studies – Liquid Manure Land Application		
New Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of lagoons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009 – Phase IV)[7]	1.4	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3

Evaluation

The only VOC emissions data that were available for liquid manure land application at a California dairy were from Schmidt and Card's Phase IV flux chamber study at a dairy located in Merced County. Total VOCs (as methane) were measured from the dry soil prior to land application and following application of liquid manure. VOC flux measurements from land application of chemical fertilizer at a different site were also performed for comparison purposes. Emissions were measured immediately after irrigation and at three hours, eight hours, and 21 hours after irrigation. The net VOC flux from liquid manure land application was found to be very low and was near the detection limits of the instrumentation. Therefore, the contribution of land application to VOC emissions at the dairy was primarily the result of the very large land application area (2,500 acres) being irrigated with liquid manure three times per year. The land application area was shared with an adjacent dairy. The land application emission factor given in the study report was based on the total number of milk cows at both dairies and resulted in an annual VOC emission factor of 1.4 lb/head-year for liquid manure land application.

Conclusion

The only California data that were available to calculate VOC emissions from liquid manure land application are from Dr. Schmidt's Phase IV study; therefore, this data will be used to quantify VOC emissions from this source. Therefore, the APCO proposes an emission factor of 1.4 lb/head-year for liquid manure land application.

The study resulted in very low total VOC flux near the quantification limit. Additionally, there was an extremely low correlation for the estimated curve fit that was used to calculate overall emissions. Therefore, in future studies additional measurements are needed to better quantify the low net flux value to calculate emissions with greater accuracy. Because of the low flux value, the mass of emissions is primarily the result of the very large surface area for this process. Therefore, to more accurately assess VOC emissions from this source, additional information is needed regarding the number of times liquid manure is applied to land, the number of acres irrigated for each event, and the total land application area at dairies in relation to the number of milk cows and total herd size.

Category 7: Solid Manure Land Application

Recent VOC Emissions Studies

Recent Studies – Solid Manure Land Application		
New Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of solid manure land application with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009-Phase IV)[7]	0.33	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3

Evaluation

The only VOC emissions data that were located for solid manure land application at a California dairy were from Dr. Schmidt and Card's 2008 flux chamber study at a Merced County dairy. Total VOCs (as methane) were measured from the soil prior to land application of solid manure and following the application of solid manure. Initial emission measurements were performed for both incorporated and unincorporated solid manure. Incorporation of solid manure was found to significantly reduce ammonia emissions; however, no significant differences were found in the VOC emissions from incorporated and unincorporated solid manure. VOC emissions were measured for incorporated manure at one hour, three hours, and seven hours after application. The net VOC flux from solid manure land application was found to be very low and was near the detection limits of the instrumentation. The net VOC flux dropped back to background levels at approximately four hours after application. The contribution of solid manure land application to VOC emissions at the dairy was the result of solid manure being applied to the very large application area (2,500 acres) twice per year. The annual VOC emission factor from the study for solid manure land application based only on milk cows was 0.33 lb/head-year.

Conclusion

The only California data that were available to calculate VOC emissions from solid manure land application are from Dr. Schmidt's Phase IV study; therefore, the data in that study will be used to quantify VOC emissions from this source. Therefore, the APCO proposes an emission factor of 0.33 lb/head-year for solid manure land application.

The study resulted in very low total VOC flux near the quantification limit and the mass of emissions is primarily the result of the very large surface area for this process. To more accurately assess VOC emissions from this source, additional information is needed regarding the number of times solid manure is applied to land and the total land application area at dairies in relation to the number of milk cows and total herd size.

Category 8: Separated Solids Piles

Recent VOC Emissions Studies

Recent Studies – Separated Solids Piles		
New Studies	**Emission Factors from Recent Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of separated solids piles with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 - Phase III)[6]	0.06	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3

Evaluation

The only California data that were available to calculate VOC emissions from separated solids plies are from Dr. Schmidt and Card's 2005 study. Flux chambers were used to measure emissions at a dairy located in Merced County and SCAQMD Method 25.3 was used to quantify total VOC flux. Dr. Schmidt also measured this source in 2004 using TO-15 to quantify emissions. The total VOC emissions measured using SCAQMD Method 25.3 were approximately twice the emissions measured using TO-15. But the overall emissions quantified with either method were very low, possibly because of the high solubility of the volatile compounds emitted from dairies, which may have resulted in many of these compounds remaining in the liquid manure when solids were removed. The annual VOC emission factor for separated solids resulting from the 2005 study using SCAQMD Method 25.3 adjusted for only milk cows is 0.06 lb/head-year.

Conclusion

The APCO has determined that the total VOC measurements from Dr. Schmidt's Phase III study provide the best available data to quantify VOC emissions from separated solids. All available studies indicate that VOC emissions from separated solids are very low. However, the earlier 2005 study used only TO-15 and focused on a very limited number of compounds. SCAQMD Method 25.3, which was used in Dr. Schmidt's later studies, captures a more complete range of compounds, including volatile fatty acids and amines. Therefore, the APCO proposes an emission factor of 0.06 lb/head-year for manure separated solids. Given the very low emissions measured, future dairy emission studies do not need to focus on VOC emissions from this source.

Category 9: Solid Manure Storage

Dairies in the San Joaquin Valley will typically have stockpiles of solid manure consisting of stored separated solids that can be used as bedding in freestalls or applied to cropland and scrapings from exercise pens and corrals that are applied to the dairy's cropland or transported offsite to be applied to the cropland of other farms.

Recent VOC Emissions Studies

Recent Studies – Solid Manure Storage		
New Studies	**Emission Factors from New Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of lagoons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 – Phase III)[6]	0.15	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3

Evaluation

The only recent California data that were available to calculate VOC emissions from stored solid manure are from Dr. Schmidt and Card's 2005 study. Flux chambers were used to measure emissions at two dairies located in Merced County and Kings County. The annual VOC emission factor from the study for solid manure storage adjusted for only milk cows is 0.15 lb/head-year.

Conclusion

The only California data that were available to calculate VOC emissions from separated solids are from Dr. Schmidt's 2005 study; therefore, the data from this study will be used to quantify VOC emissions from this source. Therefore, the APCO proposes an emission factor of 0.15 lb/head-year for solid manure storage.

Category 10: Silage Piles

Recent VOC Emissions Studies

Recent Studies –Silage Piles		
New Studies	**Average VOC Flux from Recent Studies ($\mu g/m^2$-min)**	**Notes**
Flux chamber sampling with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 – Phase III)[6]	Silage Pile Average Flux: 29,335 $\mu g/m^2$-min (8.65×10^{-3} lb/ft^2-day) Seasonally and Time Adjusted Average Flux based on 2008 Study: 21,435 $\mu g/m^2$-min (6.32×10^{-3} lb/ft^2-day)	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3 Highest reported flux from freshly disturbed silage: 49,329 $\mu g/m^2$
Flux chamber sampling during summer and winter seasons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009 – Phase IV)[7]	Seasonally and Time Adjusted Average Flux: 39,405 $\mu g/m^2$-min (1.16×10^{-2} lb/ft^2-day)	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3 Highest reported flux from freshly disturbed silage: 85,240 $\mu g/m^2$ and 81,374 $\mu g/m^2$ Although higher average flux was measured in 2008, the higher per head EF in the report is also due to an additional silage pile being open at each dairy during the Phase IV study.
Flux chamber sampling of ROG from with analysis by GC/MS (Krauter, 2009)[8]	Average flux Disturbed silage: 19,170 $\mu g/m^2$-min (5.65×10^{-3} lb/ft^2-day); Undisturbed silage: 4,229 $\mu g/m^2$-min (1.25×10^{-3} lb/ft^2-day)	Analysis and speciation by GC/MS Time dependent data not provided but highest reported flux from freshly disturbed silage (75,977 $\mu g/m^2$ and 72,698 $\mu g/m^2$) is very similar to highest flux reported in Schmidt Phase IV study.

Recent Study for Comparison Purposes – Thin Layers of Loose Silage		
New Studies	**Average VOC Flux ($\mu g/m^2$-min)**	**Notes**
Flux chamber sampling with analysis of VOC by PTRMS and INNOVA photoacoustic analyzer (Zhang, 2010)[9]	Loose Corn Silage*: Ave. Flux: 1.17 g/m^2-hr (~ 19,400 $\mu g/m^2$-min) Loose Alfalfa Silage*: Ave. Flux: 1.00 g/m^2-hr (~ 16,700 $\mu g/m^2$-min)	Major VOC measured by PTRMS: methanol, acetic acid, and acetaldehyde. INNOVA analyzer measured ethanol and methanol. Based on Cumulative Emissions measured over 12 hours

*For total VOC flux the methanol values by PTRMS and the INNOVA analyzer were averaged

Evaluation

The recent California research that is available to quantify emissions from silage piles at dairies is based on three studies conducted at dairies in the San Joaquin Valley. In addition, the average flux rates measured for loose silage from the ARB research project led by Dr. Ruihong Zhang of UC Davis will also be briefly discussed for comparison purposes.

Dr. Schmidt and Card's Phase III study used flux chambers and SCAQMD Method 25.3 to quantify emissions at two dairies located in Merced County and Kings County. As previously mentioned, Schmidt and Card performed a follow-up study in 2008 (Phase IV) using flux chambers to quantify emissions at the same two dairies. In the Phase IV study, some samples were collected during the winter season to characterize seasonal effects on the VOC emissions rates. The study showed that winter VOC emissions rates from the feed sources were lower than the summer rates. This information was used to adjust the summer data from the Phase III and Phase IV studies to arrive at an annual average considering seasonal variability. Additionally, measurements were taken at one of the dairies throughout the day to characterize how emissions changed with time. The VOC emissions from the silage piles were the highest when the silage was initially disturbed to remove feed for the TMR but declined with time. The silage that had not been disturbed had much lower emissions. The operational practices observed at the dairy were used to simulate emissions and arrive at an average annual VOC emission factor. The adjustment factors from the Phase IV study were also used to adjust the emissions measurements from the Phase III study. The following average flux values were derived from these studies: corn silage: 1.02E-02 lb/ft^2-day (34,681 µg/m^2-min); alfalfa silage: 5.15E-03 lb/ft^2-day (17,458 µg/m^2-min); and wheat silage: 1.29E-02 lb/ft^2-day (43,844 µg/m^2-min).

For reference purposes, the measured flux and process surface areas for the open faces of the silage piles can also be used to calculate the seasonally adjusted VOC emission factor based on the number of milk cows at the dairies. This would result in an average VOC emission factor of approximately 6.5 lb/head-year for the uncovered faces of the silage piles. However, the lb/head-year emission factor may overestimate VOC emissions from silage since the silage piles at the Merced dairy also served other dairies with additional milk cows that were not counted when determining this value. Additionally, because emissions from this source are more dependent on the exposed area of the silage piles than the number of cows at the dairy, using the average flux values to calculate VOC emissions is more appropriate for this source. This is illustrated by the fact that a significant portion of the increased lb/head-year silage pile VOC emission factor reported in the Phase IV study conducted in 2008 as compared to the Phase III study conducted in 2005 can be attributed to an additional silage pile being open and utilized at each dairy during the Phase IV study.

The study by Dr. Krauter and Dr. Blake also used flux chambers to measure VOC emissions from the silage piles at six dairies in the San Joaquin Valley. GC/MS was used to analyze and quantify VOC flux. Sampling occurred during the winter, early summer, and fall but no seasonal effects were found for VOC emissions from feed sources. This study reported maximum VOC flux values for freshly disturbed silage that were similar to the maximum VOC flux values for freshly disturbed silage reported in Dr. Schmidt's Phase III and Phase IV dairy studies, particularly the higher values in the Phase IV study report. However, the average VOC flux values reported for silage piles were significantly less than the seasonally-adjusted averages from Dr. Schmidt's Phase III and Phase IV dairy studies. The reason for this difference is not known at this time but may be related to the time measurements were taken after initial disturbance of the silage and how these values were averaged. Additional time-dependent emissions data for dairy feed sources would be useful for better characterizing emissions from this source and determining representative emission values. There was also a great deal of variability in the flux measured from the silage at the dairies. The variability may be related to the types of silage used or silage compaction; however, the study report does not provide all of this information but states that an upcoming report may contain at least some of this information.

During the Krauter and Blake study INNOVA analyzers were also used to quantify alcohol emissions from sources at the dairies. The INNOVA analyzer measurements were taken at the same source within 10 minutes of the canister samples analyzed with GC/MS. In the report to ARB for the Krauter and Blake study it was noted that the INNOVA analyzer alcohol measurements for silage were consistently three to four times the values obtained with the canister samples analyzed by GC/MS and that Dr. Donald Blake of UC Irvine and other project collaborators had questioned the ability of the GC/MS system to extract all of the water soluble gasses, such as alcohols, from the canisters when they are analyzed. However, the results in the report indicating higher alcohol emissions measured with the INNOVA analyzer as compared to GC/MS were based on preliminary information from an earlier progress report submitted to ARB in April 2007. Later measurements performed by the researchers indicated general agreement between the GC/MS alcohol measurements and the INNOVA analyzer alcohol measurements.[13] Researchers at CSU Fresno that were involved in the project were contacted and they indicated that the apparent difference between the two methods occurred in the first year (2006) and possibly the early part of the second year (2007) of the monitoring study while the methodology was still being developed and the field collection and lab analysis techniques were still being modified. Dr. Krauter and other researchers involved with the project stated that the data from the later years, 2007- 2009, including the measurement values in the main body of the final report to ARB, showed much better agreement and are more reliable than their preliminary work

[13] Chung M., Beene M., Ashkan S., Krauter C., Hasson A. (2009) Evaluation of non-enteric sources of non-methane volatile organic compound (NMVOC) emissions from dairies. Atmospheric Environment 44, 786-794.

that indicated differences between the GC/MS alcohol measurements and the INNOVA analyzer alcohol measurements.

The primary purpose of the study led by Dr. Ruihong Zhang was to identify and quantify significant VOC compounds emitted from silage and dairy manure storage for the purpose of developing process-based models to quantify emissions from dairy sources. As part of the study, samples of corn and alfalfa silage were spread in thin layers and flux chambers were used to measure emissions using PTRMS and an INNOVA photoacoustic analyzer to measure alcohols. Four major compounds were detected with high certainty by PTRMS: methanol, acetic acid, acetaldehyde, and acetone (an exempt compound). The INNOVA analyzer was used to measure ethanol and methanol. Emissions from the loose silage samples were measured over a twelve-hour period. The average VOC flux rates from the main compounds reported in this study are presented for comparison purposes only since the thin layers of loose silage samples that were measured are not representative of the condition of the majority of silage in silage piles, which is densely compacted to slow aerobic spoilage and preserve nutritional value. The average flux measurements for the major VOCs reported for thin layers of loose corn and alfalfa silage are generally similar to the average silage pile emission numbers reported by Dr. Krauter and Dr. Blake. These average flux values were less than the seasonally-adjusted average flux for corn silage from Dr. Schmidt's Phase III and Phase IV dairy studies and similar to the seasonally-adjusted average flux for alfalfa silage. This is likely because of the limited number of compounds for which the flux rates were reported since emissions are known to increase with increased porosity and loose silage samples would be expected to have a higher average flux rate than silage in silage piles, most of which would be densely compacted.

Conclusion

The APCO has determined that the total VOC flux measurements from Dr. Schmidt's Phase III and Phase IV studies provided the best available data to quantify VOC emissions from silage piles at dairies. Because emissions from this source are more directly related to the exposed area of the silage piles, the measured flux will be used to calculate emissions on a per area basis rather than a per cow basis. The APCO proposes that the following average flux values be used to calculate emissions from the silage piles at a dairy on a per area basis: corn silage: 1.02E-02 lb/ft^2-day; alfalfa silage: 5.15E-03 lb/ft^2-day; and wheat silage: 1.29E-02 lb/ft^2-day.

The study by Krauter and Blake resulted in very similar maximum VOC flux rates but lower average VOC flux using GC/MS. Additional time-dependent emissions data for dairy feed sources would be useful to better characterize emissions from this source and determine representative emission values. The difference in the average flux values may also be related to the types of silage used or other factors. The study report states that some of this information may be provided in another report. As mentioned above, preliminary results of the Krauter and Blake study had initially indicated higher alcohol flux using INNOVA analyzers; however these preliminary results were based on measurements that were taken while the field and lab procedures were still being developed. Later measurements demonstrated general agreement between the values obtained by GC/MS and the INNOVA analyzer and the researchers involved with the project state that these later results are more reliable. Dr. Schmidt's Phase IV study found seasonal variation that was not found in the Krauter and Blake study but the winter data set from Dr. Schmidt's Phase IV study was very limited. Therefore, additional data may need to be collected in the winter and/or fall seasons to better quantify seasonal variability of VOC emissions from this source.

The average flux rates of major VOCs emitted from thin layers of loose silage that were identified in the study led by Dr. Zhang were presented for comparison purposes. The average VOC flux rates from this study were similar to the average flux rates for silage piles in the Krauter and Blake study and less than the average flux rates for silage piles from the Schmidt and Card Studies. This is likely because of the limited number of major compounds for which flux rates were reported since loose silage will generally have higher emission fluxes than densely compacted silage piles.

Category 11: Total Mixed Ration

Recent VOC Emissions Studies

Recent Studies – Total Mixed Ration (TMR) (feed placed in front of cows)		
New Studies	**Average VOC Flux from Recent Studies ($\mu g/m^2$-min)**	**Notes**
Flux chamber sampling with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 – Phase III)[6]	TMR Average Flux: 40,061 $\mu g/m^2$-min (1.18×10^{-2} lb/ft^2-day) Seasonally and Time Adjusted Average Flux based on 2008 Study: 15,415 $\mu g/m^2$-min (4.55×10^{-3} lb/ft^2-day)	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3
Flux chamber sampling during summer and winter seasons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009 – Phase IV)[7]	Seasonally and Time Adjusted Average Flux: 10,696 $\mu g/m^2$-min (3.15×10^{-3} lb/ft^2-day)	Total non-methane, non-ethane VOC as methane determined by SCAQMD 25.3
Flux chamber sampling of ROG from TMR with analysis by GC/MS (Krauter, 2009)[8]	TMR Average flux: 8,260 $\mu g/m^2$-min (2.44×10^{-3} lb/ft^2-day)	Analysis and speciation by GC/MS

Evaluation

The recent California research that is available to quantify emissions from Total Mixed Ration (TMR) at dairies is based on three studies conducted at dairies in the San Joaquin Valley.

Schmidt and Card's Phase III study used flux chambers and SCAQMD Method 25.3 to quantify emissions at two dairies located in Merced County and Kings County. The later Phase IV study used the same methodologies but with a focus on seasonal and temporal variability from important emission sources. The VOC emissions from the TMR, the feed placed to be consumed by the cows, were the highest when the feed was first placed but declined with time. The TMR was the largest source of VOC emissions at the dairies and also had the most variability. The maximum flux measured from the TMR at the Kings County dairy was significantly higher than the flux measured from the TMR at the Merced County dairy. The operational practices observed at the dairies were used to simulate emissions and arrive at an average annual VOC emission factor. However, the original exponential curve fit used in the report to calculate VOC emissions from the milk cow TMR had a very low correlation value - so low that it could be argued that there was no true correlation between the data set and the exponential equation used. Therefore, the emission factor for the TMR used in this report is based on a slightly more conservative linear curve fit of the 2008 data set that had a higher correlation value. The adjustment factors derived from the 2008 study were also used to adjust the emissions measurements from the 2005 study for both temporal and seasonal variability. For reference purposes, the measured flux and process surface areas for the TMR can be used to calculate the seasonally adjusted VOC emission factor based on the number of milk cows at the dairies, which results in an average VOC emission factor of approximately 11.8 lb/head-year for the TMR. However, as with silage piles, the other feed emission source, it has been determined that using the average flux value and the area of the TMR placed for the cows to calculate VOC emissions is more appropriate for determining emissions from this source. The following average flux value derived from Schmidt and Card's Phase III and Phase IV dairy studies can be used to calculate emissions from the TMR on a per area basis: 3.85E-03 lb/ft^2-day (13,056 µg/m^2-min).

The Krauter and Blake study (2009) also used flux chambers to measure VOC emissions from the TMR at six dairies in the San Joaquin Valley. Sampling occurred during the winter, early summer, and fall. No seasonal effects were found for VOC emissions from feed sources. However, as in Schmidt and Card's studies, emissions from the TMR were found to decrease with time after placement of the feed. The average flux values reported for this study can be compared to the average flux values reported for the studies by Schmidt and Card. This study resulted in average VOC flux values for the TMR that were less than the values reported by Schmidt and Card but were more similar to the average flux values reported by Schmidt and Card after they had been adjusted to account for temporal and seasonal variability in VOC emissions from feed. The study also resulted in lower emissions from the TMR for the fictitious dairy described in the report. As mentioned earlier, preliminary results of the Krauter and Blake study had initially indicated higher alcohol flux using INNOVA analyzers compared to the values obtained by GC/MS; however these preliminary results were based on measurements that were taken while the field and lab procedures were still being developed. Later measurements demonstrated general agreement between the values obtained by GC/MS and the INNOVA analyzer[13] and the researchers involved with the project state that these later results, including the values contained in the main body of the final project report to ARB, are more reliable. More data were collected on TMR emissions at two of the dairies but these data were not presented in the current project report. The report states that these data will be presented in a forthcoming report.

Conclusion

The APCO has determined that the total VOC measurements from the Schmidt and Card Phase III and Phase IV studies provide the best available data to quantify VOC emissions from TMR at dairies. Therefore, the APCO proposes that the following average flux value be used to calculate emissions from the TMR on a per area basis: 3.85E-03 lb/ft^2-day.

The Krauter and Blake study resulted in a slightly lower average VOC flux than the values reported by Schmidt and Card, once these values had been adjusted to account for temporal and seasonable variability. Additional data may need to be collected in the winter and/or fall seasons to better quantify seasonal variability of VOC emissions from this source. Additionally, the correlations for the curve fits that were examined to calculate emissions from TMR based on data from the Phase IV Schmidt Study were all low. Additional time-dependent emissions data are needed to better characterize changes in emissions from dairy feed sources over time and determine representative emission values.

Category 12: Composting

Composting		
Process or Constituent	**Emission Factor (lb/hd-yr)**	**Basis for Emission Factor**
Composting	TBD, > 0	N/A

Although unknown quantities of VOCs may be emitted during composting of dairy manure solids, no California emissions data could be located that were representative of this source. Therefore, the APCO will consider the emissions from this source to be of the category to be determined but greater than zero. Further research is recommended to quantify emissions from this source.

Summary of Dairy Emission Factors

In summary, the tables below show the dairy emission factors that were developed based on the best information available to the APCO and will be used for each source and constituent:

Dairy Emission Factors based on Studies Summarized in this Document

Per Cow Dairy VOC Emission Factors	
Process or Constituent	**Emissions (lb/hd-yr)**
1. Enteric Emissions from Cows	4.1
2. Milking Parlor(s)	0.03
3. Freestall Barns	1.8
4. Corrals/Pens	6.6
5. Liquid Manure Handling (Lagoons, Storage Ponds, Basins)	1.3
6. Liquid Manure Land Application	1.4
7. Solid Manure Land Application	0.33
8. Separated Solids Piles	0.06
9. Solid Manure Storage	0.15
12. Composting & Manure Disturbance	TBD, >0
Total not including Feed	**15.8**

The dairy emission factors that are summarized in the table above were developed based on the studies reviewed and summarized in this document; however, the APCO has determined that during the time that the majority of these studies were performed, measures were being implemented that would reduce VOC emissions below the levels that would otherwise have been measured. In order to calculate the uncontrolled dairy emission factors for the period when no controls/mitigation measures were implemented (i.e. prior to District Rule 4570), the dairy emission factors developed in this document were adjusted to remove control efficiencies for certain practices that reduced emissions. Details of how this calculation was performed can be found in Appendix 8 and the uncontrolled dairy VOC emission factors to be used for dairies that are not required to implement measures from Phase I of District Rule 4570 are summarized in the table below.

Dairies not Implementing Phase I of District Rule 4570 (< 1,000 milk cows)

Uncontrolled Per Cow Dairy VOC Emission Factors	
Process or Constituent	**Emissions (lb/hd-yr)**
1. Enteric Emissions from Cows	4.3
2. Milking Parlor(s)	0.04
3. Freestall Barns	1.9
4. Corrals/Pens	10.0
5. Liquid Manure Handling (Lagoons, Storage Ponds, Basins)	1.5
6. Liquid Manure Land Application	1.6
7. Solid Manure Land Application	0.39
8. Separated Solids Piles	0.06
9. Solid Manure Storage	0.16
12. Composting & Manure Disturbance	TBD, >0
Total not including Feed	**20.0**

VOC Emissions from Dairy Feed Sources

Silage Pile VOC Emissions Flux*	
10. Silage Piles	**Emissions Flux (lb/ft^2-day)**
1. Corn Silage	1.02E-02
2. Alfalfa Silage	5.15E-03
3. Wheat silage	1.29E-02

*Assuming silage piles are completely covered except for the “face” from where feed can be removed

Average Total Mixed Ration (TMR) VOC Emissions Flux	
11. Average TMR	**Emissions Flux (lb/ft^2-day)**
TMR	3.85E-03

Previous Dairy VOC Emission Factor for Reference

For comparison purposes only, the District's previous dairy emission factor (adopted August 1, 2005) is provided in the table below. The District's revised dairy emission factors represent a significant improvement because it specifically addresses many areas of the previous dairy emission factor for which there was a need for additional research to better quantify emissions under California dairy conditions.

District's Previous Dairy Emission Factors (Adopted August 1, 2005)	
Process or Constituent	**Emissions (lb/hd-yr)**
1. Emissions from Cows and Feed in Environmental Chamber	1.4
2. Ethylamines from specific dairy processes	0.2
3. VOCs (except VFAs and Amines) from miscellaneous dairy processes	1.2
4. VOCs (except VFAs and Amines) from lagoons and storage ponds	1.0
5. Volatile Fatty Acids	15.5
6. Phenols (from dairy processes)	TBD, > 0
7. Land Application	TBD, > 0
8. Feed storage, settling basins, composting, & manure disturbance	TBD, > 0
Total not including Feed	**19.3**

Summary of Future Research Recommendations

The APCO believes that future research will continue to improve the quality of dairy emission factors and recommends future research on the following items:

- Additional data are needed on different process emissions and effects of management practices on emissions to develop practical measures to mitigate emissions from important sources at dairies.
- Additional data need to be collected using real-time emission measurement techniques to better characterize changes in emissions from dairy feed sources over time and to compare these values with total VOC and other canister methods analyzed in a laboratory.
- Additional information is needed to better assess seasonal variability of emissions sources at dairies, particularly feed sources.
- Research should continue to determine which specific VOC compounds (e.g. alcohols, VFAs, aldehydes, esters) have the greatest contribution to the total mass of VOC from emitted from important sources at dairies and which of these compounds may have greater potential for ozone formation.
- Research should be conducted to determine if representative compounds can be measured to represent general categories of similar compounds (e.g. alcohols, VFAs, aldehydes) for purposes of assessing potential mitigation strategies.
- Additional information is needed comparing the effects of different sample collection techniques (e.g. flux chambers and wind tunnels) on calculated emissions rates
- Additional information is required regarding total land application area in relation to the number of milk cows and/or total head at a dairy and the frequency of land application of solid and liquid manure

Appendix 1 – Partial List of Emissions Studies Papers and Presentations Reviewed

Previous Papers and Presentations Reviewed to Establish the 2005 Dairy VOC Emission Factor

Cassel, T. Flocchini, R. Green, P. Higashi, R. Goodrich, B. Beene, M. Krauter, C. (Jan 2005). On-Farm Measurements of Methane and Select Carbonyl Emission Factors for Dairy Cattle. Presented at the Livestock Emissions Research Symposium held on January 26, 2005 at the San Joaquin Valley Air Pollution Control District Office, Fresno, CA
ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/cassel05jan26.pdf

- Carbonyl Emission Factors by DNPH

Hobbs, P.J. Webb, J. Mottram, T.T. Grant, B. Misselbrook, T.M. (2004) Emissions of Volatile Organic Compounds Originating from UK Livestock Agriculture. 2004©. Society of Chemical Industry. J Sci Food Agric 84:1414-1420
http://www.valleyair.org/busind/pto/dpag/VOC_from_UK_livestock.pdf

- Non-methane VOCs emitted from slurry manure in an enclosed chamber measured using adsorbent material and thermal desorption GC/MS

Mitloehner, F. Trabue, S. Koziel, J.A. Research Proposal Summary (~2004) - Measurement of airborne volatile fatty acids emitted from dairy cows and their waste using sorbent tubes
http://www.valleyair.org/busind/pto/dpag/Appendices/Appendix%2024%20%20Plan%20of%20work%20VFAs_FMM.pdf

- VFAs by sorbent tubes and analyzed on a thermal desorption TDS/GC-MS system

Krauter, C. Goodrich, B. Dormedy, D. Goorahoo D., and Beene, M. 2005. Monitoring and Modeling of ROG at California Dairies. Presented at the EPA 14th Emissions Inventory Conference, April 13, 2005, Las Vegas, NV
http://www.epa.gov/ttn/chief/conference/ei14/session1/krauter.pdf
http://www.epa.gov/ttn/chief/conference/ei14/session1/krauter_pres.pdf

- VOC Concentration by EPA Method TO-15; Speciation by GC/MS; Emission Modeling by IST-STv3:

Krauter, C. Goorahoo, D. Goodrich, B. Beene, M (2005). Monitoring and Modeling of ROG at California Dairies, Presented at the Livestock Emissions Research Symposium held on January 26, 2005 at the San Joaquin Valley Air Pollution Control District Central Office, Fresno, CA
ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/krauter05jan26.pdf

McGinn, S. M. Janzen, H. H. Coates, T. (2003). Atmospheric Ammonia, Volatile Fatty Acids, and Other Odorants near Beef Feedlots. J. Environ. Qual. 32:1173-1182

- VFAs (acetic, propionic, butyric, isobutyric, isovaleric, valeric, and caproic acids), cresols, phenol, indole, and skatole from beef feedlots by sorbent tubes and GC

Mitloehner, F. (2005). Volatile Organic Compound Emissions from Dairy Cows and Their Excreta. Presented at the Livestock Emissions Research Symposium held on January 26, 2005 at the San Joaquin Valley Air Pollution Control District Central Office, Fresno
ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/mitloehner05jan26.pdf)

- Cows in an environmental chamber oxygenated VOCs (i.e. Ketones, Aldehydes, Alcohols, Carbonyls, Phenols, and Volatile Fatty Acids (VFAs)) by PTR/MS; TO-15 VOCs by GC/MS; total non-methane, non-ethane organic compounds by GC-FID; VFAs by GC/MS thermo-desorption

Schmidt, C. Card, T. Gaffney, P. (2005). Assessment of Reactive Organic Gases and Amines from a Northern California Dairy Using the USEPA Surface Emission Isolation Flux Chamber. Presented at the Livestock Emissions Research Symposium held on January 26, 2005 at the San Joaquin Valley Air Pollution Control District Central Office, Fresno
ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/schmidt05jan26.pdf

- Flux Chambers with VOCs by EPA Method TO-15 (GC/MS); Amines by NIOSH 2010 (GC/IC); Aldehydes & Ketones by EPA Method TO-11 (GC/HPLC); Volatile Organic Acids by EAS Method (UV-VIS)
- Process units measured: Flush lanes; Solids storage piles; Lagoon (inlet and outlet of lagoon); Solids in Solids separator; Bedding in pile for freestall; Freestall area; Barn turnout and corral area; Manure piles in turnout; Heifer pens (dry cow area); Open feed storage in barn feed lanes; and Milk parlor wastewater effluent stream

Schmidt, C. E. (2005). Technical Memorandum: Results of the Dairy Emissions Evaluation Using Flux Chambers Merced Dairy- Summer Testing Event. April 2005. Final Report to the Central California Ozone Study (CCOS) group.
http://www.valleyair.org/Workshops/postings/PriorTo2008/2005/7-11-05/Appendix%206%20Schmidt%20ARBDairy.TM.02.pdf

Rabaud, N.E. Ebeler, S.E., Asbaugh, L.L, and R.G. Flocchini. 2002©. The application of Thermal Desorption GC/MS with Simultaneous Olfactory Evaluation for the Characterization and Quantification of Odor Compounds from a Dairy. Crocker Nuclear laboratory and department of Viticulture and Enology. American Chemical Society, 10.1021/jf020204u

Ngwabie, N.M. and Hintz, T. 2005©. Mixing Ratio Measurements and Flux Estimates of Volatile Organic Compounds (VOC) from a Cowshed with

Conventional Manure Treatment Indicate Significant Emissions to the Atmosphere. Geographical Research Abstracts, Vol. 7, 01175, 2005 Sref-ID: 1607-7962/gra/EGU05-A-01175

Koziel, J.A., Spinhirne, J.P., and Back, B.H. Measurements of Volatile Fatty Acids Flux from Cattle Pens in Texas. Texas Agricultural Experiment Station, Texas A&M University. Paper #04-A-646-AWMA

Additional VOC Papers and Presentations Reviewed

Schmidt, C. Card, T. (2009) 2008 Dairy Emissions Study: Summary of Dairy Emission Factors and Emission Estimation Procedures. August 2009. Final Report to San Joaquin Valley Air Pollution Control District

Schmidt, C. Card, T. (2009) Recent Sampling of Total Organic Gas Emissions from Dairies. Presented at the UC Davis Green Acres, Blue Skies II Conference, June 1, 2009, Davis, CA
http://airquality.ucdavis.edu/pages/events/2009/greenacres.html

Krauter, C. Blake, D. (2009) Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions in the San Joaquin Valley (May 01, 2009). Final Report for California Air Resource Board (ARB)
http://www.arb.ca.gov/research/single-project.php?row_id=64648

Zhang, Ruihong. (2010) Process-Based Farm Emission Model for Estimating Volatile Organic Compound Emissions from California Dairies. May 2010. Final Report for California Air Resource Board (ARB)
http://www.arb.ca.gov/research/single-project.php?row_id=64722

Alanis, P. Sorenson, M. Beene, M. Krauter, C. Shamp, B. Hasson, A. S. Measurement of non-enteric emission fluxes of volatile fatty acids from a California dairy by solid phase micro-extraction with gas chromatography/mass spectrometry, Atmospheric Environment 42 (2008) 6417–6424

Alanis, P. Ashkan, S. Krauter, C. Campbell, S. Hasson, A. S. Emissions of volatile fatty acids from feed at dairy facilities, Atmospheric Environment 44 (2010) 5084–5092

Sun, H. Trabue, S. Scoggin, K. Jackson, W. Pan, Y. Zhao, Y. Malkina, I.L. Koziel, J.A. and Mitloehner. F.M. (2008) Alcohol, volatile fatty acid, phenol, and methane emissions from dairy cows and fresh waste, Journal of Environmental Quality. Volume 37 (March–April 2008) 615-622.

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Appendix 2

San Joaquin Valley Air Pollution Control District Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies, August 1, 2005

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Appendix 3

Mitloehner, F. Trabue, S. Koziel, J.A. (2006) Volatile Fatty Acids, Amine, Phenol, and Alcohol Emissions from Dairy Cows and Fresh Waste (May 31, 2006). Final Report to California Air Resource Board (ARB)

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Appendix 4

Schmidt, C.E. Card, T. Gaffney, P. Hoyt., S. California Air Resource Board (ARB) and Central California Ozone Study (CCOS) Project: Assessment of Reactive Organic Gases and Amines from a Northern California Dairy Using the USEPA Surface Emissions Isolation Flux Chamber. 14th USEPA Annual Emissions Inventory Conference Las Vegas, Nevada, April, 2005

a. Technical Paper
http://www.epa.gov/ttn/chief/conference/ei14/session1/schmidt.pdf

b. Presentation
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Appendix 5

Schmidt, C. Card, T. (2006) Dairy Air Emissions Report: Summary of Dairy Emission Estimation Procedures (May 2006). Final Report to California Air Resource Board (ARB)

a. Dairy Air Emissions Report: Summary of Dairy Emission Estimation Procedures
http://www.arb.ca.gov/ag/caf/SchmidtDairyEmissions2005.pdf

b. Technical Memorandum: Results of the Dairy Emissions Evaluation Using Flux Chambers Phase III Merced and Kings County Dairies
http://www.arb.ca.gov/ag/caf/SchmidtDairyTestData2005.pdf

c. Technical Memorandum: Results of the Dairy Emissions Evaluation Using Flux Chambers Phase III Volatile Fatty Acids (VFAs) Verification and Validation Tasks
http://www.arb.ca.gov/ag/caf/SchmidtVFAValidation2005.pdf

Appendix 6

Schmidt, C. Card, T. (2009) 2008 Dairy Emissions Study: Summary of Dairy Emission Factors and Emission Estimation Procedures. August 2009. Final Report to San Joaquin Valley Air Pollution Control District

a. 2008 Dairy Emissions Study: Summary of Dairy Emission Factors and Emission Estimation Procedures

b. Technical Memorandum: DAIRY EMISSIONS EVALUATION - Results from the Phase 4 Continued Research, “Dairy Emissions Evaluation Using the Surface Isolation Flux Chamber: Feed Sources, Corrals/Turnouts, and Land Application Sources”

Appendix 7

Krauter, C. Blake, D. (2009) Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions in the San Joaquin Valley (May 01, 2009). Final Report for California Air Resource Board (ARB)

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Appendix 8 – Calculation of Uncontrolled VOC Emission Factors for Dairies with less than 1,000 milk cows

Uncontrolled Dairy Emission Factors

In order to calculate the uncontrolled dairy emission factors for the period when no controls/mitigation measures were implemented (i.e. prior to the implementation of District Rule 4570), the dairy emission factors developed in this document were adjusted to remove control efficiencies for certain practices being implemented that reduced emissions. The District's dairy emission factor of 15.8 lb/head-year was used as the basis for this calculation. This emission factor was adjusted to account for the control measures that were being applied at the time when the emission measurements took place. The following control measures are assumed to have been in place at the dairies where the emission measurements were taken:

- Feed according to the NRC guidelines
- Flush or hose milk parlor immediately prior to, after, or during each milking
- Removal of manure from the corrals
- Clean manure from corrals at least once between April and July and at least once between October and December
- Manage corrals such that the depth of manure in the corral does not exceed 12" at any point or time, except for in-corral mounding[14]
- Maintain corrals and pens to ensure drainage and prevent water from standing more than 24 hours after a storm, slope the surface of the pens at least 3% where the available space for each animal is 400 square feet or less or at least 1.5% where the available space for each animal is more than 400 square feet per animal, or rake/harrow/scrape pens to maintain a dry surface[14]
- Inspect water pipes and troughs and repair leaks
- Install all shade structures uphill of any slope in the corrals
- Remove solids from the liquid manure handling system, prior to the manure entering the lagoon
- Incorporation of solid manure applied to land
- Not allowing liquid manure to stand in fields for more than 24 hours after application

Based on the 2006 staff report for District Rule 4570, a conservative control efficiency of 10% was applied to many of the mitigation measures. Therefore, a 10% control efficiency will be assumed for each of the mitigation measures that was being implemented at the time the studies were performed unless otherwise noted. For mitigation measures that were only being implemented at one of two dairies that were measured or were being partially being implemented, a 5%

[14] 5% control efficiency will be used for this measure since one of the two dairies that were sampled did not include this measure when the testing was performed. Therefore, the average of the two dairies was taken (10%/2=5%)

VOC control efficiency was assumed. Removing the assumed control efficiencies for the mitigation measures that were being from the District's dairy emission factor of 15.8 lb/head-year results in an uncontrolled dairy emission factor of 20.0 lb/head-year. This emission factor will be used to calculate emissions from dairies that are not implementing the mitigation measures outlined in Phase I of District Rule 4570 (i.e. < 1,000 milk cows). The table below shows the mitigation measures that were assumed to be implemented during the emission studies and the respective control efficiencies that were assumed for each measure.

The following sample calculation shows how the uncontrolled emissions were calculated:

Sample Calculation for Uncontrolled Enteric Emissions:

4.1 lb/head-year ÷ (1-Control $\text{Efficiency}_{\text{Feed to NRC Guideline}}$)
4.1 lb/head-year ÷ (1-0.05) = 4.32 lb/head-year

Appendix 8: Calculation of Uncontrolled VOC Emission Factors for Dairies

		Feed	Milking Parlor	Exercise Pens and Corrals					Liquid Manure	Land Application		
Source	District Dairy Emission Factors	Feed to NRC Guidelines	Flush parlor after each milking	Clean manure between Apr. - July & Oct. - Dec.	Depth of manure not exceed 12 " in corral	Ensure drainage, slope surface, or-harrow/rake	Inspect Water pipes	Install Shades uphill	Remove solids with a separator	incorporation	Not allow liquid manure stand in field > 24 hours	Uncontrolled District Dairy Emission Factors
1. Enteric Emissions	4.1	5%	-	-	-	-	-	-	-	-	-	4.32
2. Milking Parlor(s)	0.03	5%	10%	-	-	-	-	-	-	-	-	0.04
3. Freestalls (lanes)	0.8	5%	-	-	-	-	-	-	-	-	-	0.84
Freestall beds	1.0	5%	-	-				-	-	-	-	1.05
4. Corrals/Pens	6.6	5%	-	10%	5%	10%	5%	5%	-	-	-	10.0
5. Liquid Manure Handling (Lagoons, Storage Ponds)	1.3	5%	-	-	-	-	-	-	10%	-	-	1.52
6. Liquid Manure Land Application	1.4	5%	-	-	-	-	-	-	-	-	10%	1.64
7. Solid Manure Land Application	0.33	5%	-	-	-	-	-	-	-	10%	-	0.39
8. Separated Solids Piles	0.06	5%	-	-	-	-	-	-	-	-	-	0.06
9. Solid Manure Storage	0.15	5%	-	-	-	-	-	-	-	-	-	0.16
Total not including Feed	**15.8**											**20.0**

Appendix 9 – Responses to Comments on Proposed Dairy VOC Emission Factors

Comments from C. Alan Rotz, Sasha Hafner, and Felipe Montes of USDA - Agricultural Research Service (ARS)

1. Comment: We have general concern for developing emission factors for these compounds given the very limited data and the relatively poor understanding of these processes that currently exists. Given that you are required to develop these factors, we generally agree that you are working with the best data available. Some further discussion and qualification of the uncertainty of the derived emission factors would be good.

   Response: The purpose of this report was to use the best available research that was useful in determining dairy emission factors. As noted in the comment, the District is required to develop emission factors for this important VOC source and the resulting emission factors are based on the best science available at the time. Measurement uncertainties are discussed in some of the specific project reports. The District's dairy emissions factors are primarily based on studies that measured VOC flux rates at California dairies. Using VOC measurements from actual dairies has clear advantages. However, one factor related to the use of flux measurements to estimate VOC emissions at dairies is that only small areas of the source can be measured at specific times and these measurements are then used to represent emissions from much larger sources that are not completely uniform and emissions from many of these sources vary with time. Additionally, there is a large amount variability in the management practices on different dairies in the San Joaquin Valley and these differing practices can affect VOC emissions. Because of the very large size of the emission sources at dairy operations and the variability in dairy management practices, many of the factors related to uncertainty are basically unavoidable regardless of the emission measurement techniques used. That being said, although additional data are generally desirable, the District used the best data that were available to develop VOC emission factors that are representative of dairy operations in the San Joaquin Valley. The District supports additional studies that will increase the knowledge related to VOC emissions from dairies and the understanding of the underlying processes that affect these VOC emissions.

2. Comment: The EPA emission isolation flux chamber method does not provide accurate measurement of VOC emission rates from manure and silage surfaces on farms and at the end of the report, additional research on differences between flux chambers and wind tunnels is recommended. Some studies have already been completed that address this issue. The emission isolation flux chamber method was designed for use in systems where emission rate is independent of the air speed across the emitting surface. Parker showed that VOC emission rate from cattle manure and wastewater is sensitive to air velocity. Measurements made in our laboratory show that the emission rate of ethanol from compressed

silage (analogous to the exposed face of a silage pile) and loose silage depend heavily on air velocity. A similar response would be expected for TMR.

Response: The studies that were chosen for inclusion in the report were studies that were found to be the most complete and valid for the purpose of generating VOC emission factors for dairy operations. The San Joaquin Valley is generally characterized by low average wind speeds, which will reduce the affect that wind will have on VOC emissions. As previously noted, the information that was used was the best information available to develop emission factors. It is not possible to determine the magnitude of the effect that wind speed will have on the VOC emission rates or adjust measured emission rates without full speciation of the compounds measured. The majority of the studies that were determined to be the most useful for generating VOC emission factors used total VOC methods without speciation because total VOC methods have been found to capture a higher proportion of the total VOC emissions when compared to other methods. Additionally, there are currently no validated procedures to adjust the measured VOC emission rates from dairy emission sources to account for differing wind velocities.

It is also important to note that although research efforts have investigated the effects of wind speed on emissions, many important research efforts have identified turbulence at the emitting surface rather than wind speed itself as an important variable that affects emissions and have concluded that wind speed is only important because of the turbulence it creates at the emitting surface. The majority of studies that have investigated the effects of wind speed on emissions have used small wind tunnels. Because of the small size of the wind tunnels used, even at lower velocities there will be increased turbulence inside the tunnels, which is very likely to artificially increase emissions above levels that would be seen if the tunnels were not present. Therefore, researchers are not in agreement regarding the use different measurement techniques and further research is needed. However, the District is using the most complete scientific data that were available to update the dairy emission factors.

As noted in the comment, the District encourages further research regarding quantification of emissions using different measurement techniques. In conclusion, the District is using the most complete scientific data available to update the dairy emission factors. As with other emission factors, the dairy VOC emission factors will be periodically updated if new scientific information indicates that revisions may be necessary.

3. Comment: Two other problems limit the accuracy of measuring VOC emission from silage. First, since silage is highly porous, sweep gas leakage may occur. Second, high VOC concentrations in silage can lead to high vapor phase VOC concentrations and result in suppression of emission (Kienbusch 1986). Measurements in our laboratory show that both of these problems occur when

measuring ethanol emission from loose corn silage using the emission isolation flux chamber method (Hafner et al).

Response: The District encourages further research regarding quantification of emissions using different measurement techniques. The District is using the most complete scientific data available to update the dairy emission factors. As with other emission factors, the dairy VOC emission factors will be periodically updated if new scientific information indicates that revisions may be necessary.

4. Comment: VOC emission rates from silage and TMR are dependent on porosity, depth, temperature, and exposure time. Mass transport theory also indicates that emission rates are directly proportional to the initial VOC concentration in silage. It would be useful to report the values of these variables for which the proposed emission factors are thought to be accurate.

   Response: The proposed emission factors for silage and TMR are based on emission measurements at dairy farms in the San Joaquin Valley and the District's dairy emission factors are expected to be representative of dairy operations in the San Joaquin valley. The atmospheric temperature would be representative of the San Joaquin Valley. Additional information characterizing the silage and TMR used in the study and the timing of the emission measurements relative to removal of silage from pile and placement of the TMR can be found in the reports for the studies by Schmidt and Card and Krauter and Blake, which have been attached as appendices to the final report. It does not appear that the initial ethanol concentration in the silage was reported but the report by Krauter and Blake does provide limited information on silage density. The District encourages further research regarding characterization of silage and how feed composition affects emissions. As previously mentioned, the District is using the best scientific data that were available to update the dairy emission factors and these factors will be periodically updated if new scientific information indicates that future revisions may be necessary.

5. Comment: The unit used for silage and TMR fluxes ($\mu g/m^2$-min) may not be the best choice. The mass unit (μg) and time unit (min) seem unreasonably small, and it may be confusing to give fluxes in an SI unit while emission factors are given in US customary units. Alternative units are lb/ft^2-day. Also, presenting five digits in the fluxes implies a level of accuracy that is not present.

   Response: The District agrees with the comment. In the final report the flux rates for silage and TMR have been given in lb/ft^2-day.

6. Comment: Page 7, second paragraph: There is some confusion here in the units. I assume these values are all in lb/head-year. Some are listed as per day, which would be very high.

   Response: The reference to lb/head-day has been corrected to lb/head-year.

7. Comment: Page 9, last sentence of third paragraph states that District Rule 4570 has resulted in more than 20 tons per day reduction in VOC emissions. Can you provide a reference that documents this improvement?

   Response: The Health Benefit Analysis for the Proposed Re-Adoption of District Rule 4570 (Confined Animal Facilities) (June 18, 2009) indicated that in the District's 2007 Ozone Plan, District Rule 4570 was estimated to achieve approximately 20 tons per day of VOC reductions by 2012. According to the San Joaquin Valley Air Pollution Control District 2010 Ozone Mid-Course Review (June 2010), District Rule 4570 accounted for 22.8 tons of VOC reductions per day in 2010. However, this statement has been updated to say that significant VOC reductions are expected from implementation of the District Rule 4570 Phase II mitigation measures.

8. Comment: Page 18, last sentence of second paragraph: Can these two emission sources be added? Is the stall bedding that which is emitted by the actual stall while the other value is that occurring simultaneously from the flush lane? If so, then we agree that they can be added. This is not clear as currently presented.

   Response: VOC fluxes were measured from two separate sources in freestall barns, the bedding in the stalls where the cows rest and the flush lanes where manure from the cows was deposited; therefore, it is appropriate to add these sources to represent emissions from the total area contained in the freestall barns.

9. Comment: Page 29, second paragraph: The exposed area of a silage pile should be better defined. The surface area of fresh silage exposed each day may be much less than the actual open surface area. After a surface is exposed for 24 hours, the emission rate from that area will be low because the surface VOCs will have been volatilized.

   Response: The exposed area is generally intended to mean the uncovered "face" of the silage pile from which silage can be removed for feeding. The silage flux rate developed from Dr. Schmidt's research is an average rate based on daily removal of feed over the entire uncovered face of the silage piles, as was observed during the studies. The average daily rate reflects the higher emissions immediately after removal of silage and lower emissions from silage that has not recently been disturbed. The District will consider further evaluating emissions from specific dairies that implement unique silage management practices.

10. Comment: Page 31: It would be helpful to know the surface area per animal that was used to convert this to a per head basis to allow for comparison among farms even if the emission factor is given on a per unit area basis.

Response: The approximate lb/head-year VOC emission value for TMR was based on the averages from the Phase III and Phase IV studies performed by Dr. C. Schmidt and T. Card. The estimated area for the TMR during the studies is included in the study reports, which have been attached as appendices to the final report.

11. Comment: Pages 32 and 33: Not all farms will have all of these components. For example, freestall barns and corrals/pens or liquid and solid manure storage. Therefore, the "Total not including feed" may be overestimated.

    Response: All of these components are typically found at dairies in the San Joaquin Valley and were present on dairies that were studied. In the San Joaquin Valley freestall barns are generally open structures in which cows will continue to have access to exercise pens or corrals. This differs from other parts of the country in which cows in freestall barns typically do not have access to exercise pens or corrals. In addition to ponds for waste storage, dairies in the San Joaquin Valley will typically have stockpiles of solid manure consisting of stored separated solids and scrapings from exercise pens and corrals that are stored for use as bedding or for application to cropland. These components are all typically present for dairies in the San Joaquin Valley and were present at dairies where emissions were measured.

Comments from the Center on Race, Poverty, & the Environment

1. Comment: The District Should Consider Wind Speed Effects on VOC Flux. Research on the effect of wind speed on VOC flux should be included in the new emission factor. The flaw of the flux chamber sampling methodology is that it creates an artificial, wind free environment. Wind is present in California dairies, including artificial "wind" from fans within free stall barns. The District has ignored the effects of wind speed and only recommended evaluation of flux chambers and wind tunnels for future research.

   Response: Please see response to Comment #2 from C. Allan Rotz, Sasha Hafner, and Felipe Montes above. Additionally, it must be noted that cooling fans in freestall barns are designed to direct air at the level of cows rather than ground level where feed is placed and because air velocity profile, these fans are not expected create significant air movement on the TMR.

2. Comment: The District Should Consider Alcohol Sampling Deficiencies. The District also reports the sampling variability between the flux chamber and the INNOVA analyzer when analyzing alcohol compounds. The use of canisters as a means of storing analyte appears to significantly underestimate alcohol compounds. Values for alcohols should be adjusted to account for this analytical error.

Response: The comment is in reference to the report for the Krauter and Blake dairy VOC emission study in which higher alcohol measurements were noted when using an INNOVA analyzer compared to the canister samples analyzed by GC/MS. The report also noted that Dr. Donald Blake had questioned the ability of the GC/MS system to extract all of the alcohols from the canisters. However, the results in the report indicating higher alcohol emissions measured with the INNOVA analyzer as compared to GC/MS were based on preliminary information from an earlier progress report submitted to ARB in April 2007. Later measurements performed by the researchers indicated general agreement between the GC/MS alcohol measurements and the INNOVA analyzer alcohol measurements as mentioned in the following journal article: *Chung M., Beene M., Ashkan S., Krauter C., Hasson A. (2009) Evaluation of non-enteric sources of non-methane volatile organic compound (NMVOC) emissions from dairies. Atmospheric Environment 44, 786-794*. Researchers that were involved in the project indicated that the apparent difference between the two methods occurred in the first year (2006) and possibly the early part of the second year (2007) of the monitoring study while the methodology was still being developed and the field collection and lab analysis techniques were still being modified. These researchers stated that the data from the later years, 2007- 2009, including the measurement values in the main body of the final report to ARB, showed much better agreement and are more reliable than their preliminary work that indicated differences between the GC/MS alcohol measurements and the INNOVA analyzer alcohol measurements. In addition, the project report only provides a small amount of the preliminary INNOVA analyzer measurement data and the reported information is not sufficient to estimate emissions using the INNOVA analyzer measurements. However, after the initial development of the field collection and lab analysis techniques, no significant differences were found between the GC/MS alcohol measurements and the INNOVA analyzer measurements and Dr. Krauter has stated that the primary standard for the project report is the GC/MS measurements. Therefore, the District used the most complete scientific data that were available to update the dairy emission factors.

3. Comment: The District Should Consider the Volatile Fatty Acid Research Conducted at Fresno State University. The District does not discuss research on non-enteric Volatile Fatty Acids conducted at Fresno State University. Alanis (2008) reported 11 kg/cow/year of non-enteric volatile fatty acid emissions. The most significant source was TMR, with a reported flux of 160 g/m2-hr. The District does not consider this research when proposing an emissions estimate for Total Mixed Rations and fails to explain why such research was excluded.

   Response: This comment refers to results of research reported in the following publication: *Alanis, P. Sorenson, M. Beene, M. Krauter, C. Shamp, B. Hasson, A. S. Measurement of non-enteric emission fluxes of volatile fatty acids from a California dairy by solid phase micro-extraction with gas chromatography/mass spectrometry, Atmospheric Environment 42 (2008) 6417–6424*. The purpose of the study was to develop a method using a flux chamber coupled to solid phase micro-extraction (SPME) fibers followed by analysis using gas chromatography/mass spectrometry to quantify volatile fatty acid (VFA) emissions from sources at a dairy. The research was performed at a small research dairy at California State University Fresno (CSUF). The paper reports that the dairy typically used corn silage and that acetic acid contributed 70-90% of the VFA emissions from the sources measured.

The comment incorrectly states that the measured volatile fatty acid (VFA) flux rate from the TMR was 160 g/m^2-hr. The study reported that the highest VFA flux rates were for the silage and TMR, 1.84 g/m^2-hr and 1.06 g/m^2-hr, respectively. Flux rates from other sources were generally two orders of magnitude lower than this and had higher levels of uncertainty. The VFA flux measurements are similar to the total VOC flux rates that the District proposed for silage and TMR, which were based total non-methane non-ethane VOC measurements by Schmidt and Card. However, the VOC flux rates proposed by the District are annual average VOC flux rates that have been adjusted for daily temporal and seasonal variation while there are factors that indicate the VFA emission measurements reported by Alanis et el (2008) are higher than what would be considered representative of a typical commercial dairy in the San Joaquin Valley.

One factor that should be considered is that the article mentions that silage samples were spread to a depth to perform the VFA emission measurements. Removing silage from the pile and spreading it will increase porosity. It is known that greater porosity will generally increase emissions. It is expected that this effect would be more pronounced when measuring VFAs because of their tendency to adhere to surfaces that they contact. Therefore, these emission measurements are likely to be higher than VFA emissions from the compacted open surface of silage piles.

In addition, subsequent research using the same methodologies has also indicated that the VFA flux rates reported by Alanis et el (2008) are much higher than those that are typically observed. Many of the same researchers that were involved with development of the methodology using SPME fibers to collect VFA emissions from dairies used SPME fibers to measure VFA emissions from six dairies in the San Joaquin Valley over a fifteen-month period. The results are reported in *Alanis, P. Ashkan, S. Krauter, C. Campbell, S. Hasson, A. S. Emissions of volatile fatty acids from feed at dairy facilities, Atmospheric Environment 44 (2010) 5084–5092.* Based on the information gathered during this study using SPME fibers to collect VFAs, average annual acetic acid emissions were estimated to be 0.7 g/m^2-hr for silage and 0.2 g/m^2-hr for TMR. VFA emissions from the non-feed sources were typically below the detection limits of the methods used. As noted in the report, these measurements are more comprehensive than the measurements in the previous study and resulted in considerably lower emissions. The Alanis (2010) study reports an estimate of 1.7 kg/cow-year for acetic acid emissions from dairy feed sources (compared to an estimate of 6.4 kg/cow-year from the previous study). Because the total mass of

VFAs are dominated by acetic acid, total VFAs measured are also substantially less than the total VOC flux rates proposed by the District, particularly for TMR.

Acetic acid emissions from thin layers of loose silage samples were also measured using flux chambers and PTR-MS for an ARB project: *California Environmental Protection Agency. Zhang, Ruihong. (2010) Process-Based Farm Emission Model for Estimating Volatile Organic Compound Emissions from California Dairies. May 2010. Final Report for California Air Resource Board (ARB)*. The project report states that, over a twelve-hour period, acetic acid emissions measured from corn silage were 7.0 g/m^2-hr (average flux of 0.58 g/m^2-hr) and were 5.0 g/m^2-hr (average flux of 0.42 g/m^2-hr) for alfalfa silage.

As demonstrated, the District's proposed VOC emission flux rates for dairy feed sources are actually much higher than recent VFA emission measurements from dairy feed sources, including a more comprehensive dairy emissions study performed by the same researchers that were involved with development of the methodology for the use of SPME fibers to collect VFA emissions from sources at dairies. Because the District's proposed VOC emission flux rates are much higher than VFA emission estimates from recent studies and was based on a total VOC method, it is reasonable to believe that these emissions are already included in the District's emission factor and, therefore, the VFA emission measurements from these studies will not be added to the proposed emission flux rate.

4. Comment: The District Should Propose for Public Comment and Adopt a Methanol Emission Factor. Because methanol is a hazardous air pollutant and a toxic air contaminant, the District should present the best available methanol emission factor for comment and adoption.

   Response: The purpose of this document is to adopt a total VOC emission factor to quantify VOC emissions from dairies. The District is committed to using the best information available to quantify toxic emissions from dairies.

Comments from ARB

1. Comment: Overall, the SJV Air Pollution Control District did a good job in deriving and justifying the new emission factors for dairy emissions. The District made it clear that their emission-factor approach is based on best science available at the time the revision was written. The document is informative and educational on issues regarding dairy emission regulations.

   Response: Comment noted and the District thanks ARB for continued support in helping the District develop and fund research to increase the scientific information available pertaining to air emissions from dairies.

2. Comment: ARB would like to request that the District include more comprehensive descriptions of the relevant studies that helped determine the revised emission factors. Since the original experimental description and data are not part of the current document, it is difficult to understand how the conversion from flux data to the emission factor (lb/head-year) was made.

   Response: The current document contains brief descriptions of the studies that were used. More comprehensive descriptions of the experimental descriptions are contained in the original study reports, many of which have been added as appendices to the final report. For enteric emissions of alcohols from cattle, the District's emission factor used unpublished data from Dr. Mitloehner; the environmental experiment was conducted as described in Dr. Zhang's ARB project report but used only the measurements from the time before manure began to accumulate in the environmental chamber.

   For emissions factors that required conversion from measured flux rates to lb/head-year emission rates, the conversion was performed using the data gathered during each respective study. The measured or average flux rate was multiplied by the observed source area and divided by the estimated number of milk cows that were onsite during the measurements.

3. Comment: What are the uncertainties associated with the estimated emission factors? Was the diurnal and seasonal variability considered in the calculation and how?

   Response: Regarding the uncertainties associated with the estimated emission factors, please see the response to Comment #1 from C. Allan Rotz, Sasha Hafner, and Felipe Montes above.

   Based on the measurements by Schmidt and Card (2009), the District's dairy VOC emissions factors for corrals/pens incorporated an adjustment for seasonal variation with no adjustment for diurnal variability since no diurnal pattern was observed for emissions from this source. Also based on measurements from the same study, the District's VOC emissions factors for feed sources incorporated adjustments to account for seasonal variation as well as daily variations in emissions as a result of feeding practices and the reduction in the VOC emission rate from silage after it is removed from the silage pile and feed after it is placed for cattle. Adjustments for diurnal and seasonal variation were not incorporated into the remaining dairy emissions factors.

4. Comment: The report should include the old emission factors in all the emission factor tables. In places the document said that "the EF was not as high as previously thought" but did not give specific numbers to support the assertion.

   Response: The places where the document notes that emissions are not as significant as previously thought are regarding VFA emissions from non-feed sources and VOC emissions from storage ponds/lagoons. Of the District's previous dairy VOC emission factor of 19.3 lb/head-year, 15.5 lb/head-year were attributed to VFA emissions with 8.3 lb/head-year attributed to enteric VFA emissions with nearly all the remaining VFA emissions attributed to wet processes, such as lagoons. As indicated in the report, subsequent research measured much lower emissions of VFA emissions from non-feed sources. Additional references to the District's previous dairy emissions factors have been added to the report and a table listing the District's previous dairy VOC emission factor has been added for reference purposes.

5. Comment: There was no mention of Dr. Ruihong Zhang's work in the draft report. ARB believes that due to the significance of her research related to dairy VOC emissions, Dr. Zhang's report should be mentioned, followed by an explanation of why it was not included. The District should also mention that they will review Dr. Zhang's findings for inclusion in the next revision to the report, as well as mention specific information from the report that will be useful for future updates to the District's dairy VOC emission factors.

   Response: When the District initially completed the draft dairy emission factor report the final report for the study led by Dr. Zhang's was not yet available. The District needed to complete the draft report and proceed with updating the dairy emission factors so more accurate dairy VOC emission factors could be used when the District revised District Rule 4570. Since that time, the District has reviewed the final report and agrees that it provides useful information and has advanced that the state of research regarding quantification and modeling of emissions from dairy feed sources. Some information from Dr. Zhang's report has been added to the final District report. Dr. Zhang's continued work will be particularly useful for developing and evaluating potential mitigation measures to reduce VOC emissions from dairy feed sources.

6. Comment: ARB suggests that it would be valuable for SJVAPCD to rank the various emission factors from strongest to weakest, and to prioritize which factors the District believes should be updated (as research funds become available, or to encourage/direct future funding) so as to develop a somewhat specific roadmap for where SJVAPCD plans to go from here.

   Response: The purpose of this document is to adopt a total VOC emission factor to quantify VOC emissions from dairies. However, the District has begun the process to develop a document explaining the District's priorities for future dairy emissions research. The District will continue to work with ARB, scientists, and dairy stakeholders to establish priorities for future dairy research efforts. One of the District's main priorities will be the development and evaluation of practical measures to reduce emissions from significant sources of emissions, such as silage and TMR.

Comments from Dairy Cares

1. Comments on the Report's General Conclusions: We agree with the following overarching conclusions of your report:
    a. Accurate dairy emissions factors are required for proper implementation of applicable air quality regulations and also for the evaluation of appropriate technologies and practices to reduce emissions;
    b. The District has gained a great deal of experience in the evaluation of emissions from agricultural sources through collaborative efforts with other institutions, agencies and interested stakeholders;
    c. The revised VOC emissions factors for dairies proposed in the report is based on a detailed review of available scientific research findings; and
    d. The District has given appropriate emphasis to studies performed on California dairies and/or in conditions representative of California dairies.

    Response: Comment noted.

2. Comments on the Approach to Categorizing and Quantifying Emissions: The scientific basis for the dairy emission factors has improved and there is considerably more detailed information regarding emissions from specific sources within dairy facilities, such as silage piles (which were not included in the APCO's 2005 dairy VOC emissions estimates), corrals and pens, and more.

    Dairy Cares supports the transition the District has made from reporting the emissions as chemical subsets, for example "volatile fatty acids" or "ethyl amines," as took place in the 2005 report. The current draft report more appropriately focuses on identifying and quantifying emissions in process-specific categories. This not only represents a great improvement in the scientific basis for estimations from those processes, but sets a better context for proposing and evaluating potential emissions reduction techniques and strategies.

    The District has taken the added step of grouping the process categories under the following headings: Per Cow Dairy Emissions Factor, Silage Pile VOC Emissions Flux, and Average Total Mixed Ration (TMR) VOC Emissions Flux. In doing so, the District has rationally concluded that these newly characterized emissions sources (silage piles and TMR) are appropriately calculated based on exposed area rather than on a per head basis. Dairy Cares agrees with the District on this point and notes that this will provide a more solid, science-based foundation for discussion of emissions reduction strategies. Conversely, including these new emissions under a per-cow factor would likely lead to large, built-in systematic errors in calculating VOC emissions on many individual dairies.

    Response: Comment noted and the District thanks Dairy Cares and other dairy stakeholders that helped facilitate the California dairy studies that were used to develop the District's dairy emission factors.

3. Comment: Where possible, we have reviewed the proposed emission factors and the underlying research studies. We generally concur that the District has selected the most appropriate studies as a basis for its decisions. We do not have any major disagreements with the District's analysis and conclusions either on individual process factors, fluxes or on the overall totals. While these appear generally accurate and representative of the underlying research, we would note for the record a few important caveats:
   a. Most of the research to date has been limited to a few dairies and covers a relatively limited range of seasonal conditions. While there has been a vast improvement in the data used for District development of emissions factors and fluxes, these may not adequately reflect variability on individual sites. As such, dairies may wish to undertake site-specific analysis in some cases and future revisions in the emissions factors and emissions fluxes may also be necessary.
   b. In the case of "Per Cow Dairy Emissions Factor" process #1, "Enteric Emissions," the District notes in the report that the determination for the emission factor of 4.1 pounds/head-year is partially derived from an environmental chamber study that was completed in late 2009by Dr. Frank Mitloehner. Because that work has not been published or peer reviewed, and has not been reviewed by Dairy Cares, we can only conditionally support this factor pending future review of the data. However, we also note that similar work by Dr. Mitloehner has been important in estimating California dairy emissions. We remain strongly supportive of the District's approach of relying on studies performed on California dairies or conditions representative of California dairies.
   c. We would like to continue our discussion to further refine the simulation of practices that are associated with silage and TMR flux rates included in the draft report. Both rates are averages based on observed data; we feel additional work is needed to ensure that the rates accurately reflect management practices implied in the simulations.

   Response: As previously mentioned, the District report used the best data that were available to develop VOC emission factors that are representative of typical dairy operations in the San Joaquin Valley. The District supports continued efforts to refine dairy feed VOC emission measurements to better account for management practices that may be implemented at specific dairy operations and looks forward to working with Dairy Cares and other dairy stakeholders regarding this matter.

4. Comments on Future Research Recommendations: The draft report included recommendations for future research to improve the quality of dairy emission factors. We concur that from an academic standpoint, additional research would be helpful to further refine the factors. However, we also are of the view that in some categories of VOC emissions from dairies, a point of diminishing return may be developing on the value of gathering additional data on VOC-generating processes versus investment in research on other pollutant categories and/or

mitigation. According to the District's own health benefit analysis in 2009, the entirety of actions under Phase I of District Rule 4570 resulted in modeled reductions of only 1.5% annually or less for population exposure to ozone. As such, any future research recommendations must be reviewed to ensure there is some possibility they would generate discernible health benefits. With that cautionary note, we remain nevertheless dedicated to collaborating with your agency on determining appropriate ways to improve our understanding and mitigation of emissions.

Response: Because the San Joaquin Valley Air basin is classified as an extreme nonattainment area for the Federal ozone standard, even relatively modest reductions in ozone and ozone precursors can make cumulatively significant contributions towards helping the District reach attainment with health-based ambient air quality standards and accurate characterizations of emissions sources are an important part of this process. However, the District agrees that one of the primary focuses of future research should be development of practical measures that will reduce VOC emissions, in general, and practices that will reduce emissions of the most reactive compounds to provide increased health benefits through greater reductions in ozone formation.