San Joaquin Valley
Unified Air Pollution Control District

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Air Pollution Control District

Air Pollution Control Officer's Revision of the Dairy VOC Emissions Factor

January 2010

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Introduction

This report provides the bases for the District's revision to the District's Volatile Organic Compound (VOC) emissions factor for dairies, which was previously established on August 1, 2005 in the report, entitled "*Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies*"[1]. The emissions factor explained 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 current dairy VOC emissions factor 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 emissions factor, as well as 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 emissions 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. Emissions 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 emissions 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 Ag-Tech Committee and the Dairy Subcommittee.

The revised VOC emissions factor for dairies proposed in this report is based on a detailed review of the available science. There have been significant additional scientific researches conducted since the development of the initial 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 will cross reference these new studies with the studies that were used to develop the initial emission factor. As would be the case with emissions factors for other sources, the District's dairy emissions factor will be revised to reflect the latest scientific information that is currently available.

In revising the dairy emissions factor, the District will continue to adhere to the sound guiding principles which were used to establish the District's original dairy emissions factor. Continued adherence to these principles ensures that the revised dairy emissions factor is 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 emissions factor is 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 waste. In establishing the revised dairy emissions 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. Chuck Schmidt, a private consultant based in California. This draft 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 continues to support continued and ongoing research at California dairies to further refine and supplement these emission factors.

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 is currently classified as a serious non-attainment area for the health-based, Federal eight-hour ozone standard. However, EPA has been requested to reclassify 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 and this reclassification is expected to occur in the near future. 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 waste excreted 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 have a significant adverse impact on efforts to achieve attainment with health-based air quality standards.

VOC Emissions 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

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[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 emissions factor of 12.8 lb/head-yr 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 emissions factor for dairy permitting and emissions inventory purposes. However, the basis for the 12.8 lb/head-yr 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 emissions factor, there was a great deal of uncertainty as to whether the 12.8 lb/head-yr emissions 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 a revised dairy VOC emissions factor of 19.3 lb/hd-day. This is the emissions factor that the District currently uses for permitting dairy operations in the San Joaquin Valley. This emissions 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-yr. However, the emissions 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 the first time around.

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 lbs/hd-yr, 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 threshold;

[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.

therefore, District permitting for these smaller dairy operations was not initially required. However, on August 1, 2005 the District revised the Dairy VOC emissions factor from 12.8 lb/head-yr to 19.3 lb/head-yr using the best available science. As a result of the revised emissions 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 (CARB), 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 is also currently 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 is currently 12.5 tons (25,000 lbs) of NOx or VOC, but will be reduced to 5 tons (10,000 lbs) of NOx or VOC after EPA approval of re-designation of the San Joaquin Valley as Extreme Nonattainment 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 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 has 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. District Rule 4570 has resulted in more than 20 tons per day of emission reductions of smog-forming VOCs in the San Joaquin Valley.

The District recently began the process to amend 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 may involve lowering the applicable threshold and/or requiring additional practices to reduce VOC emissions. Using the most accurate emissions information available will be critical to the District's process to amend Rule 4570. The revised dairy emission factor proposed in this document will allow for a more accurate assessment of sources that contribute to emissions at a dairy and allow these emission sources to be targeted for cost-effective emission control strategies.

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 performed 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 recorded as alcohol emissions. In order to obtain accurate data; Dr. MItloehner recreated the entire study with the proper filters in place. The study was recently completed (October 2009) and as such, a final report has not been generated. At the request of District staff, the resulting data, minimal but sufficient, has been provided by the researcher to the District so that emissions can be estimated[5].
- Two studies conducted by Dr. Chuck Schmidt, (Dairy emissions using flux chambers, 2006, Phase III[6] and 2009, Phase IV[7]) which measured various emission compounds along with total VOCs from dairy waste 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.

[4] Mitloehner, Frank, May 2006. Volatile Fatty Acids, Amine, Phenol, and Alcohol Emissions from Dairy Cows and Fresh Waste from Environmental Chambers
[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.E. 2006. Results of the Dairy Emissions Evaluation Using Flux Chambers **Phase III**
[7] Schmidt, C.E. 2009. Results of the Dairy Emissions Evaluation Using Flux Chambers **Phase IV**

- A series of studies led by Dr. Charles Krauter in which flux chambers were used to evaluate VOC emissions from sources at two dairies in the San Joaquin Valley[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.

Important findings of the latest dairy research studies include:

- Manure storage ponds and lagoons, which were previously thought to be a major source of VOC emissions at dairies, 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) are important but not as significant as previously estimated during the first revision of the dairy VOC emissions factor;
- 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 contributes 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 emissions factor, will be evaluated to update the current VOC emissions factor that is used to permit dairies in the San Joaquin Valley.

[8] Krauter, Charles, January 2009. Dairy Operations: An evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions in the San Joaquin Valley

The Purpose of this Revision to the Dairy VOC Emissions Factor

The District is charged with the responsibility of adopting emissions 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 emissions factor that is most suitable. In these cases the District must use its expert judgment to evaluate the scientific information available to establish an appropriate emissions factor. This District did exactly this during the original revision to the dairy VOC emissions factor. However, as stated earlier, dairy emission research that better reflect the conditions at California dairies have 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 emissions factor 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 first revision to the dairy VOC emission factor, the contents of this draft report will go through a public process in which comments on the proposed emissions factor will be addressed.

<u>Guiding Principles Used by the APCO for Determining Appropriate Emissions Factors</u>

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 emissions factors, the District reviewed several different studies in the first revision to the dairy VOC emissions factor. This current revision will reevaluate the dairy VOC emissions 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 current dairy emissions 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 emissions 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 emissions 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 emissions factors.

5. When no valid source of quantitative VOC data that could be linked to dairy processes is found, no emissions factor is to be determined, and the constituent or process emissions 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 Current VOC Emissions Factor

Basis of the Current Dairy VOC Emissions Factor – Enteric Emissions (Previous Category 1: Emissions from Cows and Feed in Environmental Chamber)		
Process or Constituent	**Emissions Factor (lb/hd-yr)**	**Basis for Current Emissions Factor**
Emissions from Cows and Feed	1.4	Emissions from Cows and Feed in Environmental Chamber with analysis by PTR/MS (Mitloehner, 2005)[9]

VOC emissions from cows, feed, and fresh manure were measured in environmental chambers by Dr. Frank Mitloehner of UC Davis using Proton Transfer Reaction Mass Spectroscopy (PTRMS). VOC emissions were estimated to be 1.6 lb/hd-yr. 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 lbs/hd-yr.

Recent VOC Emissions Studies

Recent Studies – Enteric Emissions		
Recent Studies	**Emissions Factors from New 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	Preliminary Data

[9] Mitloehner, Frank (study conducted in 2005, but published in 2007). *Emissions from Cows and Feed in Environmental Chamber with analysis by PTR/MS*

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 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 emissions 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 discovered 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 recently completed by Dr. Mitloehner in late 2009 and is not yet published. 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, which used INNOVA analyzers without ammonia filters. 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/hd-yr will be added to represent the measured value for enteric emissions of phenols and cresols from the second chamber study and 2.6 lb/hd-yr 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/hd-yr.

Category 2: Milking Parlor (waste emissions)

California VOC Emissions Studies

Milking Parlor (waste emissions)		
Process or Constituent	**Emissions Factor (lb/hd-yr)**	**Basis for Current Emissions 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)[10]

Dr. Chuck Schmidt 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/hd-yr

[10] Schmidt, C.E. April 2005. Results of the Dairy Emissions Evaluation Using Flux Chambers Merced Dairy- Summer Testing Event

and amines were found to contribute an additional 0.01 lb/hd-yr. Therefore, total VOCs from the milking parlor were 0.03 lb/hd-yr 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.

Conclusion

The only California data available to calculate VOC emissions from milking parlors are from Dr. Schmidt's 2004 study; therefore, the APCO proposes an emissions factor of 0.03 lb/hd-yr 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 (waste emissions)

Recent VOC Emissions Studies

Recent Studies – Freestall Barns (bedding and flush lanes)		
Recent Studies	**Emissions Factors from New 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)[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 VOC (including VFAs and amines) as methane measured by SCAQMD 25.3

Recent Studies – Freestall Barns (bedding and flush lanes)		
Recent Studies	**Emissions Factors from New Studies (lb/hd-yr)**	**Notes**
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)	Measured 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 (completed in 2006) by Dr. Chuck Schmidt and used flux chambers to quantify emissions at two dairies located in Merced County and Kings County. EPA 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 emissions 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 emissions 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 emissions factors based only on milk cows. The resulting VOC emissions factors were 0.8 lb/hd-yr for the flush lanes and 1.0 lb/hd-yr for the stall bedding, for a total of 1.8 lb/hd-yr from the freestall barns.

A recently completed study performed by Dr. Charles Krauter measured VOC flux from six dairies in the San Joaquin Valley using flux chambers. EPA 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 Dr. Schmidt's 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 emissions 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/hd-yr for the flush lanes, which is very close to the value of 0.8 lb/hd-yr from the Dr. Schmidt's 2005 dairy study.

Conclusion

The APCO has determined that the total VOC measurements from Dr. Schmidt'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. Dr. Krauter's study resulted in similar average VOC flux from the freestall flush lanes. If the one potentially anomalous measurement is removed from Dr. Krauter's study, the average VOC flux from the freestall is equivalent or less than the average flux determined in the Schmidt 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 emissions factor from the data in Dr. Schmidt's study and the VOC emissions factor for the fictitious dairy described in the report for Dr. Krauter's 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 emissions 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 emissions factor of 1.8 lb/hd-yr for the freestall barns.

Category 4: Corrals (waste emissions)

Recent VOC Emissions Studies

Recent Studies –Corrals (waste emissions)		
New Studies	**Emissions Factors from New Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of corrals with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006)[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 VOC (including VFAs and amines) as methane measured by SCAQMD 25.3
Flux chamber sampling of corrals during summer and winter seasons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009)[7]	Seasonally Adjusted Turnout Average: **6.5 lb/hd-yr** (Average flux of 207 µg/m^2-min)	Total VOC (including VFAs and amines) as methane measured 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	Measured by GC/MS

Evaluation

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

As mentioned above, Dr. Schmidt 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 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 emissions 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 emissions factor based only on milk cows. This resulted in an annual VOC emissions factor of 6.6 lb/hd-yr for the corrals.

Dr. Krauter's 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 Dr. Schmidt's 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/hd-yr for the corrals, which is approximately half the annual average value from the 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 at dairies. Dr. Krauter's study 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 underestimated thereby resulting in lower VOC emissions. As stated above, it is more appropriate to base the emissions factor on the actual data from Dr. Schmidt's study because the surface areas used to calculate the emissions 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 emissions factor of 6.5 lb/hd-yr for the corrals.

Category 5: Lagoons, Storage Ponds, and Settling Basins

Basis of Current VOC Emissions Factor

Basis of the Current Dairy VOC Emissions Factor Previous Category 4: VOCs from lagoons and storage ponds		
Process or Constituent	**Emissions Factor (lb/hd-yr)**	**Basis for Current Emissions Factor**
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)[10] Concentration analysis by EPA TO-15 and Emissions Modeling by ISCST3 (Krauter, 2005)[11]

Dr. Schmidt 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. Dr. Krauter estimated VOC emissions from lagoons and storage ponds at two San Joaquin Valley dairies using TO-15 measurements of upwind and downwind concentrations in conjunction with atmospheric modeling techniques.

Recent VOC Emissions Studies

Recent Studies – Lagoons, Storage Ponds, and Settling Basins		
New Studies	**Emissions Factors from New Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of lagoons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006)[6]	1.3	Total VOC (including VFAs and amines) as methane measured 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 emissions 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 emissions factor based only on milk cows. This resulted in an annual VOC emissions factor of 1.3 lb/hd-yr for the liquid manure handling system.

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[11] Krauter, Charles, 2005. Concentration analysis by EPA TO-15 and Emissions Modeling by ISCST3

Conclusion

The District has determined that the VOC measurements taken 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 emissions factor of 1.3 lb/hd-yr. Therefore, the APCO proposes an emissions factor of 1.3 lb/hd-yr 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. All available studies indicated that VOC emissions from lagoons were relatively low; therefore, this source is not as significant as previously thought.

Category 6: Liquid Manure Land Application

Recent VOC Emissions Studies

Recent Studies – Liquid Manure Land Application		
New Studies	**Emissions Factors from New 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 VOC (including VFAs and amines) as methane measured by SCAQMD 25.3

Evaluation

The only VOC emissions data that were available for liquid manure land application at a California dairy were from Dr. Schmidt'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 emissions factor given in the study report was based on the total number of milk cows at both dairies and resulted in an annual VOC emissions factor of 1.4 lb/hd-yr for liquid manure land application.

Conclusion

The only California data 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 emissions factor of 1.4 lb/hd-yr 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, more information needs to be gathered 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	**Emissions Factors from New Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of lagoons with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2009- Phase IV)[7]	0.33	Total VOC (including VFAs and amines) as methane measured 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'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 non-incorporated solid manure. However, no significant differences were found in the VOC emissions from incorporated non-incorporated solid manure. VOC emissions were measured for incorporated manure at one hour, three hours, and 7 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 emissions factor from the study for solid manure land application based only on milk cows was 0.33 lb/hd-yr.

Conclusion

The only California data that is 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 emissions factor of 0.33 lb/hd-yr 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, more information needs to be gathered 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

Recent VOC Emissions Studies

Recent Studies – Separated Solids (fresh and aged)		
New Studies	**Emissions 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])	0.06	Total VOC (including VFAs and amines) as methane measured by SCAQMD 25.3

Evaluation

The only California data available to calculate VOC emissions from separated solids are from Dr. Schmidt's 2005 study. Flux chambers were used 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. The annual VOC emissions factor for separated solids resulting from the 2005 study using SCAQMD Method 25.3 adjusted for only milk cows is 0.06 lb/hd-yr.

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 emissions factor of 0.06 lb/hd-yr for solid manure separated solids. Given the very low emissions measured, future dairy emission studies do not need to focus on this source.

Category 9: Solid Manure Storage

Recent VOC Emissions Studies

Recent Studies – Solids Storage		
New Studies	**Emissions 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 VOC (including VFAs and amines) as methane measured by SCAQMD 25.3

Evaluation

The only recent California data that is available to calculate VOC emissions from stored solids are from Dr. Chuck Schmidt's 2005 study. Flux chambers were used to measure emissions at a dairy located at two dairies located in Merced County and Kings County. The annual VOC emissions factor from the study for solid manure land application adjusted for only milk cows is 0.15 lb/hd-yr.

Conclusion

The only California data that 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 emissions factor of 0.15 lb/hd-yr for solid manure storage.

Category 10: Silage Piles

Recent VOC Emissions Studies

Recent Studies –Silage Piles		
New Studies	**Emissions Factors from New Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of corrals with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 – Phase III[6])	Silage Pile Average Flux: 29,335 µg/m^2-min (4.4 lb/hd-yr) Seasonally and Time Adjusted Average Flux based on 2008 Study: 21,435 µg/m^2-min (3.2 lb/hd-yr)	Total VOC (including VFAs and amines) as methane measured by SCAQMD 25.3
Flux chamber sampling of corrals 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 µg/m^2-min (9.7 lb/hd-yr)	Total VOC (including VFAs and amines) as methane measured by SCAQMD 25.3 Highest measured flux from freshly disturbed silage: 85,240 µg/m^2 and 81,374 µg/m^2 Although higher average flux was measured in 2008, the higher per head emission factor is also due to an additional silage pile being open at each dairy during the Phase IV study.
Flux chamber sampling of ROG from open lots with analysis by GC/MS (Krauter, 2009[8])	Average flux of 19,170 µg/m^2-min for disturbed silage and 4,229 µg/m^2-min undisturbed silage	Measured by GC/MS Time dependent data not provided but highest measured flux from freshly disturbed silage (75,977 µg/m^2 and 72,698 µg/m^2) is very similar to highest flux measured in Schmidt Phase IV study.

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.

Dr. Schmidt'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, Dr. Schmidt 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 emissions 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: 34,681 $\mu g/m^2$-min; alfalfa silage: 17,458 $\mu g/m^2$-min; and wheat silage: 43,844 $\mu g/m^2$-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 emissions factor based on the number of milk cows at the dairies. This would result in an average VOC emissions factor of 6.5 lb/hd-yr for the uncovered faces of the silage piles. However, the lb/hd-yr emissions factor may slightly 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 emissions found in the Phase IV study as compared to the Phase III study can be attributed to an additional silage pile being open and utilized at each dairy during the Phase IV study.

Dr. Krauter’s study also used flux chambers to measure VOC emissions at the silage piles at six dairies in the San Joaquin Valley. GC/MS was used to quantify VOC flux. Sampling occurred during the winter, early summer, and fall but no seasonal effects were found for VOC emissions from feed sources. The flux values from this study can be compared to the flux values obtained in Dr. Schmidt’s study. This study resulted in maximum VOC flux values for the disturbed silage that were very comparable to the maximum VOC flux values from Dr. Schmidt’s Phase IV dairy studies. However, the average VOC flux values for the silage piles were significantly less than the seasonal-adjusted averages from Dr. Schmidt’s Phase III and Phase IV dairy studies. The reason for this difference is not known at this time. There was a great deal of variability in the flux measured from the silage at the dairies. The variability may be related to time of the measurements taken after initial disturbance, types of silage used, or silage compaction; however, the current study report does not provide this information but states that an upcoming report may contain at least some of this information. It must be noted that Dr. Krauter's study also used INNOVA analyzers to quantify alcohol emissions measurements from sources at the dairy. The INNOVA analyzer measurements were taken at the same source within 10 minutes of the canister samples analyzed with GC/MS but resulted in much more alcohol emissions that were three to four times the values obtained with the canister samples. Feed is not a significant source of ammonia emissions so ammonia interference does not account for this difference. The project report states that Dr. Donald Blake at UC Irvine and other project collaborators have 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, so the higher values may be more accurate. Additional information and research is needed to determine which of the values from Dr. Krauter's study are more representative of emissions from silage piles.

Conclusion

The APCO has determined that the total VOC flux measurements from Dr. Schmidt's Phase III and Phase IV studies provide 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: 34,681 $\mu g/m^2$-min; alfalfa silage: 17,458 $\mu g/m^2$-min; and wheat silage: 43,844 $\mu g/m^2$-min.

Dr. Krauter's study resulted in very similar maximum VOC flux rates but lower average VOC flux using canister samples and GC/MS. Insufficient information was provided to determine if this difference in the measured values was time-dependent, related to the types of silage used, or resulted from other factors. The currebt report states that some of this information may be provided in a forthcoming report. Dr. Krauter's study also resulted in higher average VOC flux rates using INNOVA analyzers. At this time it is not known which of the values obtained by GC/MS or the INNOVA analyzer better represent the actual VOC emissions from silage during the study period. Therefore, additional studies are needed to compare different sample collection and analyses techniques for measuring emissions from feed sources. Dr. Schmidt's Phase IV study found seasonal variation that was not found in Dr. Krauter's study but the winter data set from Dr. Schmidt's Phase IV study was very limited. Therefore, additional data also needs to be collected in the winter and/or fall seasons to better quantify seasonal variability of VOC emissions from this source.

Category 11: Total Mixed Ration (Bunker Feed)

Recent VOC Emissions Studies

Recent Studies – Total Mixed Ration (TMR) (feed placed in front of cows)		
New Studies	**Emissions Factors from New Studies (lb/hd-yr)**	**Notes**
Flux chamber sampling of corrals with analysis of Total ROG by SCAQMD 25.3 (Schmidt, 2006 – Phase III[6])	TMR Average Flux: 40,061 µg/m^2-min (38.2 lb/hd-yr) Seasonally and Time Adjusted Average Flux based on 2008 Study: 15,415 µg/m^2-min (13.6 lb/hd-yr)	Total VOC (including VFAs and amines) as methane measured by SCAQMD 25.3
Flux chamber sampling of corrals 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 µg/m^2-min (10.0 lb/hd-yr)	Total VOC (including VFAs and amines) as methane measured by SCAQMD 25.3
Flux chamber sampling of ROG from TMR with analysis by GC/MS (Krauter, 2009[8])	Average flux of 8,260 µg/m^2-min for TMR	Measured 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.

Dr. Schmidt'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 and a follow-up study, Phase IV used the same methodologies but with a focus on seasonal and temporal variability. 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 emissions 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 emissions 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. As with silage, the other feed emissions 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 this source. The following average flux value derived these studies can be used to calculate emissions from the TMR on a per area basis: 13,056 $\mu g/m^2$-min. For reference purposes, the measured flux and process surface areas for the TMR can also be used to calculate the seasonally adjusted VOC emissions factor based on the number of milk cows at the dairies, which results in an average VOC emissions factor of 11.8 lb/hd-yr for the TMR.

Dr. Charles Krauter's study (2009) also used flux chambers to measure VOC emissions at the silage piles 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, like in Dr. Schmidt's study, emissions from the TMR were found to decrease with time after placement of the feed. 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 TMR that were less than the seasonally adjusted averages from Dr. Schmidt's Phase III and Phase IV dairy studies. The study also resulted in lower emissions from the TMR for the fictitious dairy described in the report. As with the silage measurements, the INNOVA analyzer measurements resulted in much higher alcohol emissions than the canister samples analyzed by GC/MS. 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. These additional data may be useful in explaining some of the variability.

Conclusion

The APCO has determined that the total VOC measurements from Dr. Schmidt's Phase III and Phase IV studies provide the best available data to quantify VOC emissions from feed bunkers 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: 13,056 $\mu g/m^2$-min.

Dr. Krauter's study resulted in slightly lower average VOC flux using canister samples and GC/MS. However, VOC flux rates measured using INNOVA analyzers were higher and may be similar to the measurements in Dr. Schmidt's study if the decrease in emissions after placement is considered. However, the report does not contain sufficient data on the INNOVA measurements to make a determination at this time. The information in the forthcoming report for a related project may be useful in this determination. Additional studies are also needed to compare different sample collection and analyses techniques for measuring emissions from feed sources. Additional data also needs 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. Therefore, in future studies additional measurements are needed to better characterize changes in emissions over time.

Category 12: Composting

Composting		
Process or Constituent	**Current Emissions Factor (lb/hd-yr)**	**Basis for Current Emissions 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. The APCO recommends for further research to quantify emissions from this source.

Summary of Dairy Emissions

In summary, the table below shows the APCO recommended emission factor for each source and constituent:

Per Cow Dairy Emissions Factor	
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

Per Cow Dairy Emissions Factor	
Process or Constituent	**Emissions (lb/hd-yr)**
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**

Silage Pile VOC Emissions Flux	
10. Silage Piles	**Emissions Flux (μg/m^2-min)**
1. Corn Silage	34,681
2. Alfalfa Silage	17,458
3. Wheat silage	43,844

Average TMR VOC Emissions Flux	
11. TMR	**Emissions Flux (μg/m^2-min)**
Average	13,056

Summary of Future Research Recommendations

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

- Additional data are needed on different process emissions and effects of management practices on emissions.
- Additional data are needed to better assess temporal and seasonal variability of emissions sources at dairies, particularly feed sources
- Additional information needs to be gathered 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

- Additional data are needed comparing the effects of different sample collection techniques (e.g. flux chambers and wind tunnels) on calculated emissions rates
- Further information is needed to compare real-time emission measurement techniques, such as the INNOVA analyzer, and total VOC and canister methods
- Standardized methods and a target suite of compounds are needed to guide future research work regarding dairy emissions. Specific research should be undertaken to determine which gases should be included from amines, oxygenated VOCs, VFAs, phenols, and other potentially important compounds, as well as to develop improved sampling, analytical and quantification methods.

Appendix A - List of Dairy Emissions Studies Reviewed

Previous Studies Reviewed to Establish the 2005 Dairy VOC Emissions Factor

Carbonyl Emission Factors by DNPH: Cassel, Flocchini, Green, Higashi (2005). On-Farm Measurements of Methane and Select Carbonyl Emission Factors for Dairy Cattle (ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/cassel05jan26.pdf)

Non-methane VOCs emitted from slurry manure in an enclosed chamber measured using adsorbent material and thermal desorption GC/MS: Hobbs, Webb, Mottram, Grant, Misselbrook (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)

VFAs by sorbent tubes and analyzed on a thermal desorption TDS/GC-MS system: Koziel (May 2006). Measurement of airborne volatile fatty acids emitted from dairy cows and their waste using sorbent tubes sampling and thermal desorption/GC-MS analysis (http://www.valleyair.org/busind/pto/dpag/Appendices/Appendix%2024%20%20Plan%20of%20work%20VFAs_FMM.pdf)

VOC Concentration by EPA Method TO-15; Speciation by GC-MS; Emission Modeling by IST-STv3: Krauter, Goorahoo, Goodrich, Beene (2005). Monitoring and Modeling of ROG at California Dairies, (ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/krauter05jan26.pdf) (http://www.valleyair.org/busind/pto/dpag/krauter_epa_april_5.pdf)

VFAs (acetic, propionic, butyric, isobutyric, isovaleric, valeric, and caproic acids), cresols, phenol, indole, and skatole from beef feedlots by sorbent tubes and GC: McGinn, Janzen, Coates (2003). Atmospheric Ammonia, Volatile Fatty Acids, and Other Odorants near Beef Feedlots

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: Mitloehner (2005). Volatile Organic Compound Emissions from Dairy Cows and Their Excreta (ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/mitloehner05jan26.pdf)

EPA 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): Schmidt, Card, Gaffney (2005). Assessment of Reactive Organic Gases and Amines from a Northern California Dairy Using the USEPA Surface Emission Isolation Flux Chamber (ftp://ftp.arb.ca.gov/carbis/ag/agadvisory/schmidt05jan26.pdf) 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

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 T. Hintz. 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 Studies/Papers Reviewed

SJVAPCD 2008 Dairy Emissions Study (August 2009) – Summary of Dairy Emission Estimation Procedures, Prepared by Thomas Card and Dr. Charles Schmidt

California Air Resource Board (ARB) Dairy Operations: An Evaluation and Comparison of Baseline and Potential Mitigation Practices for Emissions Reductions In the San Joaquin Valley (May 01, 2009), Principal Investigator: Dr. Charles Krauter (http://www.arb.ca.gov/research/apr/past/04-343.pdf)

Phillip Alanis, Mark Sorenson, Matt Beene, Charles Krauter, Brian Shamp, Alam S. Hasson. “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

Huawei Sun, Steven L. Trabue, Kenwood Scoggin, Wendi A. Jackson, Yuee Pan, Yongjing Zhao, Irina L. Malkina, Jacek A. Koziel, and Frank M. Mitloehner. “Alcohol, Volatile Fatty Acid, Phenol, and Methane Emissions from Dairy Cows and Fresh Manure.” Journal of Environmental Quality (37:615–622), Volume 37, March–April 2008.

Stephanie L. Shaw , Frank M. Mitloehner, Wendi A. Jackson, Edward J. DePeters, James G. Fadel, Peter H. Robinson, Rupert Holzinger, Allen H. Goldstein. “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

California Air Resource Board (ARB) Volatile Fatty Acids, Amine, Phenol, and Alcohol Emissions from Dairy Cows and Fresh Waste (May 31, 2006), Frank Mitloehner, Ph.D (http://www.arb.ca.gov/ag/caf/MitloehnerDairyChamberEmissions2006.pdf)

California Air Resource Board (ARB) Dairy Air Emissions Report (May 2006) – Summary of Dairy Emission Estimation Procedures, Prepared by Thomas Card and Dr. Charles Schmidt (http://www.arb.ca.gov/ag/caf/SchmidtDairyEmissions2005.pdf)

Huawei Sun, Yuee Pan, Yongjing Zhao, Wendi A. Jackson, Lisa M. Nuckles, Irina L. Malkina, Veronica E. Arteaga and Frank M. Mitloehner. "Effects of Sodium Bisulfate on Alcohol, Amine, and Ammonia Emissions from Dairy Slurry", Journal of Environmental Quality 37:608-614. February 20, 2008

Jenny Filipy, Brian Rumburg, George Mount, Hal Westberg, Brian Lamb. "Identification and quantification of volatile organic compounds from a dairy", Atmospheric Environment 40 (2006) 1480–1494

Koziel, Jacek A., Spinhirne, Jarett P., and Lloyd, Jenny D. - Texas Agricultural Experiment Station, Texas A&M University, Amarillo, TX; Parker, David B. - West Texas A&M University, Killgore Research Center, Canyon, TX; Wright, Donald W. and Kuhrt, Fred W. - Microanalytics, Round Rock, TX. "Evaluation of Sample Recovery of Malodorous Livestock Gases from Air Sampling Bags, Solid-Phase Microextraction Fibers, Tenax TA Sorbent Tubes, and Sampling Canisters". Journal of the Air & Waste Management Association, Volume. 55:1147–1157. August 2005.

Richard, Tom L. and Wheeler, Eileen, Penn State University - Department of Agricultural and Biological Engineering; Varga, Gabriella, Penn State University - Department of Dairy and Animal Science; Kaye, Jason; and Ann Bruns, Mary, Penn State University - Department of Crop and Soil Science, 2005 Penn State Dairy Cattle Nutrition Workshop. Strategies for Reducing Gas Emissions from Dairy Farms. (2005)

Parker, David B., Caraway, Edward A., Rhoades, Marty B., Donnell, Chanci, and Spears, Jan – West Texas A&M University, Canyon, TX; Cole, N. Andy and Todd, Richard - USDA-ARS, Bushland, TX; Casey, Kenneth D. - Texas AgriLife Research, Amarillo, Texas. "Effect of Wind Tunnel Air Velocity on VOC Flux Rates from CAFO Manure and Wastewater". ASABE Meeting Presentation Paper # 08-3897 for presentation at the 2008 ASABE Annual International Meeting at Providence, Rhode Island, June 29 – July 2, 2008

Caraway, Edward A., Parker, David B., Olsen, Mark J., Donnell, Chanci, Rhoades, Marty B., and Spears, Jan – West Texas A&M University, Canyon, TX; Casey, Kenneth D. - Texas AgriLife Extension, Amarillo, Texas. "Diel VOC Emissions from a Beef Cattle Feedyard". ASABE Meeting Presentation Paper # 084136 for presentation at the 2008 ASABE Annual International Meeting at Providence, Rhode Island, June 29 – July 2, 2008

Hudson, N. and Ayoko, G.A. - International Laboratory for Air Quality and Health, School of Physical and Chemical Sciences, Queensland University of Technology. "Comparison of emission rate values for odour and odorous chemicals derived from two sampling devices". Journal of Atmospheric Environment 10:1016. March 23, 2009.

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