San Joaquin Valley
Unified Air Pollution Control District

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Air Pollution Control District

Air Pollution Control Officer's Determination of VOC Emission Factors for Dairies

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Introduction

This report presents and provides the bases for the Air Pollution Control Officer's (APCO's) determination of Volatile Organic Compound (VOC) emission factors to be used for permitting San Joaquin Valley dairies. This report was written and reviewed by District staff, under the direction of the APCO. It includes a summary of the analyses performed by the District that resulted in the determination, as well as recommendations for further research necessary to continue to improve our understanding of VOC emissions from dairy operations.

The initial proposed version of this report was issued on June 27,2005. A public workshop was held on July 11, 2005 to present the proposed version of the report. After all comments were received and addressed, this revised report was then finalized on August 1, 2005.

In addition to addressing each of the specific comments submitted regarding the APCO Dairy VOC emission factor determination, the District is also providing the following responses to address some of the general issues raised regarding the proposed emission factor determination. These responses may also eliminate some misconceptions that have arisen during the process of developing the proposed emission factors.

Dairy VOC emission factors are needed to implement the requirements of State Law. Under State law (SB 700, Florez 2003) agricultural operations, including dairies, which emit over 25,000 lb of VOCs per year are required to obtain permits. In order to determine which operations exceed this level of emissions, VOC emission factors are needed. A process-based emission factor is also needed as a first step in establishing Best Available Retrofit Control Technology for the dairies as required under state law. However, the type and level of control that will ultimately be in a regulation covering dairies will not be solely driven by the magnitude of the emission factor. The District, through a public process, will fully examine the technological feasibility, availability, and the cost of possible control measures.

Based on any viewpoint expressed in the comments we received, dairies are a significant source of VOC emissions that require controls under State law. Even if the very low partial estimates of VOC emissions proposed by dairy industry representatives were correct (one advocated a VOC emission factor as low as 3.1 lb/head-yr), dairies would still be among the largest sources of VOC emissions in the Valley. Even if these partial emission factors were used, emission levels from individual dairies would still be far higher than most other individual sources of air pollution that have been successfully implementing VOC emissions controls for many years.

San Joaquin Valley Air District staff is well qualified to develop VOC emissions factors. Although the laboratory and field data used to develop emission factors are often collected by researchers; the selection, evaluation,

and application of this data to real-world operations is almost solely the function of air agency engineers. Collectively, Valley Air District staff members directly involved in preparing and reviewing this report have over 60 years of experience in developing, evaluating, selecting and applying emission factors to real-world sources of air pollution, including agricultural operations. Furthermore, among California air districts and other agencies, Valley Air District staff members are considered the experts in this area. Technical methodologies for determining agricultural emissions that were compiled and developed by Valley Air District engineers and specialists are being used by agencies throughout California for establishing permitting requirements, determining the applicability of requirements under Title V of the Federal Clean Air Act, and developing air quality attainment plans.

The VOC emissions factors for dairies proposed in this report are based on a detailed review of available science. In order to establish the proposed emission factors in this report, the APCO and his staff reviewed the Dairy Permitting Advisory Group (DPAG) report, each presentation to DPAG, and over 15 research studies, including all recent dairy emissions studies performed at California dairies and Universities.

In an academic setting, it is entirely appropriate to withhold data and action, often for years, until all questions are answered and until we have nearly perfect science. Some have argued that the District should withhold action until we have perfect science. Unfortunately, given the Valley's air quality, public health considerations, and the strict statutory deadlines, we do not have that luxury. This, however, does not mean that we should act carelessly and without regard to the economic health of the dairy farmers in the Valley. In arriving at an emission factor for the dairies, the District has employed a number of conservative guiding principles aimed at ensuring that the proposed factor would likely represent a low-range estimate of dairy emissions that is supported by best available science.

In evaluating the research studies, California research was <u>always</u> given preference. In fact, most of the proposed emission factor values were obtained directly from California researchers. Of the five categories in which emission factor values were determined, recent California research was used for four of the five values, as well as for over 50% of the value in the fifth category.

Specifically:

1) Enteric emissions and emissions from fresh feed were determined directly from data reported by Dr Frank Mitloehner of U.C Davis;
2) Ethylamines from Dairy Processes were measured by Dr. C.E. Schmidt at a Merced County dairy;
3) VOC emissions from miscellaneous dairy processes were measured by Dr. C.E. Schmidt at a Merced County dairy;

4) VOC emissions from lagoons and storage ponds were measured by Dr. C.E. Schmidt and Dr. Charles Krauter of California State University at Fresno at a Merced County dairy, and by Dr. Charles Krauter at a Kings County dairy; and
5) Enteric Volatile Fatty Acids were determined from data reported by Dr Frank Mitloehner of U.C Davis.

Other studies (Hobbs et al and Koziel et al) were only used after considerable review to fill a data gap in one category (VFAs from dairy processes) where valid California data were not available.

Before applying <u>any</u> data from outside California, the District performed a detailed analysis comparing the research study conditions with process conditions at California dairies. For reasons described in detail in this report, no valid California research data were available for a portion of one of the VOC emissions categories, VFA emissions from dairy processes. In the absence of valid California data, other studies were reviewed to determine if any tests performed would be applicable to California dairies. After careful review, the test conditions in one study, the Hobbs et al study, were found to represent wet process conditions (flush lanes, solids separation, lagoons, etc.) at California dairies very well. The material (urine and feces from Holstein cows of similar size and milk production), the moisture content (over 90% water), the pH (7.1, approximately neutral), and the temperature were almost identical to the conditions found in wet dairy processes in the San Joaquin Valley.

In order to estimate VFA emissions from the other 40% of the manure that is captured in dry dairy processes (e.g., manure that is excreted and falls into dry exercise pens), data from another non-California study, the Koziel et al summertime studies of Texas feedlots, were used (See appendix 13). After carefully comparing the test conditions to those at California dairies, the VFA emissions rate from the Koziel et al study was adjusted downward by a factor of eight (as described in this report) to account for potential differences in diet between California dairy cattle and Texas feedlot cattle. Because VFA emissions are directly related to moisture and the Koziel et al study was based on dry summertime conditions, the proposed VFA emission factor is expected to be an underestimate of the annual emissions from dry processes.

All comments, including those from California Scientists, were considered in the development of the proposed emission factor. Although the District received input from several research scientists on the proposed report, these scientists did not always agree upon the best approach for determining emissions. For example, while comments by several scientists strongly supported the District's approach in the use of the British Hobbs study to determine VFA emissions from wet dairy processes (Dr. David Grantz of the University of California; Dr. F.M. Byers, consultant and former professor of animal nutrition at Texas A&M; Diane Bailey of the NRDC, and Dr. James Morris

of BION Corp.), others (Dr. Deanne Meyer of U.C. Davis, Matt Summers formerly of the California Dept. of Food and Agriculture, and Dr. Charles Krauter of California State University at Fresno) expressed concerns with this approach.

One researcher (Dr. Frank Mitloehner of U.C. Davis) expressed concern with the use of the enteric VFA data that he himself had provided to the Dairy Permitting Advisory Group. Dr. Mitloehner stated that the study was "not designed to accurately determine total VFA emissions", and that he was "not able to conclude that application of the ratio of inlet and outlet data from other VOC compounds measured in our study can be used to predict inlet concentration due to their completely different chemical nature". Although the District shared Dr. Mitloehner's concerns regarding the variation in the data and the potential differences in chemical nature between VFAs and other VOCs, in reviewing the results, the District found that enteric VFAs were clearly found at high levels in these tests. In fact, nine specific VFAs were detected in these tests, and the total VFA results were orders of magnitude greater than detection limits. The APCO also found that most of the potential inaccuracies associated with the measurement and calculation of VFA emissions (e.g. sampling losses) would be far more likely to underestimate the emissions than overestimate them. The data far more accurately represented enteric VFA emissions than the alternative emission factor (zero) proposed by dairy industry advocates. Therefore, in the absence of any other data for enteric VFA emissions, after considering Dr. Mitloehner's concerns, the APCO chose to use the average of the enteric VFA data reported to DPAG.

The District strongly supports further research on 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 air basin is classified as a serious non-attainment area for the health-based eight-hour federal ozone (smog) standard, a serious non-attainment area for the PM-10 (fine particulate matter) standard, and a non-attainment area for the new PM-2.5 (ultra-fine particulate matter) standard. In order to work toward meeting these air quality standards as required under state and federal law, and to protect the health of Valley residents, the District develops and adopts air quality attainment plans that include control measures aimed at further reducing emissions from a broad range of sources. For example, a control measure planned for Confined Animal Feeding Operations, including dairies, is expected to achieve a reduction of 15.8 tons per day of smog-forming VOC emissions by 2010.

San Joaquin Valley Dairies and Air Quality

Dairies are significant sources of smog-forming volatile organic compounds and of fine particulate matter in the San Joaquin Valley. Volatile Organic Compounds are emitted directly from the Valley's approximately 2.5 million dairy cows, and also from the decomposition of hundreds of millions of pounds of dairy waste excreted each day from dairy cows in the San Joaquin Valley. Although a wide range of VOC emission factors has been proposed recently, by any of the common current estimates, 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 the health-based air quality standards.

The current "interim" VOC emission factor of 12.8 lb/head-yr in use in California for dairy permitting and emissions inventory is based on estimates of total organic compounds from environmental chamber tests performed in the 1930s. Because volatile organic compounds were not directly determined in those tests and because the chamber tests did not represent most dairy processes, the more recent research discussed in this report is expected to provide much better estimates of dairy emissions.

Permitting Requirements

One key way that the Valley Air District assures compliance with air pollution control regulations and limits increases in emissions of air pollutants is by issuing conditional permits to commercial and industrial sources of air pollution. Since the 1970s, the 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 San Joaquin 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 "New Source Review" requirements, 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 sources' compliance with applicable requirements.

Removal of the Agricultural Exemption from Permitting

Until recently, under state law, agricultural sources of air pollution, including large dairies, were exempt from these permitting requirements and new source emissions limitations. That changed effective January 1, 2004, when Senate Bill 700 (Florez) amended the California Health and Safety Code to eliminate the longstanding permit exemption for operations, including dairies, that grow crops or raise animals. With the elimination of the agricultural permit exemption, Valley dairies also became subject to "New Source Review" requirements, including the requirement to apply Best Available Control Technology to new and modified operations.

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 major source thresholds. Based on dairy VOC emission factors in use in California at that time, existing dairies with 1,954 cows[1] were expected to have VOC emissions equal to or greater than one-half of the District major source thresholds, 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 major source thresholds, so permitting was deferred for these smaller operations. Under the provisions of SB 700, an air district may permit these 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 cause or contribute 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.

[1] 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. See the Districts Dairy Emissions Calculator at www.valleyair.org/farmpermits/need_permit.htm .

For dairies with 1,954 or more cows, these findings were not necessary. Permitting is specifically required under SB 700 for these agricultural sources with emissions over one-half the major source thresholds.

It should be noted that for other non-agricultural source categories, permits and Best Available Control Technology are generally required at a far lower emissions rate of 2 lb/day. For instance permits and significant air pollution controls are required of small sources of emissions such as print shops, autobody shops, gasoline stations, and dry cleaners.

Additional Requirements for Dairies Constructed or Modified after 1/1/2004

With the passage of SB 700, dairies with more than one-half the major source emissions constructed or modified on or after 1/1/2004 are required to obtain Authority to Construct from the District prior to construction. These new and modified dairies, like other new and modified sources of air pollution, are subject to the requirements of the District's New and Modified Stationary Source Review Rule, including the requirement to apply Best Available Control Technology, and, potentially, offsetting of emission increases.

Additional SB 700 Requirements for Existing Dairies

In addition to the permitting requirements described above that result from the elimination of the agricultural exemption, Section 40724.6 of the Health and Safety Code was added to require that the District establish VOC control requirements for existing dairies. This code section requires the California Air Resources Board to review all available scientific information and develop a definition for the source category of "large" Confined Animal Facilities, including dairies. The definition must be adopted by the State Board in a public hearing on or before July 1, 2005. By July 1, 2006, one year later, the District must adopt a rule requiring "Large Confined Animal Facilities", as defined by the State Board, to obtain permits to reduce emissions to the extent feasible. State law requires Large CAFs to submit applications for a permit or permit amendment to reduce emissions within six months of District adoption of this rule, and requires the facilities to implement the required emission reductions within one year of District approval of the application.

Western United Dairymen, Alliance of Western Milk Producers v. San Joaquin Valley Air Pollution Control District

In response to the District's implementation of the SB 700 requirements for dairies in 2004, dairy industry organizations filed a lawsuit in Fresno Superior Court. In the lawsuit, *Western United Dairymen, Alliance of Western Milk Producers v. San Joaquin Valley Air Pollution Control District*, dairy industry representatives alleged that the District had exceeded its lawful authority in issuing the dairy permitting requirements.

The District disputed the charges in the lawsuit, and in September of 2004, the lawsuit was settled. Under the settlement agreement (Appendix 1):

1) A Dairy Permitting Advisory Group (DPAG) was established to meet in a public process and to develop and provide recommendations and advice to the APCO on issues associated with permitting Valley dairies, including the development of an emission factor and Best Available Control Technology guidance. The DPAG was to be comprised of representatives from the District, the plaintiffs, and others with expertise and interest in dairies and dairy air quality issues.

   No later than July 1, 2005 (later extended to August 1, 2005 under mutual agreement of the parties to the settlement), the APCO would adopt a dairy emission factor after considering the information and recommendations developed by the DPAG. Under the agreement, the APCO was not limited to using information presented to the DPAG, or recommended by DPAG, to make the determination. The APCO specifically reserved the right in the agreement to "*adopt a Dairy Emission Factor other than that recommended by the Dairy Permitting Advisory Group if the APCO determines that the best available science shows that the Dairy Emission Factor is more accurate than recommended by the DPAG."*

2) The District would continue to require permits for dairies based on the "interim emission factor" of 12.8 lb/head-yr, until the APCO established the new dairy emission factor, as required.

3) The APCO would work with the DPAG, the regulated community and other interested parties in adopting a Best Available Control Technology guidance;

4) For new dairies requiring Best Available Control Technology (BACT) determinations before the completion of final Guidance, the APCO would not require the immediate installation of a lagoon cover or digester as BACT, but could require that the applicant install an anaerobic treatment lagoon based on USDA guidelines; and

5) A dairy permit unit was defined as "*any and all sources contained within one of the following five categories of dairy operations: (1) Cow Housing and Feeding (2) Dairy Waste Treatment Lagoon (3) Milking Center (4) Dairy Manure Storage and (5) Dairy Manure Land Application.*"

The Role of DPAG

One of the key tasks assigned to the DPAG was to:

> *"…develop a means for determining the volume of VOC emissions from individual dairies, including the development of a Dairy Emission Factor or Dairy Emission Factors for the dairy facility as a whole and, to the extent possible, for individual units that may be part of individual dairy operations, such as manure lagoons. "*

Under the settlement agreement, DPAG was to "work to provide the APCO with recommendations and advice for a more accurate Dairy Emission Factor than the current Interim Emission Factor. " The agreement noted, "*Several efforts to develop additional information on accurate and reliable Dairy Emission Factors are currently underway. Scientific studies of dairy air emissions are currently underway at U.C. Davis and Fresno State University. The preliminary results of those studies should be available for review within six to eight months. California Air Resources Board ("CARB") will be commencing its efforts to review dairy emission information, and develop a definition of Large Confined Animal Facilities, as required by SB 700. CARB's initial report is expected to be completed by March 2005 and must be adopted by July 1, 2005. The USDA has also convened a panel of experts to review available scientific information for purposes of creating an interim dairy VOC emission factor. This project is endorsed by U.S. EPA, and is scheduled to be completed by the end of 2004*." However, input was not limited to these studies under the agreement. To the contrary, DPAG was specifically required to *"allow all interested parties to provide meaningful input into the manner in which the District implements its dairy permitting program."*

The Final DPAG Report of Dairy Emissions Factors for VOCs

After holding nine public sessions, the DPAG completed this important task on May 6, 2005 with the issuance of the Final DPAG Report of Dairy Emissions Factors for VOCs (Appendix 2). While the DPAG was able to approve and issue the report, DPAG was not able to reach consensus on each VOC constituent. There was substantial disagreement in several areas, and DPAG reported the areas of agreement and disagreement in detail as three separate viewpoints, resulting in three differing total dairy emission factors. After substantial discussion, DPAG agreed that the table, as attached in Appendix 3 represented an adequate summary of their process-based approach to calculating the major constituents of VOC. Where there was disagreement, alternate methods for calculating an emission factor were reported for each constituent, with notes provided to explain the case for each method. The total emissions factors for each viewpoint (excluding areas where data were not available) was as follows:

	Viewpoint 1	Viewpoint 2	Viewpoint 3
VOC Emission Factor	5.6 lb/head-year	13.3 lb/head-year	38.2 lb/head-year

The DPAG report was presented to the APCO and Deputy APCO on May 31, 2005, with Mr. J.P. Cativiela of the dairy industry organization Dairy Cares and Dr. Julia Lester, a consultant hired by the dairy industry, presenting Viewpoint 1; Dr. David Grantz of the University of California presenting Viewpoint 2; and Ms. Diane Bailey of the Natural Resources Defense Council presenting Viewpoint 3.

The Responsibility of the APCO to Establish a VOC Emission factor

Under the settlement agreement, the APCO is required to adopt a dairy emission factor after considering the information and recommendations developed by the DPAG. As noted previously, however, the APCO is not limited to using information presented to DPAG, or recommended by DPAG, to make the determination. The APCO is also required to conduct a public workshop to discuss and consider the available science and recommendations of the DPAG and any other science considered by the APCO. This draft report is being provided for consideration at that presentation.

Guiding Principles Used by the APCO for Determining Appropriate Emissions Factors

The Final DPAG Report on Dairy VOC Emission Factors includes 28 different references describing 15 different research efforts. Although several of these individual research studies were deemed by the DPAG members to provide appropriate estimates for some of the VOC chemicals from some of the dairy processes, not one of these efforts was found, in any viewpoint expressed, to adequately address all the VOC constituents from all dairy processes. Therefore, in order to determine appropriate dairy emissions factors, the APCO finds it necessary to review all available research and determine the appropriate emissions factors for important classes of VOC constituents and key dairy processes individually. This is consistent with the process-based approach proposed by the DPAG.

In order to ensure that emission factors chosen were based on the best available science, the APCO used the following principles in evaluating and selecting data for use in emissions factor development:

1. Data from research studies presented to DPAG by scientists, data obtained from other dairy emissions research, and data from available recognized scientific literature are to be used to determine emission factors.

2. The methods used to collect the data are to be reviewed. Data are 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 constituent 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 are to be given preference over data from other sources. The APCO 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 emissions 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, is not to 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 can not 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: Emissions from Cows and Feed in Environmental Chamber (Except Volatile Fatty Acids)

Available Research

VOC emissions from cows, their feed, and fresh excreta were measured in environmental chambers by Proton Transfer Reaction Mass Spectroscopy (PTRMS) as described in Dr. Mitloehner's 4/13/05 presentation to DPAG (Appendix 4), 4/17/05 letter to DPAG (Appendix 5), and 7/25/05 letter to Dave Crow (Appendix 26). Dr. Mitloehner initially estimated that 3 lb VOC/head-yr were emitted based on these measurements in the letter dated 4/17/05, but revised the number downwards to 1.6 lb/hd-yr, based on the most recent letter received on 7/25/05. Since other VOC tests by Dr. Mitloehner using EPA Method TO-15 had shown that emissions from fresh excreta in the test chamber represented approximately 10% of emissions, DPAG members in all three viewpoints adjusted Dr. Mitloehner's number downward by 10% to 2.7 lb/head-yr, to obtain a value for enteric and feed emissions without the excreta. Based on the revised number from Dr. Mitloehner, and adjusting it downwards by 10%, the new value for enteric and feed emissions without the excreta is equal to 1.4 lbs/hd-yr.

DPAG Viewpoints

	Viewpoint 1	**Viewpoint 2**	**Viewpoint 3**
VOC Emission Factor Cows and Feed in Chamber	2.7 lb/head-year	3.4 lb/head-year	3.4 lb/head-year

In the DPAG report, there was consensus among the three viewpoints that Dr. Mitloehner's 2.7 lb/head-yr value provides the best available basis for estimating at least some of the enteric and feed emissions. Where the viewpoints differed is in determining what quantities of other compounds should be added to Dr. Mitloehner's 2.7 lb/head-yr value to provide a more complete estimate. However, as discussed above, the 2.7 lbs/hd-yr has been adjusted to 1.4 lbs/hd-yr based on the letter from Dr. Mitloehner dated 7/25/05.

In Viewpoints 2 and 3, as presented to the APCO on 5/31/2005, values for two specific VOC compounds (1,2,4 trimethylbenzene and 1,3,5 trimethylbenzene) were added to the 2.7 lb/head-yr (revised to 1.4 lb/hd-yr based on 7/25/05 letter) number based on TO-15 test data provided by Dr. Mitloehner, resulting in a value of 3.4 lb/head-yr. Values for these trimethylbenzene compounds were added because there were some initial indications that the PTRMS may not have

detected these compounds. Proponents of Viewpoint 1, on the other hand, proposed to use Dr. Mitloehner's estimate without further adjustment.

Evaluation

In reviewing the report and presentations, the APCO was unable to determine whether or not the addition of trimethylbenzene values from the TO-15 tests was appropriate. In Dr. Mitloehner's letter to DPAG of 4/17/2005, he indicated that the PTRMS measurements detected a number of oxygenated compounds including ketones, aldehydes, alcohols, carbonyls and phenols. He also indicated that volatile fatty acids may also be detected but with unknown accuracy due to the sticky chemical nature of these compounds. He did not include aromatic compounds like trimethylbenzenes in his lists of compounds detected by this procedure. However, other literature provided by the dairy industry from PTRMS instrument manufacturers indicated aromatic compounds such as trimethylbenzenes could be detected by PTRMS. No evidence was presented to DPAG or otherwise provided that would allow the APCO to determine with certainty whether the 2.7 lb/head-yr (revised to 1.4 lb/hd-yr based on 7/25/05 letter) estimate based on the PTRMS measurements already included the trimethylbenzenes.

The APCO did find, however, that there was ample evidence that significant quantities of other compounds present in enteric and feed emissions were not adequately measured by PTRMS, and were therefore not included in the 1.4 lb/head-yr estimate. Ethanol, for example, which was the VOC compound found at the highest concentrations in other tests of dairy feed areas by Dr. Schmidt (Schmidt's Results - Appendix 6), was not included in the PTRMS results at all due to a quirk in the test that precluded the ethanol from being detected (Goldstein E-mail - Appendix 7). Additional evidence indicated that many other compounds were probably also missed. In the words of Dr. Goldstein, who performed the PTRMS testing for Dr. Mitloehner, "It would be naïve to think that TO-15 and PTRMS together captured all the emitted compounds" (Goldstein E-mail - Appendix 7). Unfortunately, reliable data for these missing compounds are not available because the only tests that provided the environmental chamber data were the ones performed by Dr. Mitloehner.

It should also be noted that there is some evidence that the VOC emissions from Cows and Feed in environmental chambers may, at least under some circumstances, be much higher than 1.4 lb/head-yr. Test results presented by Dr. Mitloehner in the 1/27/2005 ARB Livestock Research Symposium showed that the emission factor for TO-15 compounds alone (which still only represent a fraction of VOC emissions) was over six lb/head-yr. Dr. Mitloehner later indicated to DPAG that those TO-15 results were unusually high and should not be used to generate an emission factor, so the 1.4 lb/head-year value was used.

Conclusion

Because of the lack of reliable data with which to accurately quantify emissions of the missing compounds, the APCO has chosen to use 1.4 lb/head-yr, for this category, and not add any values for additional compounds. Despite the shortcomings noted in the evaluation section, Dr. Mitloehner's value of 1.4 lb/head-year was found to be from valid tests providing process specific data for California dairy cows, consistent with Guiding Principles 1 and 2. The decision not to add an emission factor for trimethylbenzenes is consistent with Guiding Principle 5 in the previous section, which states that when no valid source of quantitative VOC data that could be linked to dairy processes is found, no emissions factor is determined. However, it must be recognized that the value chosen represents an underestimate of enteric and feed emissions, and that further research is needed to accurately quantify emissions of additional compounds for this category.

Category 2: Ethylamines from Specific Dairy Processes

Available Research

Dr. C.E. Schmidt measured ethylamine emissions from a variety of processes at a Merced County Dairy. Samples were collected using flux chambers and analysis was performed using NIOSH Method 2010. Although other references (Rabaud et al – Appendix 8) indicate that other amine compounds are present in emissions from dairy operations, other amine compounds were not reported in the Schmidt tests, and no published emission factors for the other amines were found in the literature searches.

DPAG Viewpoints

	Viewpoint 1	**Viewpoint 2**	**Viewpoint 3**
VOC Emission Factor for Ethylamines	0.2 lb/head-year	0.2 lb/head-year	11.0 lb/head-year

Proponents of Viewpoints 1 and 2 recommended using an emissions factor of 0.2 lb/head-yr for amines based on measurements of ethylamine by Dr. Schmidt. Proponents of Viewpoint 3 recommended an emissions factor of 11.0 lb/head-year, based on an average of emissions rates determined by Schmidt (Schmidt's Results - Appendix 6), Rabaud et al (Appendix 8), and Ngwabie et al (Appendix 9).

Evaluation

In reviewing the report and presentations, the APCO finds indications that the emission factor of 0.2 lb/head-yr based on measurements by Schmidt significantly underestimates dairy amine emissions. One reason to believe that the 0.2 lb/head-year is an underestimate is that the Schmidt results did not

include emissions from several important dairy processes including feed storage, land application, settling basins, and composting operations. The Schmidt results also did not include enteric amine emissions, which may also be significant, and it is still unclear whether enteric amines were effectively included in category 1 estimates above. Another reason to suspect that the 0.2 lb/head-yr emissions factor is low is that many key amine compounds found in other studies are also missing from the results (Rabaud et al – Appendix 8). These indications lead the APCO to believe that the real amine emissions factor may be much higher than the 0.2 lb/head-year estimate.

The Viewpoint 3 emissions factor of 11.0 lb/head-year was based on an average of emissions rates determined by Schmidt (Schmidt Results - Appendix 6), Rabaud et al (Appendix 8), and Ngwabie et al (Appendix 9). However, the values from Schmidt and Ngwabie studies in this average (0.2 lb/head-yr and 0.03 lb/head-yr respectively) were insignificant when compared to the value based on Rabaud et al data of 32.7 lb/head-yr. The APCO finds the value based on the Rabaud et al data to be suspect (possibly far too high), because it was calculated using a ratio of amine concentrations to VFA concentrations and, in many studies, VFA concentrations appear to have been significantly underestimated because of what Dr. Mitloehner referred to as their “sticky chemical nature” (Mitloehner 4/17/05 Letter – Appendix 5). Therefore, the emission factor for amines based on the Rabaud et al data was rejected, consistent with Guiding Principle 2b. This issue is further discussed in the VFA section of this report. The Ngwabie study value was based on only one amine (Triethylamine) and the low, single value did not significantly add to the total for amines.

Conclusion

Although the reference provided in Viewpoint 3 (Rabaud et al- Appendix 8) does strongly suggest that other amine compounds may be present in significant quantities in dairy emissions, the APCO did not find data sufficient to create an emissions factor for these other compounds at this time. This determination is consistent with Guiding Principle 5 in the previous section, which states that when no valid source of quantitative VOC data that could be linked to dairy processes is found, no emissions factor is to be determined. In recognition of the fact that the emissions of several compounds and from many processes are missing from the 0.2 lb/head-year estimate, the title of this category was revised from “Amine Emissions from Dairy Processes” to read “Ethylamine Emissions from specific dairy processes”. Further research is required to determine an emissions factor that represents all amine compounds from all dairy processes.

Category 3: VOCs from Miscellaneous Dairy Processes

Available Research

Dr. C.E. Schmidt measured VOC emissions from a variety of dairy processes using flux chambers in conjunction with EPA method TO-15, NIOSH method 2010, EPA TO-11, and an EAS UV/VIS Method (Schmidt Presentation to DPAG – Appendix 10). Samples were collected for the specific processes including those in the milker barn, dry barn, turnout area, separated solids piles, and lagoon.

Dr. Charles 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 (Krauter Presentation to DPAG - Appendix 11).

DPAG Viewpoints

	Viewpoint 1	**Viewpoint 2**	**Viewpoint 3**
VOC Emission Factor for Miscellaneous Dairy Processes	1.2 lb/head-year	1.2 lb/head-year	1.2 lb/head-year

Proponents of all three viewpoints proposed to use the Schmidt data to characterize the TO-15 VOC emissions for the areas measured, except the lagoon. The emissions factor derived from the Schmidt data from these processes was 1.2 lb/head-yr.

Evaluation

In reviewing the Schmidt data, the APCO finds that his measurements clearly missed important compounds and significantly underestimated VOC emissions from the processes measured. For instance, the EPA TO-15 test method was designed to measure emissions from industrial operations. Although the calibration standard for the TO-15 method does include dozens of organic compounds, many of those compounds, the chlorinated industrial solvents for example, are not the correct compounds for dairy emissions studies. Other important VOC compounds, which are known to be emitted from dairies, cannot be quantified using Method TO-15 because they are not included in the Method TO-15 calibration standards. Methanol, for example, which was determined to be the most abundant VOC compound in the Dr. Mitloehner's environmental chamber studies using PTRMS representing over one-half of the VOC emissions, was not included in TO-15 or any of the other analyses performed by Dr. Schmidt. In addition to missing a significant portion of the VOC compounds from dairy emissions, it was also clear that the Schmidt data do not address all dairy

processes, since important processes such as feed storage, solids separation, composting, and land application were not tested.

On the other hand, Dr. Schmidt reported that the method he used to identify which samples to analyze introduced a slightly high bias because they chose to analyze samples which were likely to contain the most emissions (to ensure that quantifiable results would be measured).

Conclusion

Even though the 1.2 lb/head-yr value derived from the Schmidt data is clearly an underestimate of VOC emissions, the APCO did agree that these tests provide the best available data for the processes tested. Although emissions from similar processes were measured by method TO-15 in aggregate by Dr. Krauter, in consideration of Guiding Principle 3b in the previous section, the Schmidt data from the specific processes were preferred. However, because data for important VOC compounds and sources are clearly missing in this category resulting in an underestimate of VOC emissions, the APCO strongly agrees with the DPAG Report recommendation that, "Standardized methods and a target suite of compounds are required to guide future research work regarding dairy emissions".

Category 4: VOCs from lagoons and storage ponds

Available Research

Dr. C.E. Schmidt measured VOC emissions from a dairy lagoon at one Merced County dairy using flux chambers in conjunction with EPA method TO-15 and other methods (Schmidt Presentation to DPAG - Appendix 10). Dr. Charles 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 (Krauter Presentation to DPAG - Appendix 11).

DPAG Viewpoints

	Viewpoint 1	**Viewpoint 2**	**Viewpoint 3**
VOC Emission Factor for Lagoons and Storage Ponds	1.0 lb/head-year	1.0 lb/head-year	1.0 lb/head-year

DPAG members reached agreement that a value of 1.0 lb/head-yr was appropriate for the VOC emissions, except VFAs and amines, based on an average of measurements by Schmidt and Krauter, consistent with Guiding Principle 3c from the previous section, which states that where test results from more than one study were deemed equivalent, an average emission factor was developed.

Evaluation

In reviewing the Schmidt and Krauter data for lagoons, the APCO finds that these measurements also clearly missed important compounds and probably underestimated the emissions. As noted earlier regarding the enteric and feed emissions, in the words of Dr. Goldstein, "It would be naïve to think that TO-15 and PTRMS together captured all the emitted compounds" (Goldstein E-mail - Appendix 7)." It would be even more naïve to think that the TO-15 test of lagoons alone, as performed by Krauter, and the limited additional testing performed by Dr. Schmidt, without the PTRMS, captured anything more than a fraction of the lagoon emissions.

Conclusion

Because data for the missing compounds is not available, the APCO agrees that these Schmidt and Krauter tests provide the best available data for this category at this time, and that 1.0 lb/head-year is the best estimate for VOC emissions from lagoons and storage ponds. Again, the APCO believes this to be an underestimate, and strongly agrees with the DPAG Report recommendation that "Standardized methods and a target suite of compounds are required to guide future research work regarding dairy emissions".

Category 5: Volatile Fatty Acids (VFAs)

Available Research

Dr. C.E. Schmidt attempted to measure volatile fatty acid (VFA) emissions at one Merced County dairy. Testing was conducted at a variety of locations (corrals, flushed lanes, lagoons, etc.), and all samples analyzed resulted in non-detect values for VFAs.

Volatile Fatty Acid concentrations were measured in significant quantities by Dr. Frank Mitloehner in his environmental chamber tests. In Dr. Mitloehner's chamber tests, the VFA samples were drawn directly into the sorbent tubes where the VFAs were collected for analysis, and not through flux chambers or sampling tubing.

Other VFA studies were also evaluated by the DPAG. Those studies included the Hobbs et al (Appendix 12) study of emissions from manure slurries, Koziel et al study of VFAs from Texas Cattle Pens (Appendix 13); and the McGinn et al study of ammonia, VFAs and other odorants near Canadian beef feedlots (Appendix 14).

DPAG Viewpoints

	Viewpoint 1	Viewpoint 2	Viewpoint 3
VOC Emission Factor for VFAs	0.7 lb/head-year	7.5 lb/head-year	17.0 lb/head-year

In the DPAG report, there was no consensus among the proponents of the three viewpoints on VFA emissions. Proponents of Viewpoint 1 chose to base an emission factor on an analysis of Dr. Schmidt's flux chamber tests by Dr. Julia Lester, a consultant hired by the Dairy Industry. Because no quantities of VFAs were actually detected in these Schmidt tests, Dr. Lester used analytical limits of detection to estimate VFA concentrations, and reported an emission factor of 0.7 lb/head-yr (Lester VFA Emission rate Technical assessment - Appendix 15). No attempt was made to include enteric VFA emissions under this viewpoint.

Proponents of Viewpoint 2 calculated VFA emissions based on two studies, the Koziel study, in which VFA emissions from a Texas feedlot were measured in very dry conditions; and the Hobbs et al study, in which VFA emissions were measured from slurry-type manure. The emissions factor from the Koziel study was used to represent emissions from dry dairy processes such as the open corrals, and the Hobbs slurry study was used to represent the wet processes such as the lagoon. The relative percentages of dairy manure in wet and dry processes were estimated from the California Regional Water Quality Control Board Fact Sheet #4 (Appendix 16) as 60% and 40% respectively, although DPAG heard testimony from a representative of the Valley's Provost and Pritchard Dairy Engineering Group that for the most common flush-type dairy, an 80%/20% ratio is perhaps more appropriate, based on the Water Board's fact sheet. An emission factor of 7.5 lbs/head-yr was calculated (DPAG Report – Appendix 3) assuming 60% of dairy manure was in wet processes, similar to the conditions in the Hobbs et al study, and 40% was in dry processes similar to the conditions in the Koziel feedlot study. However, no attempt was made in this viewpoint to estimate enteric VFA emissions.

Proponents of Viewpoint 3 calculated VFAs emissions by taking an average of VFA factors derived from three studies (11.9 lb/head-yr, from the Hobbs report, McGinn 2003 - 13.3 lb VFA/head-year and Ngwabie 2005 - 25.9 lb VFA/head-year). The McGinn and Ngwabie VFA emissions were developed using the ratio of VFA concentrations to ammonia concentrations multiplied by an ammonia emission factor for California Dairies. The VFA emission factor was determined to be 17.0 lbs/head-yr. This emission factor includes emissions from cows and from their waste.

Evaluation

In reviewing the DPAG report, presentations, and studies, the APCO attempted to determine whether non-detect VFA measurements by Dr. Schmidt, in which samples were drawn through a flux chamber and 8 feet of tubing before entering

the sorbent tubes, could be used to develop accurate emission factors for VFAs in the manner described in Viewpoint 1. One document the APCO reviewed was an e-mail from Jacek Koziel (VFA researcher at Texas A&M University). Dr. Koziel stated that, "*VFAs have a high affinity for adsorption to any surfaces (even stainless steel, Teflon or glass). Adsorption to tubing can result in underestimation of measured concentrations*." (Koziel E-mail - Appendix 17). The APCO also reviewed an e-mail from Dr Alan Goldstein (researcher at University of California at Berkeley) indicating that " *Volatile fatty acids, phenols, peroxides… may have a tendency to condense or be absorbed by many of the materials typically used in sampling lines…Therefore, these compounds often can only be detected if at sufficiently high concentrations, and then only qualitatively, as these loss processes often do not occur at correctable rates.*" (Goldstein E-mail - Appendix 7). Based on these expert opinions, the APCO concluded that the non-detect values in the Schmidt Study could be the result of the expected sampling bias, and therefore it is not appropriate to use the analytical limits of detection from these tests to estimate VFA emission factors. This deficiency in the sampling method constitutes "evidence that sample collection procedures may have resulted in the potential for significant loss of analyte" as described in Guiding Principle 2b, and, as Dr. Goldstein indicates, this deficiency is not correctable in this case. Therefore, the Schmidt VFA data was considered invalid and rejected, consistent with Guiding Principle 2b.

Proponents of Viewpoint 1, argued that this same VFA data based on the Schmidt study was the most appropriate, as it was the only study reviewed by DPAG that measured VFAs under conditions at a California dairy. While valid data from recent tests performed at California dairies may be given preference over data from other sources under some circumstances, it would be inappropriate (and inconsistent with Guiding Principle 2b) to give any preference to data found to be invalid.

Because the Schmidt VFA non-detect data was not valid, the APCO reviewed data from other research studies presented to DPAG by scientists, data obtained from other dairy emissions research, and data from available recognized scientific literature in an attempt to find data that could be used to estimate enteric VFA emissions from the cows and VFA emissions from dairy processes.

Enteric and Feed VFAs: Dr. Mitloehner and his collaborators from USDA-ARS and ISU measured VFA emissions from dairy cows, feed, and animal excreta for the purpose of determining the relative concentration of VFA components. The tests were performed with three cows inside of an environmental chamber and VFAs were collected directly onto sorbent tubes (without lengths of sampling tubing). Although Dr. Mitloehner and his collaborators advised the DPAG and the APCO that the use of VFA concentration data is scientifically invalid for determination of an emission factor because of the variation in the data and the fact that inlet measurements were not performed, the APCO determined that the lack of inlet VFA data was a correctable problem. As part of the DPAG efforts to

evaluate the VFA data, the DPAG chair, David Warner, contacted the analyst for Dr. Mitloehner's VFA data, Jacek Koziel. Koziel indicated (in an email – Appendix 17) only one factor that would preclude the use of the data – the absence of VFA inlet data. In spite of the absence of inlet data, the APCO was still able to calculate a "low-range" enteric VFA emissions estimate of 8.3 lb/head-yr by assuming that the ratio of inlet to outlet VFA emissions was similar to the ratios measured for other VOC compounds (See Low-range estimate of enteric VFA emissions - Appendix 18). Air entering the environmental chambers in the Mitloehner studies passed though a HEPA filter that may have adsorbed a significant quantity of inlet VFAs. It should be noted that this assumption that "the ratio of inlet to outlet VFA emissions was similar to the ratios measured for other VOC compounds" almost certainly results in an underestimate of VFA emissions. If inlet VFAs were adsorbed by the HEPA filter (as might be expected based on comments regarding how easily VFAs can be adsorbed by Koziel and Goldstein), and were not as high as assumed, the actual VFA emissions would be higher than the 8.3 lb/head-yr reported here.

VFAs from Dairy Processes: While California data would be preferred in accordance with Guiding Principle 3a, no valid measurements of VFA emissions from specific dairy processes were performed on California dairies. Because no valid California VFA data was available, the APCO reviewed other studies to estimate an emission factor for the VFAs from dairy processes. In accordance with principle 3a, the APCO carefully considered 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.

The APCO found strong support for the Viewpoint 2 approach for determining these non-enteric VFA emissions, in which the emission factors from the Koziel et al Texas Feedlot study were used to represent dry dairy processes, and the emissions factors derived from dairy manure slurry studies by Hobbs et al were used to represent VFA emissions from wet dairy processes.

The basis for this approach is that VFA emissions from manure vary with moisture content. The following studies strongly support the contention that **dairy VFA emissions are proportional to manure moisture levels**:

Study	Author	Statement regarding the affect between manure moisture content on VFA Emissions
Measurements of Volatile Fatty Acids Flux from cattle Pens in Texas	Koziel, et al	*"Measured flux was proportional to manure pH and moisture content…"*
In Vitro study of biochemical origin and production limits of odorous compounds in cattle feedlots	Miller and Varel	*"Earlier research has documented a 60-fold increase in odor concentrations after rainfall (Watts and Tucker, 1993; Watts et al., 1994)"*
Atmospheric Ammonia, VFA's, and other odorants near beef feedlots	McGinn, et al	*"The source strength in manure may be influenced by other factors such as precipitation events (Lunney and Lott, 1995) and thickeners and moisture content of the manure in feedlot."*
Monitoring odorous emissions from livestock manure using a chamber approach	McGinn and Coates	*"A higher moisture content of manure was shown to suppress ammonia emission. Similarly, VFA emission was initially suppressed, but after 24 h, VFA emission was greater from the wet manure compared to the drier manure."*
Strategies to reduce manure emissions	McGinn, et al	*"Adding more than 20 mm of water to manure increased volatile fatty acids emissions over a four-day period. The researchers speculate this is because of anaerobic bacterial growth"*
Dealing with the environmental impacts of livestock manure	Silsoe Research Institute	*"Volatile fatty acids (VFA) are the most important group and are commonly reported as being a major indicator of the offensiveness of odors arising from livestock slurries (Williams, 1984)"*

Comparison of Process Conditions for the Koziel et al Study: Certain areas of San Joaquin Valley dairies, including the drylot and corral areas are dry in the summer and are moist during foggy and rainy periods such as the winter months. Although the APCO agrees with the proponents of Viewpoint 2, that these drier areas of the dairy may be best represented by the Koziel et al Texas feedlot study, some specific differences in process conditions should be noted.

The Koziel et al study was performed in Texas feedlots during the summer. The summertime Texas meteorological conditions were undoubtedly warm and dry as evidenced by the very low manure moisture contents of 9-14% reported in the study (Koziel et al – Appendix 13). While the Texas feedlot conditions should be very similar to summertime conditions in the dry areas of a San Joaquin Valley dairy such as in the dry lot and corral, the emissions in the Koziel study may tend

to underestimate emissions in other San Joaquin Valley seasons when ground moisture and humidity levels are higher. Because there were no quantitative emissions data associated with this difference in process conditions, the APCO chose not to attempt to correct for this underestimation.

Comparison of Diet for the Koziel et al Study: Because feedlot cattle, not dairy cattle, were the subject of the Koziel et al study, differences in diet may have impacted the reported emissions. In a letter dated May 4, 2005 (Meyer 5/4/05 Letter – Appendix 19), Dr. Deanne Meyer of the University of California at Davis indicated that, although dairy cattle excrete more mass than feedlot cattle, the starch levels excreted by feedlot cattle may be as much as eight times higher than that of dairy cattle. Dr. Meyer also indicated that starch content would be a key factor in VFA formation. In order to adjust for the lower starch content in dairy excreta, the APCO divided the Koziel emission factor of 0.53 lb/head-yr by eight to obtain a minimum emission factor of 0.07 lb/head-yr for the dry areas of the dairy.

Comparison of Process Conditions for the Hobbs et al Study: In the Hobbs et al study, VFA emissions from containers of manure slurries were measured in the laboratory, and VFA emissions were reported in the *Journal of the Science of Food and Agriculture* (Hobbs et al - Appendix 12). Dr. Julie Lester, a consultant hired by the Dairy industry, noted that the laboratory slurry was 2-5% dry matter, that the laboratory slurry was stirred and that the slurry was kept at 59 ^{0}F, and that emissions are strongly dependent on environmental conditions.

The APCO found conditions in wet processes in real San Joaquin Valley dairies to be remarkably similar to these laboratory conditions. For instance, the average daily temperature in Fresno is 81° F in July and 45° F in January, and the annual average temperature is approximately 63° F, which is very close to the 59° F in the laboratory. Since the average temperatures of large bodies of water, such as dairy treatment lagoons and storage ponds, closely approximate average ambient temperatures, the laboratory test temperatures are found to be closely representative of actual conditions on San Joaquin Valley dairies.

Also, in typical San Joaquin Valley dairies, large percentages of a dairy are represented by wet conditions. As previously noted, the Water Quality Control Board Fact Sheet #4 states that 60 - 80% of the manure generated enters into the “wet” system. Manure is flushed with large amounts of water from flush lanes, into a wet solid separation process or processing pits, and then eventually into lagoons and/or storage ponds. Throughout this entire process, the manure remains at moisture contents far exceeding the 8 - 15% moisture represented by the dry, summertime Koziel study. In fact, the driest part of this system, the mechanical solids separation process, results in a solid effluent of a minimum of 60% moisture content.

On the other end of the moisture spectrum, dairy lagoons are expected to have a significantly higher moisture content than the 95 - 98% moisture content (2-5% solids content) in the Hobbs et al laboratory tests. The recommended (average) solids loading of 10-11 lb/1000ft^3 (NRCS Conservation Practice Standard - Appendix 20), which is equivalent to approximately 99.85% moisture content, is far above the laboratory moisture content in laboratory slurry conditions. In real lagoons, however, much of the manure sinks to the bottom, where anaerobic digestion and VFA emissions occur, and the solids concentration at the bottom of the lagoon are very similar to laboratory slurry conditions, as individual solid manure particles are surrounded by free moisture, just as they were in the Hobbs laboratory tests.

Several other operations at a dairy will have moisture contents in between these two ends of the spectrum. The flush lanes, milk barn flushing, processing pits, basin-type solids separation, and liquid manure land application processes are all wet processes that would expect to far more closely mimic the Hobbs report conditions than the dry summertime Koziel report conditions.

Therefore, the APCO finds that these Hobbs et al laboratory conditions do represent the wet processes on California dairies remarkably well, and they are much superior in representing wet process conditions to the dry summertime Texas feedlot studies that Dr. Lester and other dairy industry representatives originally recommended DPAG use to determine VFA emissions in April (Lester Analysis of Hobbs et al - Appendix 21), because the VFA emission rate is proportional to moisture content.

Comparison of Diet for the Hobbs et al Study: In her letter of May 4, 2005, Dr. Meyer (Appendix 19) questioned the use of the Hobbs et al data indicating that the diet for the animals used in the Hobbs et al study may have been different than the diet in animals from California dairies, impacting the VFA emissions determination. Dr. Meyer noted, for example, that nitrogen excretion from cattle could vary 15 to 20% based on diet.

The APCO agrees with Dr. Meyer that diets could possibly be different between California dairy cows and the UK dairy cows used in the Hobbs et al study, and that this may have had some impact (possibly even 15-20%) on the ratio of VFA to ammonia found in the study, affecting the resulting VFA emission factors. Because of the concern about the impact of diet, the APCO strongly advocates future VFA research on California dairies that includes consideration of diet. However, the fact remains that no other valid data exists to represent these wet dairy processes, and a possible deviation of 15-20% in data used to generate an emission factor, does not make the data invalid. Because of the limited availability of research data and other factors, uncertainties of this magnitude in air pollution emission factors are common, and acceptable.

Dr. Meyer also noted that the Hobbs et al study, found no significant correlation between NMVOC (Non-methane Volatile Organic Compound) emissions and ammonia emissions for the dairy cattle slurry, as the former were too low (although a significant correlation was clearly found in other manure slurries). The APCO evaluated this concern (see Appendix 22) and determined that the fact that a significant correlation could not be demonstrated from the data at low VFA concentrations was to be expected, and that this would not render the data invalid for use in emission factor development. In fact, in their study, Hobbs et al not only concluded that the dairy slurry data could be used to estimate VFA emissions from cattle, they specifically did use the data to estimate VFA emissions in their publication in the *Journal of Science of Food and Agriculture.*

Conclusion

Based on the above evaluation of all of the available VFA data, the APCO finds that the Koziel study best represents dry dairy processes in the San Joaquin Valley, and that the Hobbs study best represents the wet dairy processes.

Therefore, the non-enteric VFAs from dairy processes are calculated as follows:

Hobbs Study Emission Factor:	11.9 lb/head-yr
Koziel Study Emission Factor:	0.07 lb/head-yr
% Manure in flush (wet):	60%
% Manure left in Corral (dry):	40%

Non-enteric VFAs = (11.9 lbs/head-yr x 0.6) + (0.07 lbs/head-yr x 0.4) = **7.2 lbs/head-yr**

The total VFA emissions are then represented by the sum of the non-enteric and the enteric VFA emissions:

Total VFA emissions = **7.2 lbs/head-yr Non-Enteric**
+ 8.3 lbs/head-yr Enteric
15.5 lbs/head-yr

It should be noted that this result is very similar to the Viewpoint 3 value of 17.0 lb/head-yr, which was arrived at by a different method.

Because several of the numbers calculated above represent minimums and low-range estimates for VFA emissions, this number of 15.5 lb/head-year most probably represents an underestimate of VFA emissions. For instance, it should be noted that the Hobbs emissions calculations are based on an ammonia emission factor of 26 lb/head-year, as opposed to the ARB's higher ammonia emission factor of 74 lb/head-year. Further research is needed to obtain a stronger understanding of VFA emissions and to more accurately quantify all VFA emissions from all sources at a dairy.

Category 6: Phenols from Dairy Processes

Available Research

Phenol emissions form dairies were not quantified in any of the on-dairy California research studies presented to DPAG. Dr. Mitloehner indicated in his letter of 4/17/2005 (Appendix) that Phenols were measured in the PTRMS studies of cows, their feed and their excreta. Some data regarding phenol emissions were obtained from literature including Hobbs et al (Appendix 12) and McGinn et al (Appendix 14). In the Hobbs et al study, measured concentrations of phenols from a dairy manure slurry were determined to be equivalent to an emission rate 5.2 lb/head-year based on a comparison with ammonia emission rates. In the McGinn study at Canadian feedlots, much lower concentrations of phenols (in relation to ammonia) were measured.

DPAG Viewpoints

	Viewpoint 1	**Viewpoint 2**	**Viewpoint 3**
VOC Emission Factor for Phenols	NA	NA	2.6 lb/head-year

Proponents of Viewpoints 1 and 2 agreed that data needed to calculate a reliable emission factor for phenols was not available. Proponents of Viewpoint 3 calculated an average emissions factor of 2.6 based on an average of an emissions factor from the Hobbs et al study of 5.2 lb/head-year and a factor derived from the McGinn et al study of 0.02 lb/head-yr.

Evaluation

Dr. Mitloehner indicated in his letter of 4/17/2005 (Appendix 5) that Phenols were measured in the PTRMS studies of cows, their feed and their excreta. No new information on phenols was presented in his letter of 7/25/05. The 1.4 lb/head-yr number for enteric and feed emissions may include at least some of the phenol emissions measured in the Canadian Feedlot studies by McGinn and included in Viewpoint 3. No information was provided to the APCO regarding the formation of Phenols and the relationships to diet and process conditions, so the APCO was unable to consider specific process conditions (such as meteorological conditions, season, manure moisture content, available information on feed, etc.) in evaluating the transferability of the out-of-state Phenol data such as that provided by McGinn et al and Hobbs et al.

Conclusion

Because no information was provided to the APCO regarding the formation of Phenols and the relationship to diet and process conditions, the APCO chose to

report the Phenol emission factor as “TBD, >0” at this time. The APCO also agrees with the DPAG recommendation for further research in this area.

Category 7: Land application*, *feed storage, settling basins, composting, and manure disturbance,

Available Research

VOC emissions from land application, feed storage, settling basins, composting, and manure disturbance were not quantified in any of the California research studies presented to DPAG.

DPAG Viewpoints

	Viewpoint 1	**Viewpoint 2**	**Viewpoint 3**
VOC Emission Factor for Land Application	NA	NA	0.1 lb/head-year

Proponents of Viewpoints 1, 2, and 3 agreed that data needed to calculate an emission factor for land application was not available. Proponents of viewpoint 3 cited McGinn et al (Appendix 14), which reported high levels of VFA emissions after application of manure on fields. The VFA concentration was over five times higher than the maximum VFA level measured downwind of feedlot operations. Since an emission factor could not be determined from the report, the proponents of Viewpoint 3 used an emissions rate of 0.1 lb/head-yr as a placeholder.

Emissions from settling basins, composting, manure disturbance, and feed storage were not quantified in any of the California research. Proponents of all viewpoints agreed that data needed to calculate an emissions factor was not available, (although in Viewpoint 3, an emissions rate of 0.1 lbs/head-yr was used as a placeholder).

Evaluation

One person commented during DPAG considerations that the application of liquid and solid manure to farm land should not be considered part of the dairy, nor should the emissions from such operations be counted towards the emissions attributed to dairies. However, both District Rule 2201 (“New and Modified Source Review”) and Senate Bill 700 contradict this position.

Rule 2201 defines a stationary source as all emitting processes that are owned or operated by a single entity and are located on contiguous properties. Therefore, application of manure on land contiguous to the dairy proper must be included in a complete assessment of emissions from a dairy.
In addition, SB 700 created state law in the form of California Health and Safety Code 39011.5. This law includes, as part of the definition of an agricultural source, “...a confined animal facility, including, but not limited to, any structure,

building, installation, barn, corral, coop, feed storage area, milking parlor, or system for the collection, storage, treatment, and distribution of liquid and solid manure…" Clearly, land application of solid or liquid manure must be considered a part of the manure treatment and distribution system, and therefore, again, application of manure on land contiguous to the dairy proper must be included in a complete assessment of emissions from a dairy.

Either one of these arguments, considered alone, require that the APCO consider land application emissions a part of a dairy's emissions, in addition to the other process mentioned here: feed storage, settling basins, composting, and manure disturbance.

However, the APCO finds that insufficient data is available to estimate emissions from land application, feed storage, settling basins, composting, or manure disturbance.

Conclusion

Although it is apparent that a significant quantity of VOCs can be emitted during land application, feed storage, settling basins, composting, and manure disturbance, the APCO agreed with Viewpoints 1 and 2, that it may be premature to calculate an emissions factor based on the limited amount of data regarding emissions from these sources at this time. Therefore, the APCO will consider the emissions from these sources to be of the category "TBD, >0". The APCO also agrees with the DPAG recommendation for further research in this area.

Summary of Dairy Emissions

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

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	**19.3**

Summary of Future Research Recommendations

The APCO acknowledges that future research needs to take place and strongly agrees with DPAG's recommendations for future research on the following items:

- 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 identified in this report, as well as to develop improved sampling, analytical and quantification methods.

- Significant work is needed to better understand the role of emissions from feed versus direct emissions from cows and their waste. Direct emissions from feed appear to be important in overall VOC emissions and evidence was also presented to DPAG suggesting that diet may have an impact on emissions from cows and manure decomposition.
- Additional data are needed on different process emissions and effects of management practices on emissions.

In addition, the APCO strongly believes that future research also needs to focus on sources at a dairy where little or no data is available, such as land application, settling basins, manure storage piles, disturbance of manure piles, processing pits, composting, and identify any other sources at a dairy that have the potential to emit VOCs.