

Memorandum

October 12, 2005



VOC Project July 2005

Determination of VOC/ROG at the Bion NMS System Project at DeVries Dairy. July 12, 2005 – July 14, 2005

Introduction:

From July 12, 2005 through July 14, 2005, Bion conducted a continuation of the Atmospheric Emission Quantification Project which was described in detail in the December 22, 2004 Report “DeVries Dairy, Bion NMS Nutrient and Atmospheric Emission Quantification Project, Analytical Approach, Details and Results” (hereafter 2004 Report, see <http://www.biontech.com/technology/documents/DeVries%20Nutrient%20&%20Air%20Project%20Review%20Final%2012-22-04.pdf>). This additional study was conducted as a result of new research that identified more precise sampling and analytical methodologies for the determination of Volatile organic compounds (VOCs).

When the July 2005 study was performed the anaerobic zone of the Bion NMS had been decommissioned and therefore was not in operation as it had been in the 2004 study. However, all other components of the Bion NMS were fully functional and the Enclosed Emissions Monitoring System for the Anoxic Zone was employed using the same protocol as had been done in 2004. The actual sampling was conducted using the improved and expanded techniques described below. Since the anoxic zone accounts for about 90 percent of the total bioreactor, analysis of its emissions provides useful data relative to the prior study.

This document is a continuation of the 2004 Report and its accompanying Master Spreadsheet (see <http://www.biontech.com/technology/documents/Analysis%20Master%20Final%2012-22-04%20ro.xls>). The system, experimental apparatus, and protocols are as described in the 2004 Report unless specified otherwise. This document also refers to the VOC Project July 2005 Spreadsheet (see <http://www.biontech.com/technology/documents/VOC%20Project%20July%202005.xls>) that contains data and calculations from the July 2005 project.

The following Table compares the 2005 results with the 2004 results on a whole system basis. Emissions are expressed as pounds emitted per 1,400 pound cow per year. The ratios of the emissions for the anoxic zone to the whole system obtained in 2004 were used as a correction factor to obtain the whole system values used in this table. The procedure is described in detail below. The NMOC category reported in 2004 (with no detectable measurements) is a considerably less comprehensive category than the VOCs reported in 2005.

**Summary Results Comparing 2004 and 2005:
Comparative Total System Emissions**

Year	2005	2004
Total lbs VOC per cow-yr	0.08014	NA
Total lbs NMOC per cow-yr	NA	0.02800
Total lbs methane per cow-yr	40.33	38.49
Total lbs ammonia per cow-yr	0.60	0.20
Total lbs hydrogen sulfide per cow-yr	0.67	0.57
Total lbs nitrogen oxides per cow-yr	0.0098	0.0168

All NO_x values are placeholder numbers based on non detects
NMOC is Non Methane Organic Compounds

VOC and ROG Definitions:

Volatile organic compounds (VOCs) are defined by EPA in accordance with 40 CFR Part 51 Section 51.100 Definitions, as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.” Methane and acetone are also excluded along with a number of other, mostly halogenated, carbon compounds.

A problem with starting with this type of very broad definition and then subtracting a list of exempted substances is that it is not possible to specify a single analytical technique which can be used to quantitatively measure all of the VOCs which are included in the definition. This problem includes sample collection as well as analytical methodology. For example certain compounds may adhere to the surfaces of vacuum canisters and thus not be detected by subsequent analysis. Also, different gas chromatographic/mass spectrometric (GC/MS) methods detect different matrices of organic compounds.

Recently the California Air Resources Board (CARB) and San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) have been working with a variety of scientists and engineers to perform qualitative and quantitative determinations of the various species of organic compounds that comprise dairy emissions. This research found that the composition of the emissions previously reported as VOCs did not always include some alcohols (specifically methanol, ethanol, and isopropyl alcohol), phenols, volatile fatty acids (VFAs), and amines. This California research has indicated new techniques for more precise sampling and analysis of dairy VOCs. CARB uses the term Reactive Organic Gases (ROG) instead of VOC and provides a definition that is similar, but somewhat more restrictive than the EPA definition. This definition also suffers from the problem of not having a single analytical technique for its determination.

VOC Sampling and Analytical Methodologies:

To avoid any ambiguity or confusion for the July 2005 monitoring period VOCs (ROGs) were measured by collecting samples with vacuum canisters and three different types of sorbent tubes which were specific for phenols and cresols, amines, and VFAs. Appropriate analytical Gas Chromatography (GC) and Mass Spectroscopy (MS) methodologies were then used for each canister or tube to quantitatively determine the various constituents of the total VOC category. The application of five separate techniques was required to address the unique sampling and measurement requirements of the five categories of compounds included in the current more comprehensive VOC approach suggested by the recent California research. The collection canister or absorption tubes used were as specified for each category of compounds.

The categories of compounds making up the total VOC category are:

- 1) TVOC as Toluene (Total Volatile Organic Compounds as detected by two different MS methods.),
- 2) Methanol
- 3) Phenols and cresols,
- 4) Volatile Fatty Acids (VFAs), and
- 5) Amines.

Acetone, which is a part of the TVOCs, is also measured separately and then subtracted from the TVOC result.

Ethanol and isopropyl alcohol are part of the TVOC total as measured by MS in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), but methanol is not included in this total. Therefore methanol is measured separately using an additional MS method which gives values in parts per billion by volume (ppbV). Thus methanol becomes a separate category.

The results of all five categories are then combined to provide a final VOC value. Thus, to arrive at the VOC total as defined herein, the amount determined for TVOC minus acetone is added to the amount for methanol plus the amounts for amines, plus VFA, plus phenols and cresols. $\text{VOC} = (\text{TVOC} - \text{acetone}) + \text{methanol} + \text{phenols \& cresols} + \text{VFAs} + \text{amines}$. The specific sampling equipment, analytical methodologies, and analytical equipment used, and the constituents they detect, are listed below.

1) TVOC:

Samples collected by Summa Canisters were analyzed by EPA TO-15 using Tekmar AUTOCAN/HP5972/HP5890 II+/MS2 and Tekmar AUTOCAN/Agilent 5973inert6890N/MS8. Results were reported as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) of TVOC as Toluene. The final value is a composite result of all compounds detected by this technique. Since acetone is one of the compounds so detected it was also quantified separately and then subtracted from the total.

2) Methanol: Summa Canister samples were also analyzed by NCASI IM/CAN/WP-99.02 using Tekmar AUTOCAN/HP5970/HP5890/MS6 for Methanol, detected as parts per billion by volume (ppbV).

3) Phenols and Cresols:

Samples were collected by a Tenax Trap sorbent tube and analyzed by EPA TO-17 using PE Turbomatrix ATD/Agilent 5973N/Agilent 6890+/MS5. Detectable compounds include:

- Phenol
- o-Cresol
- m-Cresol & p-Cresol
- 2,6-Dimethylphenol
- 2,4-Dimethylphenol & 2,5-Dimethylphenol
- p-Ethylphenol
- p-Chlorophenol
- 3,4-Dimethylphenol

Results were reported as micrograms per cubic meter (ug/m³).

4) VFAs:

Samples were collected according to method CASAQL 502 as developed by Columbia Analytical Services Air Quality Laboratory using a sodium hydroxide treated silica gel tube (SKC 226-55) and analyzed by GC/MS using HP5970/HP5890 II+MS4. Detectable compounds include;

- Acetic Acid
- Propanoic Acid (Propionic)
- 2-Methylpropanoic Acid (Isobutyric)
- Butanoic Acid (Butyric)
- 2-Methyl Butanoic Acid
- 3-Methyl Butanoic Acid (Isovaleric)
- Pentanoic Acid (Valeric)
- 2-Methylpentanoic Acid
- 3-Methylpentanoic Acid
- 4-Methylpentanoic Acid (Isocaproic)
- Hexanoic Acid (Caproic)
- 2-Ethylhexanoic Acid
- Heptanoic Acid
- Octanoic Acid (Caprylic)
- Cyclohexanecarboxylic Acid

Nonanoic Acid
Benzoic Acid

Results were reported as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

5) Amines:

Samples were collected according to method CASAQL 501 as developed by Columbia Analytical Services Air Quality Laboratory using a Treated Alumina Tube (CASAQL) and analyzed by GC/NPD using Agilent 6890N/GC14/NPD. Detectable compounds include;

Dimethylamine
Ethylamine
Trimethylamine
Isopropylamine
t-Butylamine
Propylamine
Diethylamine
s-Butylamine
Isobutylamine
Butylamine
Diisopropylamine
Triethylamine
Dipropylamine

Results were reported as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

All of these results were converted into pounds per 1400 pound cow per year and then added together to provide a final measurement of VOC.

Calculations:

The "VOC Project July 2005" spreadsheet accompanying this document contains two worksheets. The first is "Raw Data" and contains the data obtained from canister and sorbent tube samples from the Anoxic Test Tank. Two ambient air samples and one field blank were also collected and analyzed and this data is also presented in this worksheet.

All data is presented as micrograms per cubic meter with two exceptions. Methane was reported as parts per million by volume, and methanol was reported as parts per billion by volume.

Field measurements for carbon dioxide, ammonia, hydrogen sulfide, methane, and nitrogen oxides were made on July 14, 2005, using the same instruments and protocol as discussed in the 2004 Report. These results are also recorded in the Raw Data sheet.

The second worksheet is titled "Calculations". This sheet converts all data into pounds per 1400 pound cow per year and then compares these numbers with the results from the 2004 Report.

Summa canister samples were taken over three hour intervals at various times of the day and sorbent tube samples were also collected during these intervals. Corrections are made using either a daytime or nighttime ambient air sample, as appropriate, for all those analytes for which the ambient air sample detected a measurable quantity. No corrections were made for non-detectable analytes in the ambient air samples. Duplicate samples were collected during consecutive intervals and these were averaged together for the purpose of obtaining a representative 24 hour daily measurement. As in the 2004 Report all non-detect measurements in the Calculations sheet are entered as one half the detection limit for computational purposes and to generate a conservative estimate of total emissions. These non-detect values are entered as ND and flagged with yellow cells in the Raw Data spreadsheet. The detection limit or MRL for Method Reporting Limit is recorded in column B for all VOC analytes.

To illustrate the general computational methodology the following discussion considers acetic acid which is presented on Row 37 of the Calculations sheet. These samples were collected in Silica Gel Tubes and were collected during the time interval identified in row 15. Since these were sorbent tube samples which did not require the three hour interval required for Summa Canister collection, when duplicate samples were taken the time of the first sample collection was at the end of the reported time interval and the second sample was collected at the beginning of the second sample time interval. As before all cells are identified by letters for columns and numbers for rows. Acetic acid has a MRL of 5.0 ug/m^3 , see cell B37, a nighttime ambient air value of 8.9 ug/m^3 (Q37) and a daytime ambient air value of 9.1 ug/m^3 (Y37).

Thus the first sample was collected sometime during the interval of 1345 to 1635 (C15) on 7/12/05 (C14). The measured value was 34 ug/m^3 (C37). Since this was considered to be a daytime sample the daytime ambient air sample value of 9.1 ug/m^3 (Y37) was subtracted from the measured value and the adjusted value of 24.9 ug/m^3 is reported in D37. Values adjusted for ambient air corrections are flagged in blue in the Calculations spreadsheet.

Samples 2 and 3 (columns E and F) were collected near 1700 (E37 & F37) on 7/13/05 (E14 & F14). These values were averaged in G37 and adjusted for the daytime ambient air correction in H37.

Sample 4, column I, was a non-detect and so it was entered as 2.5 ug/m^3 which is one-half of the MRL. This value, and all other non-detects which are entered as one half of the MRL, are flagged in yellow in the Calculations sheet. This value was not adjusted by the ambient air correction and so it was recorded in column J, the adjusted value column, as 2.5 ug/m^3 .

Sample 5 (K37) was a nighttime sample and so was adjusted for the nighttime ambient air correction (Q37) and reported in L37.

Sample 6 (M37) was also a nighttime sample but when it was adjusted for the ambient air correction the value was below one half of the MRL. Consequently the value entered for the adjusted value N37 was 2.5 ug/m³ which is one-half of the MRL. Cells containing one-half of the MRL as a result of the ambient air correction are flagged in green.

Sample 7 was a non-detect and handled as was sample 4. Sample 8 was the night ambient air sample. Samples 9 and 10 were duplicate samples and were handled as were samples 2 and 3. Since both samples were non-detect no ambient air correction was made and the final adjusted average was recorded at one half of the MRL in V37.

Sample 11 was a daytime measurement that was similar to sample 6 in that the ambient air correction dropped the value to less than one half of the MRL and so 2.5 ug/m³ was recorded in X37. Sample 12 was the daytime ambient air sample and sample 13 was the field blank.

Thus, the average value for the acetic acid concentration is 9.18 ug/m³ which is the average value for cells D37, H37, J37, L37, N37, P37, V37, and X37 as reported in AC37.

Except for the field values, all other average analyte concentrations reported in this document are calculated in a similar manner.

To determine a final VOC value the acetone concentration was subtracted from the TVOC concentration determined for the Summa Canister (AC26). Then all of the concentrations determined for the sorbent tubes as described above were added to this value (AC69).

This average concentration was then converted into pounds per cow per year. This was done by first converting the test system gas flow of 5.3 cfm (D115) into cubic meters per day [cubic feet per minute * 0.02832 cubic feet per cubic meter divided by 1440 minutes per day = cubic meters per day] (F115).

The total concentrations of VOCs measured in micrograms per cubic meter (AC69) were multiplied by the test gas flow in cubic meters per day (F115) to get the total micrograms emitted per day (C118). This was converted to grams emitted per day for the test system (divide by one million, D118) and then scaled up to the full system by multiplying by 91.9 which is the volumetric and surface area ratio of the full anoxic zone to the test system (E118). This is converted to pounds per day in F118 and finally to 0.049551 pounds of VOCs emitted per 1,400 pound cow per year in G118.

This number does not contain acetone but it also does not contain methanol since methanol was measured from the Summa Canister in parts per billion by volume (ppbV). To convert the average sample methanol concentration in ppbV to pounds of methanol

per 1400 pound cow per year first convert the test system gas flow in cfm to the methanol gas flow at one ppbV by dividing by one billion (C95). Multiply this by the methanol mass density (C87) corrected for the bioreactor temperature (C96) and multiple by 1440 minutes per day to get the test tank methanol emission in pounds per day (C97). As above this is then adjusted to represent the whole anoxic zone in C99 and converted into pounds of methanol emitted per 1400 pound cow per year in C100.

This methanol value is added to the VOC total calculated from the mass concentration data to yield a final VOC value of 0.049879 pounds of VOC emitted per 1400 pound cow per year (G117).

Methane, which is not part of the VOC definition, was similarly calculated from the Summa Canister measurements and compared with the field test readings. Since the field test readings gave a higher value the field test readings were used in the summary presentations.

Field test readings were all calculated as in the 2004 Report and are included in the summary presentation for comparative purposes.

To extrapolate the results of the July 2005 study, which only had the anoxic zone in service, with the 2004 Report which reported anoxic zone, anaerobic zone, and total system emissions, a total system to anoxic zone ratio was calculated and called the Tot/Anoxic Factor. This factor was calculated for the methane, ammonia, hydrogen sulfide, and nitrogen oxide data from the 2004 Report and used to extrapolate the July 2005 data to a whole system projection. This information is displayed in columns A through I, rows 158 through 183 of the Calculations sheet.

Note that the nitrogen oxides factor is based solely on non-detects. Since VOCs as defined herein were not measured in 2004, and the NMOC category that was reported in 2004 was all non-detect, an estimated factor of 1.61 (D167), consisting of the average of the methane, ammonia, and hydrogen sulfide data, was used to estimate the extrapolation of the VOC data to the whole system. (Note that this average factor is almost identical to the 2004 nitrogen oxide factor of 1.59 (D175) which was calculated based on the non-detects.) The comparison of the 2004 data with the extrapolated data from the 2005 study shows generally good agreement for the low emission levels measured.