Tier III Data Validation Report Summary

Client: Chevron Environmental Management Company – Chevron Cincinnati Facility	Laboratory: Air Toxics LTD
Project Name: Hooven Vapor Investigation	Sample Matrix: Air
Project Number: 500-016-012	Sample Start Date: 07/01/2009
Date Validated: 08/18/2009	Sample End Date: 07/01/2009
Parameters: Volatile Organic Compounds (VOCs) by Modified Method TO-15, and Helium and Fixed Gases by Modified Method ASTM D-1946	
Laboratory Project ID: 0907205A and 0907205B (TO-15 MOD) and 0907205C (ASTM D-1946 MOD)	
Data Validator: Andy Smith, Environmental Chemist	

DATA EVALUATION CRITERIA SUMMARY

A Tier III data validation was performed by Trihydro Corporation on the analytical data report package generated by Air Toxics, LTD, evaluating samples from the Chevron Site located in Cincinnati, Ohio.

Precision, accuracy, method compliance, and completeness of this data package were assessed during this data review. Precision was determined by evaluating the calculated relative percent difference (RPD) values of samples from laboratory duplicate pairs. Laboratory accuracy was established by reviewing the demonstrated percent recoveries of laboratory control samples (LCS) to verify that none of the data were biased. Method compliance was established by reviewing holding times, detection limits, surrogate recoveries, method blanks, and the LCS recoveries against method specific requirements. Completeness was evaluated by determining the overall ratio of the number of samples planned versus the number of samples with valid analyses. Determination of completeness included a review of the chain-of-custody, laboratory analytical methods, and any other documents associated with this analytical data set.

Data were evaluated in general accordance with validation criteria set forth in the USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Superfund Organic Methods Data Review, document number USEPA-540-R-08-01, June 2008 with additional reference to USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Organic Data Review, document number EPA 540/R-99-008 of October 1999. Review of duplicates is conducted in accordance with USEPA Region 1 Laboratory Data Validation Function Guidelines for Evaluation of Organic Analysis, December 1996. In addition to the above mentioned guidance documents, the USEPA Hazardous Waste Support Branch Validating Air Samples Volatile Organic Analysis of Ambient Air in Canister by Method TO-15, SOP # HW-31, October 2006 document and the applicable methods were used for verification of the data.

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SAMPLE NUMBERS TABLE

Client Sample ID	Sample Number
VW-139(5), 070109	0907205A and C-01A
VW-139(10), 070109 [a, b]	0907205A and C -02A
VW-139(15), 070109	0907205A and C -03A
VW-139(20), 070109	0907205A and C -04A
VW-139(30), 070109	0907205A and C -05A
OA-1,070109	0907205B-06A

[a] – A laboratory duplicate was prepared from this sample for Method TO-15 analyses.
[b] – A laboratory duplicate was prepared from this sample for Method ASTM-D-1946 analyses.

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The samples were analyzed for client-specified analytes. The samples were shipped to Air Toxics LTD under proper chain-of-custody procedures. The laboratory data were reviewed to evaluate compliance with the required methods and the quality of the reported data. A leading check mark (✓) indicates that the referenced data were deemed acceptable. A preceding crossed circle (⊗) signifies problems with the referenced data that may have warranted attaching qualifiers to the data.

- ✓ Data Completeness
- ✓ COC Documentation
- ✓ Holding Times and Preservation
- ✓ Laboratory Blanks
- ⊗ Calibrations
- ✓ System Monitoring Compounds (i.e. Surrogates)
- ⊗ Laboratory Control Samples (LCS)
- ✓ Laboratory Duplicates

OVERALL DATA PACKAGE ASSESSMENT

Based on a data validation review, the data are acceptable as delivered. The purpose of validating data and assigning qualifiers is to assist in proper data interpretation. Data which are not qualified meet the site data quality objectives. If values are assigned qualifiers, the data may be used for site evaluation, with the reasons for qualification being given consideration when interpreting sample concentrations. Data points which are assigned an R qualifier should not be used for any site evaluation purposes. A total of 26 data points were qualified due to out of range calibration data, and LCS recoveries.

Data qualifiers used during this validation included:

J – Estimated concentration

UJ – Estimated reporting limit

DATA COMPLETENESS

The analyses appeared to be performed as requested on the chain-of-custody records. The associated samples were received by the laboratory and appeared to be analyzed properly. No data points were rejected. The data completeness measure for these data packages are 100%.

TABLE 1. GENERAL VALIDATION CRITERIA CHECKLIST	
1. Did the laboratory identify any non-conformances related to the analytical data?	Yes
The reported CCV for each daily batch may be derived from more than one analytical file due to the client's request for non-standard compounds. Non-standard compounds may have different acceptance criteria than the standard TO-15 compound list as per contract or verbal agreement. As per project specific client request the laboratory has reported estimated values for target compound hits that are below the Reporting Limit but greater than the Method Detection Limit. Laboratory comments: 0907205A (TO-15 MOD): The laboratory noted that a seven point initial calibration was analyzed on 07/15/2009 on instrument MSD-X. The following compounds used 0.3 ppbv as the lowest calibration concentration: 1,3-butadiene, chloroform, benzene, 1,2-dibromoethane, styrene, cumene, 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene. The laboratory noted that the analytes sec-butylbenzene and butylbenzene were not present in the LCS spiking compound. 0907205B (TO-15 MOD): The laboratory noted that an initial calibration curve was analyzed on 03/19/2009 on MSD-Z. The instrument was set up to do full scan and selective ion monitoring (SIM) simultaneously. The 0.1 ppbv level of this ICAL was reanalyzed due to the anomalous unacceptable linearity for 2-butanone. 0907205C (ASTM D-1946 MOD): The laboratory noted that a seven point initial calibration was analyzed on GC-9 on 04/29/2009. As noted on the accompanying analytical run log, calibration level 6 was reanalyzed due to an unacceptable linearity for compound butane.	
2. Were sample chain-of-custody forms complete?	Yes
Comments: The COC record from field to laboratory was complete, and custody was maintained as evidenced by field and laboratory personnel signatures, dates, and times of receipt.	
3. Were detection limits in accordance with the QAPP, permit, or method, or indicated as acceptable by the Tier I validator?	Yes
Comments: The detection limits were acceptable. For Method TO-15, the laboratory reported required dilutions between 1.73 and 4.76 times. For Method ASTM D-1946, the laboratory reported required dilutions between 2.29 to 2.47 times.	
4. Were the requested analytical methods in compliance with the QAPP, permit, or COC?	Yes
Comments: The requested analytical methods were performed in accordance with the chain-of-custody form.	
5. Were samples received in good condition within method specified requirements?	Yes
Comments: Samples were received intact and in good condition. The final vacuums from the field and receipt vacuums measured by the laboratory were compared and the vacuums appeared to be acceptable. Pressure/vacuum changes from the field to the laboratory were less than five inches of mercury for each sample. The canisters used for sampling were 100% certified by the laboratory. The canister certification results were also reviewed and found to be acceptable. Compounds of interest were quantified in canisters used for sampling; however, the detections were at concentrations less than the reporting limit. Laboratory and field helium results were compared. The differences between the results were within acceptable limits.	
6. Were samples analyzed within method specified or technical holding times?	Yes
Comments: The samples were analyzed within method specified holding times.	
7. Were reported units appropriate for the associated sample matrix/matrices and method(s) of analyses?	Yes
Comments: The results for Method TO-15 were reported in units of part per billion by volume (ppbv) and micrograms per cubic meter ($\mu g/m^3$). The results for Method ASTM D-1946 for fixed gases were reported as percentages (%). These units are appropriate for the air matrix and for the methods used.	

TABLE 1. GENERAL VALIDATION CRITERIA CHECKLIST	
8. Do the laboratory reports include all constituents requested to be reported as indicated by the Tier I validator?	Yes
Comments: The requested constituents were reported as requested.	
9. Were the reporting requirements for flagged data met?	Yes
Comments: The reporting requirements for flagged data were met. **<u>Method TO15</u>: In samples VW-139(5), 070109; VW-139(10), 070109; VW-139(15), 070109; and VW-139(20), 070109, the laboratory used a J flag to indicate estimated concentrations for results between the method detection limit and the reporting limit. These qualifications were carried over as a result of this review.** **In samples VW-139(5), 070109, VW-139(20), 070109, and VW-139(30), 070109, and OA-1, 070109 the analytes 2-propanol (isopropanol) and acetone were qualified as E by the laboratory to indicate that they were detected at levels that exceeded the calibration range. These analytes were qualified as J to indicate estimated concentrations.** In sample OA-1, 070109 the analyte MTBE was qualified by the laboratory as UJ due to a low bias in the continuing calibration verification. Data qualification related to this laboratory observation is discussed in the calibration section, below.	
10. Were the field duplicates collected equal to at least 10% of the total number of samples, or as required by the project guidelines, QAPP, SAP, or permit, or as indicated by the Tier I validator?	No
Comments: Field duplicate samples were not collected during this event.	
11. Were field duplicate RPD values less than the upper RPD limit (soil [50%], water [30%], or air/vapor [25%]), as specified by the laboratory or method?	N/A
Comments: Field duplicate samples were not collected during this event.	
12. Was the number of equipment, trip, or field blanks collected equal to at least 10% of the total number of samples, or as required by the project guidelines, QAPP, SAP, or permit, or as indicated by the Tier I validator?	No
Comments: There were no equipment blank, trip blank, or field blank samples associated with this sample set.	
13. Were detections found in trip blanks, equipment blanks, or field blanks?	N/A
Comments: There were no equipment blank, trip blank, or field blank samples associated with this sample set.	

TABLE 2. VALIDATION CRITERIA CHECKLIST FOR VOC ANALYSES (METHOD TO-15)	
1. Were the initial and continuing calibration verifications within acceptable limits?	No
Comments: Calibration criteria were met for the samples and analyses with the following exceptions. **0907205A: In the initial calibration analyzed between 07/15/2009 at 08:15 and on 07/20/09 at 09:30 the percent relative standard deviation (%RSD) for 1,3-butadiene was outside data validation QC limits of 0-30% at 30.815%. As 1,3-butadiene was not detected in associated samples VW-139(5), 070109; VW-139(10), 070109; VW-139(15), 070109; VW-139(20), 070109; and VW-139(30), 070109; it was qualified as UJ to indicate estimated reporting limits.** **0907205B: In the continuing calibration analyzed on 07/22/2009 at 09:52 the percent difference for MTBE was outside data validation QC limits of 0-30% at 38.813231%. As MTBE was not detected in associated sample OA-1,070109, it was qualified as UJ to indicate an estimated reporting limit.**	
2. Were the instrument tunes within method control limits?	Yes
Comments: The Gas Chromatography/Mass Spectrometry (GC/MS) instrument tunes were within method control limits.	
3. Were the internal standards within method control limits?	Yes
Comments: The internal standard area counts differences were within TO-15 QC limits of ±40% of the internal standard area and within ±0.50 minute of the internal standard retention time.	
4. Was the total number of method blank samples prepared equal to at least 5% of the total number of samples, or analyzed as required by the method?	Yes
Comments: Method blank samples were analyzed for this data set on a greater than 5% basis.	
5. Were method blank detections reported for this data set?	No
Comments: There were no detections of target analytes reported in the method blank samples.	
6. Was the total number of laboratory control samples analyzed equal to at least 5% of the total number of samples, or analyzed as required by the method?	Yes
Comments: Laboratory control samples were analyzed for this data set on a greater than 5% basis.	
7. Were laboratory control recoveries within acceptable limits?	No
Comments: LCS recoveries were within acceptable limits with the exceptions noted below. Please note that sec-butylbenzene and butylbenzene were not added to the LCS spike mix. As these analytes are unusual target analytes, this omission has been determined to be acceptable. **0907205A: In the LCSs analyzed on 7/20/09 and 7/21/09 the recoveries of ethanol were outside laboratory QC limits of 70-130% at 51% and 53%, respectively. Since ethanol was not detected in the associated samples, VW-139(5), 070109; VW-139(10), 070109; VW-139(15), 070109; VW-139(20), 070109; and VW-139(30), 070109, it was qualified as UJ to indicate estimated reporting limits.** **0907205B: In the LCS analyzed on 7/22/09 the recoveries of 1,2,4-trichlorobenzene and hexachlorobutadiene were outside laboratory QC limits of 70-130% at 65% and 65%, respectively. Since these analytes were not detected in the associated sample, OA-1, 070109, they were qualified as UJ to indicate estimated reporting limits.**	
8. Was the total number of matrix spike samples prepared equal to at least 5% of the total number of samples, or analyzed as required by the method?	N/A
Comments: Matrix spike samples are not required by Method TO-15.	
9. Were matrix spike recoveries within acceptable limits?	N/A
Comments: Matrix spike samples are not required by Method TO-15.	
10. Were surrogate recoveries within control limits?	Yes
Comments: Surrogate recoveries were within control limits.	

TABLE 2. VALIDATION CRITERIA CHECKLIST FOR VOC ANALYSES (METHOD TO-15)	
11. Were laboratory duplicate RPD values within laboratory-specified limits?	Yes
Comments: A laboratory duplicate was prepared from sample VW-139(10),070109. Laboratory duplicate RPD values were within laboratory specified limits.	

TABLE 3. VALIDATION CRITERIA CHECKLIST FOR METHANE AND FIXED GAS ANALYSES (ASTM D-1946 MOD)	
1. Were the initial and continuing calibration verifications within acceptable limits?	Yes
Comments: The initial and continuing calibration verifications were within acceptable limits.	
2. Were the instrument tunes within method control limits?	N/A
Comments: Instrument tunes are not required by Method ASTM D-1946 MOD.	
3. Were the internal standards within method control limits?	N/A
Comments: Internal standards are not required by Method ASTM D-1946 MOD.	
4. Was the total number of method blank samples prepared equal to at least 5% of the total number of samples, or analyzed as required by the method?	Yes
Comments: The total number of method blank samples analyzed for this data set was greater than 5% of the number of samples analyzed.	
5. Were method blank detections reported for this data set?	No
Comments: There were no detections of target analytes in the method blanks.	
6. Was the total number of laboratory control samples analyzed equal to at least 5% of the total number of samples, or analyzed as required by the method?	Yes
Comments: The total number of laboratory control samples analyzed for this data set was greater than 5% of the number of samples analyzed.	
7. Were laboratory control recoveries within acceptable limits?	Yes
Comments: Laboratory control sample recoveries were within laboratory QC limits.	
8. Was the total number of matrix spike samples prepared equal to at least 5% of the total number of samples, or analyzed as required by the method?	N/A
Comments: Matrix spike samples are not required by Method ASTM D-1946.	
9. Were matrix spike recoveries within acceptable limits?	N/A
Comments: Matrix spike samples are not required by Method ASTM D-1946.	
10. Were surrogate recoveries within control limits?	N/A
Comments: Surrogate recoveries are not required by Method ASTM D-1946.	
Comments A laboratory duplicate was prepared from sample VW-139(10),070109. Laboratory duplicate RPD values were within laboratory specified limits.	

DATA QUALIFICATION SUMMARY

Analyte	Method	Field Sample ID	Lab Sample ID	Result	Limit	Units	Detect Flag	Reviewer Qualifier	Reviewer Qualifier Reason
1,3-Butadiene	TO-15	VW-139(10), 070109	0907205A-02A		2.5	ug/m3	False	UJ	The CCV was below the acceptable limits indicating a possible low bias.
1,3-Butadiene	TO-15	VW-139(15), 070109	0907205A-03A		2.6	ug/m3	False	UJ	The CCV was below the acceptable limits indicating a possible low bias.
1,3-Butadiene	TO-15	VW-139(20), 070109	0907205A-04A		5.3	ug/m3	False	UJ	The CCV was below the acceptable limits indicating a possible low bias.
1,3-Butadiene	TO-15	VW-139(30), 070109	0907205A-05A		5.2	ug/m3	False	UJ	The CCV was below the acceptable limits indicating a possible low bias.
1,3-Butadiene	TO-15	VW-139(5), 070109	0907205A-01A		4.4	ug/m3	False	UJ	The CCV was below the acceptable limits indicating a possible low bias.
Benzene	TO-15	VW-139(15), 070109	0907205A-03A	0.54	3.7	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Benzene	TO-15	VW-139(20), 070109	0907205A-04A	3	7.6	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Benzene	TO-15	VW-139(5), 070109	0907205A-01A	1.1	6.3	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Ethanol	TO-15	VW-139(10), 070109	0907205A-02A		8.6	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
Ethanol	TO-15	VW-139(15), 070109	0907205A-03A		8.8	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
Ethanol	TO-15	VW-139(20), 070109	0907205A-04A		18	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
Ethanol	TO-15	VW-139(30), 070109	0907205A-05A		18	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
Ethanol	TO-15	VW-139(5), 070109	0907205A-01A		15	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
Ethylbenzene	TO-15	VW-139(10), 070109	0907205A-02A	4.2	5	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.

Analyte	Method	Field Sample ID	Lab Sample ID	Result	Limit	Units	Detect Flag	Reviewer Qualifier	Reviewer Qualifier Reason
Ethylbenzene	TO-15	VW-139(20), 070109	0907205A-04A	2.2	10	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Ethylbenzene	TO-15	VW-139(5), 070109	0907205A-01A	3.8	8.6	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Isopropanol	TO-15	VW-139(20), 070109	0907205A-04A	3600	23	ug/m3	True	J	The ICV was above the acceptable limits indicating a possible high bias.
Isopropanol	TO-15	VW-139(30), 070109	0907205A-05A	2700	23	ug/m3	True	J	The ICV was above the acceptable limits indicating a possible high bias.
Isopropanol	TO-15	VW-139(5), 070109	0907205A-01A	2700	19	ug/m3	True	J	The ICV was above the acceptable limits indicating a possible high bias.
m,p-Xylene	TO-15	VW-139(20), 070109	0907205A-04A	3.1	10	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
m,p-Xylene	TO-15	VW-139(5), 070109	0907205A-01A	1.7	8.6	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Toluene	TO-15	VW-139(15), 070109	0907205A-03A	0.89	4.4	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
Toluene	TO-15	VW-139(20), 070109	0907205A-04A	5	9	ug/m3	True	J	Flagged by the Lab: Result between MDL and RL.
1,2,4-Trichlorobenzene	TO-15	OA-1,070109	0907205B-06A		6.4	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
Acetone	TO-15	OA-1,070109	0907205B-06A	230	2	ug/m3	True	J	The ICV was above the acceptable limits indicating a possible high bias.
Hexachlorobutadiene	TO-15	OA-1,070109	0907205B-06A		9.2	ug/m3	False	UJ	The LCS and/or LCSD recovery(ies) were below the acceptable limits indicating a possible low bias.
MTBE	TO-15	OA-1,070109	0907205B-06A		0.62	ug/m3	False	UJ	The CCV was below the acceptable limits indicating a possible low bias.