

## Appendix E – Laboratory Analyses Quality Assurance

### 1.0 Quality Assurance Program Plan

The quality assurance methods (precision and accuracy evaluations) were conducted to ensure accurate results were obtained and the method applied varied by type of parameter evaluated. For the criteria pollutants (PM<sub>2.5</sub>, SO<sub>2</sub>, CO) quality assurance was primarily conducted in the field since measurements were made with continuous monitoring instruments. In-house quality assurance was performed by comparing the results for the criteria pollutants and meteorological parameters with data from other monitors in the state. For the VOCs and carbonyls the quality assurance requirements outlined in the QAPP were used and are discussed in further detail in (this Appendix) Section 3.0.

The BAQS participates in USEPA's National Air Toxics Trends System (NATTS) and follows the guidelines outlined the Technical Assistance Document (USEPA 2007) for quality assurance evaluations. Some discrepancies between the QAPP (Table A.7.1) and procedures outlined in the NATTS program were identified. A revised table (**Table E1**) correcting the discrepancies and the changes are discussed below.

A precision and accuracy evaluation was conducted on all three criteria pollutants (the QAPP reported only evaluations for PM<sub>2.5</sub>) and the acceptance threshold applied for both types of evaluations was +/- 10%.

For the VOCs and carbonyls, the accuracy thresholds set by the NATTS performance program (accuracy evaluation) were used and are shown in **Table E1**.

**Table E1** Study Data Quality Indicators and Expected Metrics

Parameter	Availability	Precision	Accuracy	Sensitivity
Volatile organic compounds	>75%	+/- 25%	+/- 25%	100 pptv
Carbonyls	>75%	+/- 25%	+/- 25%	100 pptv
Fine particulate matter (PM <sub>2.5</sub> )	>75%	+/- 10%	+/- 10%	100 ng/m <sup>3</sup>
Sulfur dioxide (SO <sub>2</sub> )	>75%	+/- 10%	+/- 10%	0.1 ppb
Carbon monoxide (CO)	>75%	+/- 10%	+/- 10%	0.02 ppm
Meteorological parameters	>75%			

Units: pptv = parts per trillion volume, ppbv = parts per billion volume, ppmv = parts per million volume, ng/m<sup>3</sup> = nanograms per cubic meter.

#### 1.1 Data Availability

The overall data availability for the Study was high as shown in **Table B2**, exceeding the QAPP target of 75% and greater than the NATTS requirement of 85%.

**Table E2** Percent Data Availability<sup>1</sup> by Sites

Parameter	BISP	BTRS	GIBI	SPWT
Canister Samples	95	97	93	95
Carbonyl Samples	92	93	92	95
TEOM (Continuous PM <sub>2.5</sub> )	97	98	93	96
Carbon Monoxide (CO)		98		
Sulfur Dioxide (SO <sub>2</sub> )		97		
Collocated Canister Samples				
Collocated Carbonyl Samples				
<b>Meteorological Parameters</b>	<b>BISP</b>			
Wind Speed	95			
Wind Direction	95			
Relative Humidity	99			
Barometric Pressure	95			
Temperature	99			

## 2.0 Quality Assurance – Criteria Pollutants and Meteorological Parameters

### Criteria Pollutants

The criteria pollutants were monitored using continuous instruments. Therefore, precision and accuracy checks were conducted in the field. Results for these checks have been reported to USEPA’s Air Quality System and only a summary is provided in this report.

#### *PM<sub>2.5</sub>*

PM<sub>2.5</sub> results were graphed to verify that the data were within expected range of values as compared to results obtained from the Buffalo and Niagara Falls monitors.

Precision checks for the TEOM instruments were conducted monthly by the field operator and consist of an instrument flow rate and temperature check. The results of these two precision checks on all four instruments were within the 10% acceptance limit.

Accuracy checks are an independent audit conducted on a bi-annual basis. Staff from the Department’s Bureau of Quality Assurance conducted these tests using a different device than the one used by the field operator. These checks verify instrument flow rate and temperature. The results of the accuracy checks on all four instruments were within the 10% acceptance limit.

#### *Carbon monoxide*

<sup>1</sup> Data availability is calculated based on the number of valid samples collected during the Study period.

Carbon monoxide results were graphed to verify that the data were within expected range of values as compared to results obtained from the Buffalo and Niagara Falls monitors.

Precision checks on the CO instruments were conducted by the field operator and include a zero and span check every week. Every two weeks the field operator conducts an additional precision check by challenging the instrument with CO gas at concentrations near the National Ambient Air Quality Standard (NAAQS). Results of the precision checks were within 4%, well below the 10% acceptance limit.

The accuracy check is a multi-point audit performed quarterly by field operators using the same equipments as the precision checks. Twice a year, staff in the Department's Quality Assurance Bureau perform a multi-point audit using a different device than the one used by the field operator. All precision checks are included in the multi-point audit. Results of the precision checks were within 4%, well below the 10% acceptance limit.

#### *Sulfur dioxide*

Sulfur dioxide results were graphed to verify that the data were within expected range of values obtained from the Buffalo and Niagara Falls monitors.

Precision checks on the SO<sub>2</sub> instruments were conducted by the field operator and include a zero and span check every week. Every two weeks the field operator conducts an additional precision check by challenging the instrument with SO<sub>2</sub> gas at concentrations near the NAAQS. Results of the precision checks were within 4%, well below the 10% acceptance limit.

The accuracy check is a multi-point audit performed quarterly by field operators using the same equipment as the precision checks. Twice a year, staff in the Department's Bureau of Quality Assurance perform a multi-point audit using a different device than the one used by the field operator. All precision checks are included in the multi-point audit. Results of the precision checks were within 4%, well below the 10% acceptance limit.

### **Meteorological Parameters**

Meteorological parameters were graphed to verify that the data are within expected values as compared with data obtained from Buffalo and Niagara Falls monitors.

## **3.0 Quality Assurance – VOCs and Carbonyls**

Quality assurance evaluations for VOCs and carbonyls include precision and accuracy analysis, sensitivity testing and checks for interferences (blanks).

### **3.1 Precision – Replicate Analysis and Collocated Sampling Results**

Precision refers to agreement between independent measurements performed according to identical protocols and procedures and applies to both sample collection and laboratory analysis. To evaluate laboratory precision, samples collected from the GIBI site were analyzed twice. The first analysis is labeled "primary" and the subsequent analysis of

this sample is a “replicate”. To evaluate overall sample precision, which includes collection and laboratory analysis, a second canister and cartridge sample were collected at the GIBI site. These second samples (called collocated) were handled by field and laboratory personnel using the same protocols as the primary samples. Both types of precision measurements are assessed by calculating a percent difference (PD)<sup>2</sup> for results obtained at concentrations greater than five times the method detection limit. Comparisons within +/- 25% PD are considered acceptable.

**Results for VOCs Samples**

Of the 53 samples<sup>3</sup> (22%) replicated, the acceptance threshold for precision was demonstrated across all analysis runs, although some individual analytes exceeded the threshold. Therefore, no corrective actions were implemented.

Of the 53 samples (22%) collocated, the acceptance threshold for precision was demonstrated across all analysis runs, although some individual analytes exceeded the threshold. Therefore, no corrective actions were implemented.

**Table E3** summarizes the replicates and collocated results. Exceedance of the threshold was found for a number of acrolein<sup>4</sup> comparisons. These results are not surprising given that acrolein is a difficult air toxic to measure accurately. We have elected to report the results but the risk evaluation<sup>5</sup> with acrolein will be noted as an estimate.

**Table E3** VOC Precision Exceedances

VOC	Replicates	Collocated
1,3-Butadiene		1
Acrolein	6	13
Benzene		1
Dichlorofluoromethane		1
m,p-Xylene		2

<sup>2</sup> Percent difference is expressed as the difference between two measurements divided by the average, expressed as a percent. NATTS recommends a relative percent difference for precision calculations. We have opted to show the direction of error as opposed to taking an absolute value.

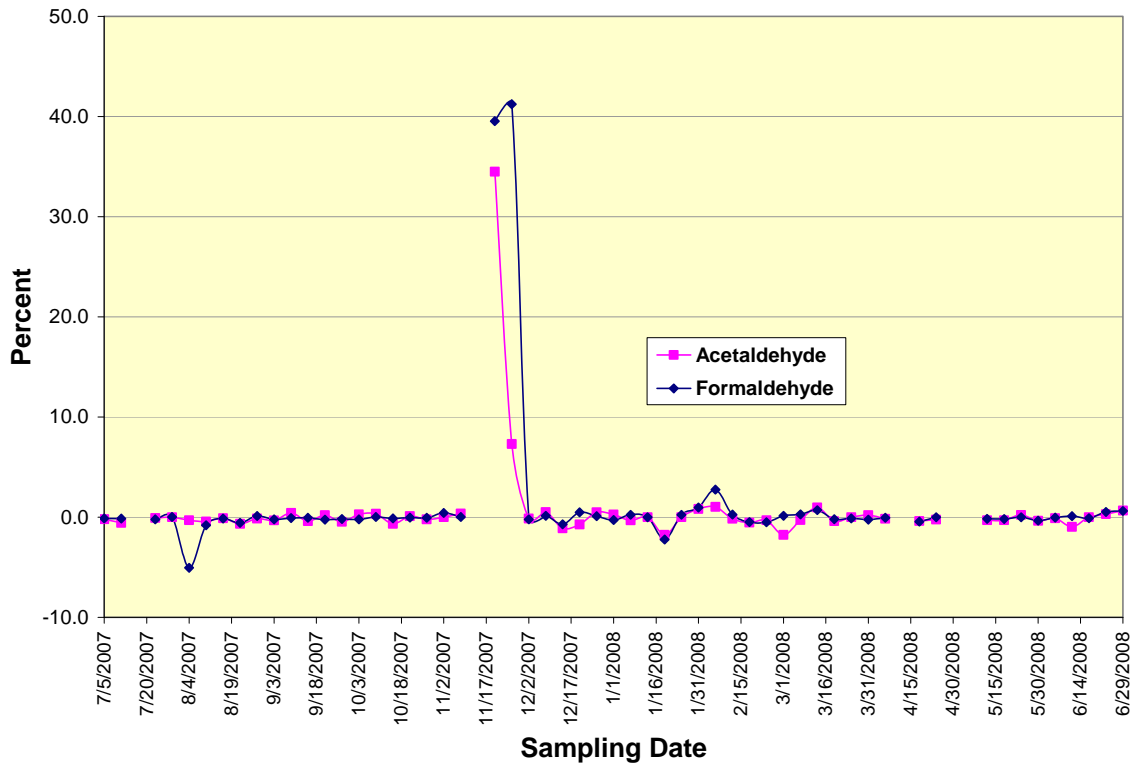
<sup>3</sup> We did not specify in the QAPP the number of replicate and collocated samples that would be obtained in this study. The NATTS requirement for VOC and carbonyl precision measurements is 10% of the samples obtained. We exceeded the NATTS requirement for all replicate and collocated sampling for both VOCs and carbonyls analysis.

<sup>4</sup> The determination of acrolein has inherent analytical and sampling issues cited by various state agencies during the implementation of acrolein by the NATTS program. The Varian Ion Trap has a very low response to acrolein as compared to most of the other analytes of interest. As an illustration, benzene has 15 times the response of acrolein at the same concentration. A subtle change in acrolein peak shape can result in a greater precision difference. Acrolein is a polar compound causing the analytical peak shape to broaden rather than being a tight Gaussian shaped peak. The polar nature of acrolein also causes reactivity in the presence of water associated with the humidity at the time of sampling. Samples are collected with a final pressure of 1 – 3 psi to reduce this affect. Canisters also have an affect on acrolein sampling. There may be a loss or gain of acrolein. Only glass lined canisters were used for sample collection to minimize this effect. The results from the collocated analysis show a possible canister effect.

<sup>5</sup> Section 7 - Public health interpretation of measured air concentrations

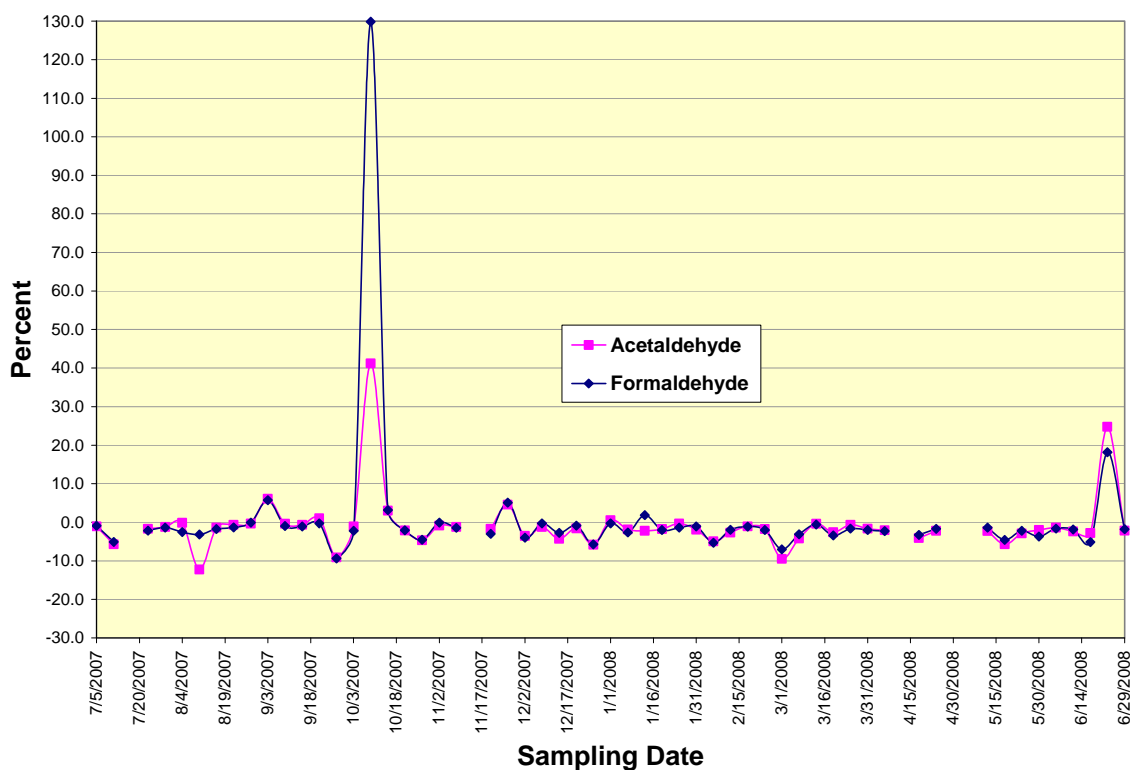
### Results for Carbonyl Samples

Twenty-three percent (57 samples) of the Study samples were replicated. Across the analysis runs, replicate comparisons demonstrated high precision. For the two carbonyls of interest, acetaldehyde and formaldehyde, **Figure E1** shows the individual comparison results. We focus on these two carbonyls since these are more commonly found in the urban environment at levels close to health comparison values. Corrective action was taken for the two dates outside the acceptance threshold. **Table E4** summarizes the results of the replicated analysis.



**Figure E1** GIBI Replicate Analysis Percent Difference Results

Twenty-three percent (57 samples) of the Study samples were collocated. Across the analysis runs, the collocated comparisons demonstrate high precision. **Figure E2** shows the results for acetaldehyde and formaldehyde. The collocated samples collected on two exceedance dates, appeared to be handled consistent with the primary sample. Therefore, no further actions were taken. The graph demonstrates that these two aldehydes track one another and shows a consistent negative bias, most likely the result of minor flow rate differences between the two sampling systems. **Table E4** summarizes the results of the collocated analysis.



**Figure E2** GIBI Collocated Analysis Percent Difference Results

**Table E4** Summary Carbonyl Replicate and Collocated Results

Carbonyl	Replicates	Collocated
2-Butanone	2	1
Acetaldehyde	1	1
Benzaldehyde	3	3
Crotonaldehyde	1	1
Formaldehyde	2	1
Hexanal	0	0
Methacrolein	0	0
m-Tolualdehyde	1	0
n-Butyraldehyde	0	2
Propionaldehyde	2	1
Valeraldehyde	1	7

### 3.2 Accuracy – Proficiency Testing

Accuracy is defined as the degree of agreement between the laboratory analytical (observed) concentration and the actual (true) concentration. The BAQS laboratory participates in the NATTS program which includes a periodic evaluation of the laboratory’s accuracy through testing of VOC and carbonyl proficiency samples.

Accuracy is assessed by calculating a percent error from the true value<sup>6</sup> and comparisons within +/- 25% are considered acceptable.

### Volatile Organic Compounds

The NATTS proficiency tests do not include all compounds which are included in the Study. The proficiency tests results before, during and after the Study are shown in **Table E5**. Ninety-one percent of the results are within acceptable limits and this illustrates the strength of BAQS' laboratory performance in the NATTS proficiency testing program.

**Table E5** NATTS Proficiency Test Results for VOC Analysis (expressed as percent)

Chemical	January 2007	February 2007	March 2007	April 2007	January 2008	January 2009
1,1,2,2-Tetrachloroethane	-16.7	3.7	0	0	-4.3	-3.1
1,2-Dibromoethane	-4.2	2	-12	-6.6	-6.6	13.5
1,2-Dichloroethane	0	1.8	-8.5	-6.2	-11.6	13.7
1,2-Dichloropropane	9.2	7.1	2.5		-3	11.6
1,3-Butadiene	3.6	-16.6	-2.5	-3.9	29.3 (O)	24.8 (W)
Acrolein	25.5 (O)	-32.9 (O)	-11.9	8.4	-23.7 (W)	-4.9
Benzene	2.6	3.1	-7.5		-9.2	-4.3
Carbon tetrachloride	-10.6	0.9	-5.9	-31.6 (O)	-28.6 (O)	-7
Chloroform	0	2	-14.7		-2.9	12.8
cis-1,3-Dichloropropene	2.9	6.8	5.4		-1.6	18.5
Dichloromethane	10	-4.4	12	8	-16.2	6.9
Tetrachloroethylene (PERC)	7.9	3.1	-2.5		-3	8.9
trans-1,3-Dichloropropene	-9.2	1.2	-1.4		-8.3	20.6 (W)
Trichloroethylene	-4.1	-0.9	0.8	3.1	-10.5	12.5
Vinyl chloride	-4.3	-6.7	0		0	9.9

Codes: (W) Warning +/- 20%, (O) Outside Control Limits +/- 25%  
Blank cells indicate VOC not included as analyte in proficiency testing.

### Carbonyls

The USEPA NATTS proficiency testing program periodically provides the laboratory with an unknown quantity of acetaldehyde and formaldehyde to extract and analyze. **Table E6** includes results for proficiency tests before, during and after the Study period. The NATTS audits suggest the laboratory accuracy improved over this period to approximately 10% (+/-) of the true value.

<sup>6</sup> Formula for percent error from true value = (true concentration - observed concentration) / (true concentration) × 100

**Table E6** NATTS Proficiency Test Results for Carbonyl Analysis (expressed as percent)

Chemical	April 2007	November 2007	April 2008	January 2009
Acetaldehyde	-21.2 (W)	-14.0	7.4	-8.0
Formaldehyde	-27.5 (O)	-18.8	10.4	-10.3

Codes: (W) Warning +/- 20%, (O) Outside Control Limits +/- 25%

### 3.3 Sensitivity – Method Detection Limit Evaluation

The sensitivity analysis expresses, the confidence of detecting an analyte's signal above background noise and is quantified through calculation of a method detection limit (MDL). The MDL is defined as the lowest value at which we can be 99% confident that the true concentration is nonzero as outlined in the *Code of Federal Regulations* (Title 40, Part 136, Appendix B, Revision 1.11).

There is less accuracy and precision with results obtained close to the MDL and data users are cautioned not to place too much reliance on these values. Background noise is a greater percentage of the total instrument signal when the measured result is near the MDL. Results in this range place greater emphasis on the technician's ability to separate the baseline noise from the instrument's response to an analyte's signal.

#### Volatile Organic Compounds

To verify the sensitivity of the analytical system, seven replicates of the TO-15 standard were analyzed on 12/18/2007 and 7/8/2008 and MDLs were derived<sup>7</sup> from these results. System linearity<sup>8</sup> was reconfirmed concurrently with the MDL evaluation. The MDL results were used in the precision assessment (discussed in Section 5.5.1). **Table E7** shows the comparisons between the MDL reported in the QAPP and the values obtained in the laboratory at each six month interval in the Study. As shown, all MDL evaluations met or surpassed the QAPP requirement.

**Table E7** MDL Evaluations for VOCs (ppbv)

Compound	QAPP MDL	12/18/2007 MDL	7/8/2008 MDL
1,1,1-Trichloroethane	0.04	0.01	0.01
1,1,2,2-Tetrachloroethane	0.04	0.01	0.01
1,1,2-Trichloroethane	0.05	0.01	0.02
1,1-Dichloroethane	0.04	0.01	0.01
1,1-Dichloroethylene	0.04	0.01	0.01
1,2,4-Trichlorobenzene	0.04	0.01	0.04
1,2,4-Trimethylbenzene	0.05	0.02	0.004
1,2-Dibromoethane	0.04	0.02	0.01

<sup>7</sup> MDL formula:  $[(3 \times \text{the standard deviation of 7 replicate analyses}) / (\text{the average of the same replicates})] \times (\text{the concentration of the analytes})$

<sup>8</sup> System linearity is consistent correspondence between sample concentration and instrument response.



Compound	QAPP MDL	12/18/2007 MDL	7/8/2008 MDL
1,2-Dichlorobenzene	0.05	0.01	0.01
1,2-Dichloroethane	0.03	0.01	0.01
1,2-Dichloroethylene	0.04	0.02	0.01
1,2-Dichloropropane	0.05	0.02	0.02
1,3,5-Trimethylbenzene	0.06	0.01	0.01
1,3-Butadiene	0.03	0.02	0.02
1,3-Dichlorobenzene	0.05	0.01	0.01
1,4-Dichlorobenzene	0.05	0.01	0.02
A-chlorotoluene (Benzylchloride)	0.06	0.01	0.02
Acrolein <sup>a</sup>	0.03	--	--
Benzene	0.05	0.02	0.01
Bromodichloromethane	0.05	0.01	0.01
Bromomethane	0.04	0.01	0.01
Carbon disulfide <sup>a</sup>	0.03	--	--
Carbon tetrachloride	0.05	0.01	0.01
Chlorobenzene	0.04	0.01	0.01
Chloroethane	0.05	0.03	0.02
Chloroform	0.04	0.01	0.01
Chloromethane	0.07	0.02	0.03
cis1,3-Dichloropropylene	0.05	0.01	0.01
Dichlorodifluoromethane	0.04	0.01	0.01
Dichloromethane	0.02	0.02	0.01
Dichlorotetrafluoroethane	0.03	0.01	0.004
Ethylbenzene	0.07	0.01	0.01
Hexachloro-1,3-butadiene	0.06	0.02	0.01
m,p-Xylene	0.12	0.02	0.01
Methyl tert butyl ether	0.05	0.01	0.01
o-Xylene	0.05	0.01	0.01
Styrene	0.1	0.01	0.01
Tetrachloroethylene	0.04	0.01	0.01
Toluene	0.05	0.01	0.01
trans1,3-Dichloropropylene	0.04	0.01	0.01
Trichloroethylene	0.05	0.01	0.01
Trichlorofluoromethane	0.04	0.01	0.01
Trichlorotrifluoroethane	0.05	0.01	0.01
Vinyl Chloride	0.07	0.01	0.01

<sup>a</sup> Acrolein and carbon disulfide are not among the 42 target compounds in the NYS Toxics Air Monitoring Network. MDL checks for these two compounds were not conducted at the two six-month intervals.

### Carbonyls

For the carbonyls, sensitivity analysis considers all dilutions and concentrations resulting from the sample extraction (preparation) process and instrument analysis. The results are expressed in terms of ambient air concentration by assuming that a total volume of air of

1440 liters was collected for a twenty-four hour sample. Variable analytical inputs include final extract volume (5.0 mL) and injection volume (20 µL).

The MDL evaluations are shown in **Table E8** and most surpass the QAPP requirement. For the two carbonyls of primary interest, acetaldehyde and formaldehyde, the QAPP specifications were unmet for at least one of the sensitivity checks. However, since these two compounds were found in all samples collected at levels well above the MDL, no further actions were necessary.

**Table E8** MDL Evaluations for Carbonyls (ppbv)

Compound	QAPP MDL	March 2008 MDL	November 2008 MDL
2-Butanone	0.009	0.006	0.008
Acetaldehyde	0.004	0.01	0.01
Benzaldehyde	0.004	0.004	0.001
Crotonaldehyde	0.009	0.006	0.006
Formaldehyde	0.007	0.015	0.006
Hexanal	0.008	0.004	0.002
Methacrolein	0.005	0.006	0.002
m-Tolualdehyde	0.003	0.003	0.001
n-Butyraldehyde	0.007	0.006	0.004
Propionaldehyde	0.004	0.006	0.002
Valeraldehyde	0.011	0.003	0.003

### 3.4 Interferences - Blank Evaluations

Control over sample contamination is essential when attempting to measure concentrations at the parts-per-billion or parts-per-trillion level. Contamination arises from principally four sources: the environment from which the sample was collected and/or analyzed, the reagents used in the analysis, the apparatus used, and introduction by staff performing the analysis. The potential for sample contamination interferences are possible at any stage of sampling and/or analysis and determining the source is achieved through evaluation of blank samples. The laboratory routinely incorporates a number of blank samples into its quality assurance program, including cleaning (VOCs only), field (carbonyls only), lot (carbonyls only) and lab blanks.

### Volatile Organic Compounds

**Cleaning Blank:** One canister was selected from a cleaning batch of 10 for each quarter of the Study. **Table E9** shows the maximum result for each quarter. As demonstrated, the pre-deployment acceptance criterion of 0.2 ppbv for any target compound or three times the detection limit of the compound, whichever is higher<sup>9</sup> has been met in all cases.

<sup>9</sup> Although both pre-deployment cleaning criteria were referenced in the QAPP, the integration of the two as specified in the NATTS Technical Document (USEPA 2007) was not stated.

**Table E9** Summary Results Quarterly Cleaning Blanks

Compound Name	MDL (ppbv)	3rd Quarter 2007 Max (ppbv)	4th Quarter 2007 Max (ppbv)	1st Quarter 2008 Max (ppbv)	2nd Quarter 2008 Max (ppbv)
1,1,1-Trichloroethane	0.04	0.022	0.010	0.024	0.018
1,1,2,2-Tetrachloroethane	0.05	0.025	0.014	0.028	0.031
1,1,2-Trichloroethane	0.05	0.024	0.010	0.000	0.025
1,1-Dichloroethane	0.04	0.023	0.022	0.022	0.018
1,1-Dichloroethylene	0.04	0.024	0.009	0.023	0.017
1,2,4-Trichlorobenzene	0.06	0.039	0.050	0.033	0.070
1,2,4-Trimethylbenzene	0.06	0.028	0.010	0.027	0.126
1,2-Dibromoethane	0.04	0.028	0.010	0.021	0.020
1,2-Dichlorobenzene	0.04	0.022	0.014	0.026	0.037
1,2-Dichloroethane	0.03	0.020	0.009	0.022	0.015
1,2-Dichloroethylene	0.04	0.023	0.010	0.022	0.024
1,2-Dichloropropane	0.05	0.021	0.009	0.017	0.021
1,3,5-Trimethylbenzene	0.05	0.026	0.008	0.027	0.081
1,3-Butadiene	0.03	0.028	0.011	0.021	0.018
1,3-Dichlorobenzene	0.05	0.019	0.011	0.023	0.036
1,4-Dichlorobenzene	0.05	0.077	0.019	0.089	0.039
aChlorotoluene	0.05	0.016	0.009	0.023	0.061
Benzene	0.05	0.030	0.031	0.021	0.026
Bromodichloromethane	0.05	0.021	0.007	0.019	0.015
Bromomethane	0.04	0.021	0.009	0.020	0.022
Carbon tetrachloride	0.05	0.021	0.011	0.021	0.017
Chlorobenzene	0.04	0.024	0.011	0.021	0.020
Chloroethane	0.05	0.000	0.000	0.000	0.150
Chloroform	0.04	0.022	0.009	0.022	0.012
Chloromethane	0.07	0.022	0.029	0.000	0.042
cis1,3-Dichloropropylene	0.05	0.017	0.008	0.020	0.020
Dichlorodifluoromethane	0.04	0.023	0.010	0.020	0.022
Dichloromethane	0.02	0.067	0.143	0.000	0.011

<b>Compound Name</b>	<b>MDL (ppbv)</b>	<b>3rd Quarter 2007 Max (ppbv)</b>	<b>4th Quarter 2007 Max (ppbv)</b>	<b>1st Quarter 2008 Max (ppbv)</b>	<b>2nd Quarter 2008 Max (ppbv)</b>
Dichlorotetrafluoroethane	0.03	0.024	0.009	0.000	0.017
Ethylbenzene	0.07	0.025	0.009	0.023	0.024
Hexachloro1,3Butadiene	0.024	0.017	0.015	0.043	0.033
m,p-Xylene	0.12	0.046	0.016	0.051	0.056
Methyl tert butyl ether	0.05	0.016	0.005	0.019	0.010
o-Xylene	0.06	0.024	0.010	0.026	0.028
Styrene	0.04	0.023	0.007	0.019	0.033
Tetrachloroethylene	0.04	0.022	0.009	0.023	0.023
Toluene	0.05	0.028	0.016	0.023	0.023
trans1,3-Dichloropropylene	0.04	0.029	0.008	0.020	0.022
Tribromomethane	0.10	0.019	0.008	0.019	0.015
Trichloroethylene	0.05	0.021	0.009	0.022	0.023
Trichlorofluoromethane	0.04	0.012	0.005	0.012	0.018
Trichlorotrifluoroethane	0.05	0.016	0.019	0.022	0.014
Vinyl chloride	0.07	0.021	0.013	0.019	0.013

Footnote: The maximum quarterly result for each compound has been displayed to illustrate that each run meet pre-deployment acceptance criteria.

Lab Blank: Blanks were generated in the GC/MS system by sampling pure nitrogen through the cryogenic trap. These checks assure no carryover during the batch analysis process. No interferences were identified during these checks.

### **Carbonyls**

Lot blanks: To assure carbonyl adsorbent tubes are suitable for use, tubes are tested and certified prior to use. Upon arrival of each shipment, three lot blanks were randomly selected from the shipment and were analyzed using normal procedures. A cartridge certificate of analysis is received with each batch lot and this was verified against the method quality control criteria. All cartridges were found acceptable for use upon receipt and the background method blank results closely matched cartridge contamination levels stated by the manufacturer.

Field blanks: The two aldehydes of primary concern, acetaldehyde and formaldehyde, were found in blanks well below thresholds of concern. Acetaldehyde and formaldehyde sample concentrations were approximately 50 and 100 times, respectively, of blank concentrations as illustrated in **Table E10**. The lowest sample concentration was at an order of magnitude higher than the blanks, indicating that the blanks were not an analytical interference. No other target analytes were found in the blanks.

**Table E10** Results of the Field Blank Evaluation for Acetaldehyde and Formaldehyde

<b>Parameter</b>	<b>Acetaldehyde (ppbv)</b>	<b>Formaldehyde (ppbv)</b>
Average blank	0.008	0.013
Maximum blank value	0.009	0.017
Standard deviation	0.000978	0.00373
3 Sigma blank QC limit	0.011	0.024
Lowest sample result	0.176	0.221

## **4.0 Data Review and Assessment**

### **Volatile Organic Compounds**

The results were reviewed by importing the data into USEPA's VOCdat software for analysis. This software allows a reviewer to assess the data for consistency by plotting a time based graph and facilitates sample to sample or analyte to analyte comparisons.

VOC results were reviewed quarterly by graphing each individual site and combining all four sites. VOCs with common sources such as automotive exhaust and those known to

be ubiquitous<sup>10</sup> were compared. Additionally, the Study data were compared to historical and concurrent data from other industrial, urban and rural sites in the State's air toxics monitoring network. Summary statistics were prepared (e.g., range, mean, median and standard deviation) for each VOC. Anomalies were noted and the raw data reviewed for errors. In cases where errors were confirmed, the results were flagged.

An example of a comparison with ubiquitous VOCs at the State's background monitor (Whiteface Mountain) is shown in **Table E11**. The results for the Whiteface monitor are similar to the levels found at all Study site monitors. This comparison adds an extra level of validity to the data set.

**Table E11** Annual Average Concentrations of Ubiquitous Compounds

Compound	Whiteface 2007 (ppbv)	Whiteface 2008 (ppbv)	BISP (ppbv)	BTRS (ppbv)	GIBI (ppbv)	SPWT (ppbv)
Carbon tetrachloride	0.098	0.093	0.11	0.11	0.11	0.11
Chloromethane	0.51	0.53	0.53	0.48	0.48	0.48
Dichlorodifluoromethane	0.53	0.54	0.53	0.53	0.53	0.53
Trichlorofluoromethane	0.16	0.23	0.18	0.18	0.18	0.18
Trichlorotrifluoroethane	0.076	0.081	0.10	0.09	0.08	0.08

### Carbonyls

The results were reviewed by importing the data into USEPA's VOCdat software for analysis.

A 2008, laboratory audit revealed analytical problems which compromised sample validity for samples analyzed from, July 5, 2007 through September 21, 2007. A retention time shift in samples caused later eluting compounds<sup>11</sup> to be misidentified and resulted in unrecoverable data loss. Consequently, the laboratory discarded results of the later eluting compounds. Two early eluting compounds, acetaldehyde and formaldehyde were unaffected because the retention time shift had not moved their peaks outside the identification window and these results were determined to be valid. Samples collected September 27, 2007 and forward were unaffected.

In February 2008, a new HPLC replaced the older unit. For three consecutive sampling dates, samples were run on both instruments for comparison to verify the new instrument would provide comparable results.

<sup>10</sup> Ubiquitous VOCs are those with little variability across the statewide network such as carbon tetrachloride, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and trichlorotrifluoroethane.

<sup>11</sup> Later eluting carbonyls are heavier in weight which is the following in our Study: 2-butanone, benzaldehyde, crotonaldehyde, hexanal, m-Tolualdehyde, methacrolein, n-Butyraldehyde, propionaldehyde, and valeraldehyde.