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NORTH CAROLINA
Environmental Quality

DAQ-03-004.5 Standard Operating Procedure (SOP)

Thermo Ultimate 3000 UHPLC-UV-MS Urban Air Toxics (UAT) and Photochemical Assessment Monitoring Station (PAMS) Carbonyl Analysis Instrument

for the North Carolina Division of Air Quality (DAQ)

Raleigh Central Office Responsibilities

NORTH CAROLINA
Department of Environmental Quality

1.0 APPROVAL SIGN-OFF SHEET

I certify that I have read and approve of the contents of the DAQ-03-004.5 Standard Operating Procedure for Thermo Ultimate 3000 UHPLC-UV-MS Urban Air Toxics (UAT) and Photochemical Assessment Monitoring Station (PAMS) Carbonyl Analysis Instrument RCO Responsibilities SOP written here with an effective date of February 18, 2022.

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DISCLAIMER:

This document, and any revision hereto, is intended solely as a reference guide to assist the user in the validation of UAT and PAMS Carbonyl sampling and analysis data for the DAQ's Ambient Monitoring Program.

ACRONYMS:

AQS - Air Quality System (EPA's Air database)
CAR – Corrective Action Report
CV – Coefficient of Variation
CFR – Code of Federal Regulations
Chief – Ambient Monitoring Section chief
DAQ - North Carolina Division of Air Quality
DAS – Data acquisition system
°C – Degrees Celsius
DEQ – North Carolina Department of Environmental Quality
DNPH – 2,4-dinitrophenylhydrazine
ECB – Electronics and Calibration Branch
EPA – United States Environmental Protection Agency
hr - hour
IPA – Instrument Performance Audit
KI – Potassium Iodide
LAB – Laboratory Analysis Branch
L – Liter
L/min – Liter/minute
LCL – lower control limit
MFC – Mass Flow Controller
MDL – Method detection limit
µg – Micrograms
µg/mL – micrograms per milliliter
mL – Milliliter
mm Hg – millimeters mercury
MQO – method quality objective
NATTS - National Air Toxics Trends Station
NIST – National Institute of Standards and Technology
PAMS – Photochemical Assessment Monitoring Station
POC – parameter occurrence code
PPB – Projects and Procedures Branch
ppbv – Parts Per Billion by Volume
PT – Proficiency Test
QA – Quality Assurance
QA/QC - Quality Assurance/Quality Control
QAPP - Quality Assurance Project Plan
QC – Quality control
RCO – Raleigh Central Office
RPD – Relative Percent Difference
SOP - Standard Operating Procedure
TAD – Technical Assistance Document
TSA - Technical Systems Audit
UAT – Urban Air Toxics
UCL – upper control limit
UHPLC – ultrahigh performance liquid chromatography
UV - ultraviolet

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2.0 SCOPE AND PURPOSE

The scope and purpose of this SOP is to describe the steps required to successfully perform Level 3 data validation of UAT and PAMS carbonyl sampling and analysis data and report this data to the United States Environmental Protection Agency's (EPA) Air Quality System (AQS).

3.0 OVERVIEW

This section describes the units of the sampling and analysis instrument data and conversions of units for AQS upload files.

3.1 Carbonyl Analysis Instrument Reporting Units

The ultrahigh performance liquid chromatography (UHPLC) concentration reporting units are in micrograms per milliliter (**µg/mL)**. Compound retention time reporting units are in **minutes**. Initial instrument quality control (QC) criteria are assessed the **µg/mL** and **minutes** units utilizing the data from the level 1 and level 2 approved UHPLC instrument amount summary reports, and the quality assurance (QA) summary reports. The data analysis and level 1 and level 2 review processes are described in more detail in **DAQ-03-004.2**.

3.2 Carbonyl Sampler Reporting Units

The ATEC 2200 and ATEC 8000 sampling instruments, report flows in Liters per minute (**L/min)** and total sample volume in Liters **(L)**.

The mass flow controllers (MFCs) that regulate sampler flows, are calibrated with slope and intercept values that convert instrument flows to standard conditions (25 degrees Celsius (°C) and 760 millimeters mercury (mm Hg)). This flow is recorded by the sampler's processing unit during the sample event.

The carbonyl sampler MFC slope and intercept values are updated annually during the sampler certification process described in SOPs **DAQ-03-002.1** (ATEC 2200) and **DAQ-09-002.1** (ATEC 8000).

The ATEC carbonyl sampler also contains a heated potassium iodide (KI) coated copper tubing assembly that removes ozone from the sample steam before contact with the 2,4-dinitrophenylhydrazine (DNPH) cartridge. The KI denuder temperatures are recorded by the ATEC sampler operating system in **°C**.

3.3 Unit Conversions

Carbonyl concentration unit conversions and sample volume conversions are done automatically by equations and references imbedded in the Carbonyl Master Spreadsheet, document # **DAQ-03-012**.

Level 1 and Level 2 approved sampling volume data are entered into this spreadsheet in the units of **L** and analysis instrument data are entered with the units of **µg/mL.** The spreadsheet then converts the concentration measured by the analytical instrument to parts per billion by volume (**ppbv)** for every sample and QC sample that is extracted and analyzed.

Instrument calibration and QC check standard results not extracted through a DNPH cartridge are not included in the Carbonyl Master Spreadsheet. The instrument calibration and QC check standard results are summarized in the QA Summary report and analysis instrument data files.

3.4 Rounding Conventions

The UHPLC analysis instrument reports values rounded to the third decimal place in the chromatograms, and amount summary reports.

The ATEC samplers display volumes and flows rounded to the second decimal place which are recorded on the DNPH Cartridge Sampler Information Form **DAQ-16-009.**

Carbonyl concentrations reported to AQS are rounded to three decimal places.

3.5 AQS Pipe Delimited Files

Current units reported to AQS are **ppbv**, represented by AQS unit code "**008**". Please see **Figure 1** below for an example of a UAT Carbonyl AQS ready file (pipe delimited format) showing current AQS coding for site, parameter, duration, units, method, sample date, start time, concentration, null and/or qualifier codes.

Figure 1: UAT Carbonyl Pipe Delimited Text File

```
RD|I|37|183|0014|43502|3|7|008|202|20201205|00:00|1.550||||2|3|6|||||||||
RD|I|37|183|0014|43502|3|7|008|202|20201211|00:00|1.700||||2|3|6|||||||||
RD|I|37|183|0014|43502|3|7|008|202|20201217|00:00|1.198||||2|3|6|||||||||
RD|I|37|183|0014|43502|3|7|008|202|20201222|00:00|1.792||||2|3|6|||||||||
RD|I|37|183|0014|43502|3|7|008|202|20201223|00:00||BB|||||||||||||||
RD|I|37|183|0014|43502|3|7|008|202|20201229|00:00|1.871||||2|3|6|||||||||
```

Please see **Figure 2** below for an example of a PAMS Carbonyl AQS ready file (pipe delimited format) showing current AQS coding for site, parameter, duration, units, method, sample date, start time, concentration, null and/or qualifier codes. The current sampling and analysis AQS method code using the ATEC 2200 and ATEC 8000 samplers (with heated KI denuders) and UHPLC ultraviolet (UV) detection is "**202**".

Figure 2: PAMS Carbonyl Pipe Delimited Text File

```
RD|I|37|183|0014|43502|2|5|008|202|20210603|04:00|1.627|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210603|12:00|1.493|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210603|20:00|0.845|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210606|04:00|2.954|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210606|12:00|3.318|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210606|20:00|1.513|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210609|04:00|2.671|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210609|12:00|4.440|||||||||||||||
RD|I|37|183|0014|43502|2|5|008|202|20210609|20:00|2.165|||||||||||||||
```

Additionally, the parameter occurrence codes (POC) are assigned as follows: UAT carbonyls collected at the primary Millbrook site are POC 3; UAT carbonyls collected at the collocated Millbrook site are POC 4; UAT carbonyls collected at Candor are POC 3; PAMS carbonyl collected at Millbrook are POC 2

3.6 Carbonyl Compounds Reported to AQS

Please see **Table 1** for a list of carbonyl compounds, AQS parameter codes, and current laboratory reporting limits (ppbv) for both UAT and PAMS carbonyl samples. The reportable limit values listed below are derived from the design volume.

Table 1: Carbonyl Compounds and Reporting Limits

Parameter Description	AQS Parameter Code	UAT Carbonyl Lower Limit (ppbv)	UAT Carbonyl Upper Limit (ppbv)	PAMS Carbonyl Lower Limit (ppbv)	PAMS Carbonyl Upper Limit (ppbv)
Formaldehyde	43502	0.028	8.481	0.085	25.443
Acetaldehyde	43503	0.019	5.782	0.058	17.345
Propanal	43504	0.015	4.385	0.044	13.155
Crotonaldehyde	43528	0.036	3.634	0.109	10.901
2-Butanone (MEK)	43552	0.035	3.532	0.106	10.596
Methacrolein	43515	0.036	3.634	0.109	10.901
Butanal	43510	0.035	3.532	0.106	10.597
Benzaldehyde	45501	0.024	2.400	0.072	7.200
Valeraldehyde	43518	0.030	2.957	0.089	8.871
m-Tolualdehyde	45508	0.021	2.120	0.064	6.359
Hexanal	43517	0.025	2.543	0.076	7.628

UAT reporting limits are derived using a flow rate of 1.0 L/min for 24-hour sample periods, yielding 1440L of air sampled. PAMS reporting limits are derived using a flow rate of 1.0 L/min for 8-hour sample periods, yielding 480L of sampled air.

Due to the differences between the UAT sample design volume and the PAMS sample design volume, there are two sets of reporting limits for each method.

4.0 DATA VALIDATION GENERAL OVERVIEW

The Level 3 reviewer transfers the laboratory analysis results to the Level 3 validation spreadsheet and applies AQS null codes and qualifier flags that best describe the failure of laboratory analysis issues, sample collection issues, and Level 3 data validation bias and precision issues. Additionally, the Level 3 reviewer visualizes the carbonyl data to monitor for out of ordinary results that may warrant further investigation. Finally, every calendar quarter, the Level 3 reviewer transforms the carbonyl results into text files, specifically pipe delimited text files, which are uploaded by DAQ's database manager to AQS.

4.1 Carbonyl Data Transfer

UAT and PAMS carbonyl data are transferred from the carbonyl master spreadsheet to the carbonyl data validations spreadsheet. The carbonyl data transfer process cannot commence until the Level 1 and Level 2 data reviews are complete. The Level 2 reviewer contacts the Level 3 validator when the data are ready for final validation. Detailed procedures are described in **Section 5.1** of this document.

4.2 Time Series and Ratio Control Charts

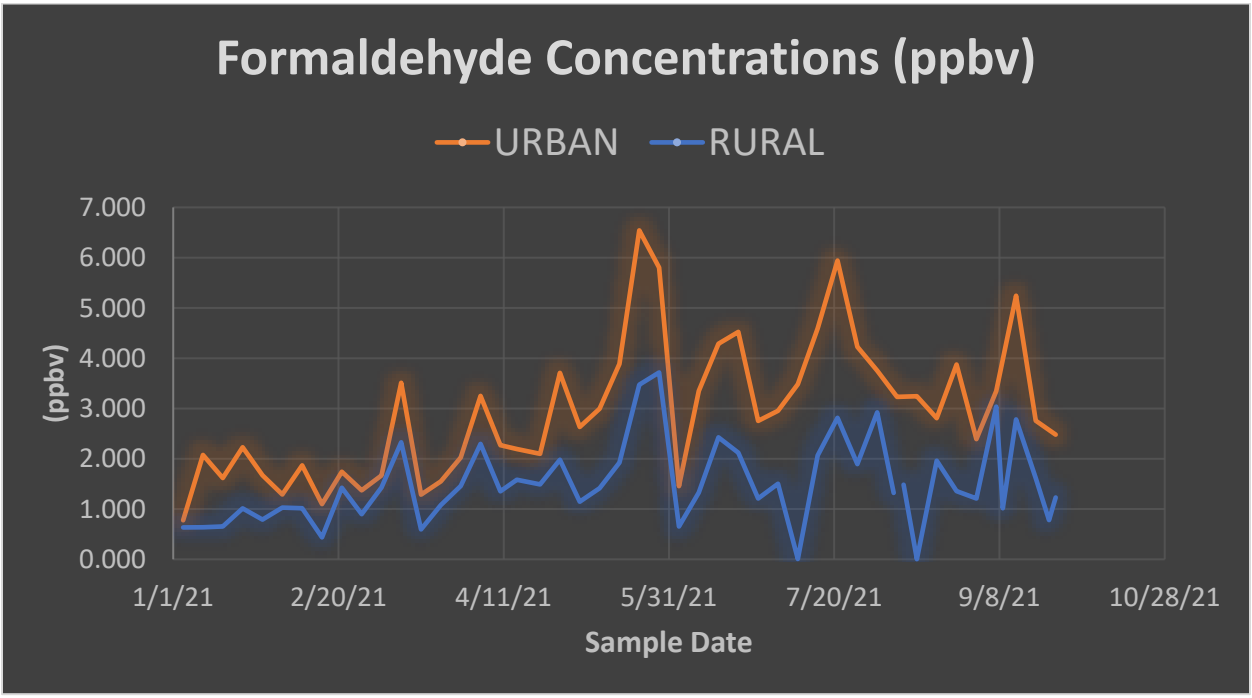
These charts are used to visually identify potential data outliers or extreme values that may require further investigation. These charts are not used to apply qualifier flags or null codes to the potential data point in question. However, the investigation to why the data outlier exists may lead to the application of a null code or qualifier flag.

Time series charts and stacked bar charts are generated and stored in the UAT and PAMS Carbonyl Data Validation Spreadsheet. Some of these charts are titled: urban vs. rural formaldehyde concentrations; formaldehyde vs acetaldehyde concentrations; and 8hr vs 24hr carbonyl concentrations. Detailed procedures on the generation of control charts are described in more detail in Section 5.3 of this document.

4.2.1 Urban and Rural Time Series Charts

Formaldehyde and acetaldehyde should be detected in all field-collected samples. Please see **Figure 3** below for an example of an urban vs. rural formaldehyde time series chart.

Figure 3: Urban and Rural Formaldehyde Time Series Chart



The intent of this chart is to quickly identify sampled cartridges where urban (Millbrook) and rural (Candor) formaldehyde concentrations do not follow the typical trend (Urban concentrations ≥ Rural concentrations). Deviations from this typical trend may indicate a sampling or analysis issue or indicate the sample was impacted by a nearby source. Additionally, instances where formaldehyde is close to 0.000 may indicate a sample collection issue.

4.2.2 Carbonyl Ratio Control Chart

Formaldehyde, acetaldehyde, and propionaldehyde should be present in all field-collected carbonyl cartridges. The ratio of formaldehyde to acetaldehyde should be ≥ 1 and the ratio of formaldehyde to propionaldehyde should be ≥ 10.

Ratios that fail their respective control limits are potentially impacted by contamination, matrix effects, or nearby sources and require a “second look” to determine if the data point should be null coded or qualified. In most cases, ratios that fail the control limits have already been null coded or qualified for failing one or more sampling and analysis measurement quality objectives.

See **Figure 4** below for a control chart of UAT and PAMS formaldehyde/acetaldehyde ratios. See **Figure 5** below for a control chart of UAT and PAMS formaldehyde/propionaldehyde ratios.

Figure 4: Formaldehyde and Acetaldehyde Ratio Chart

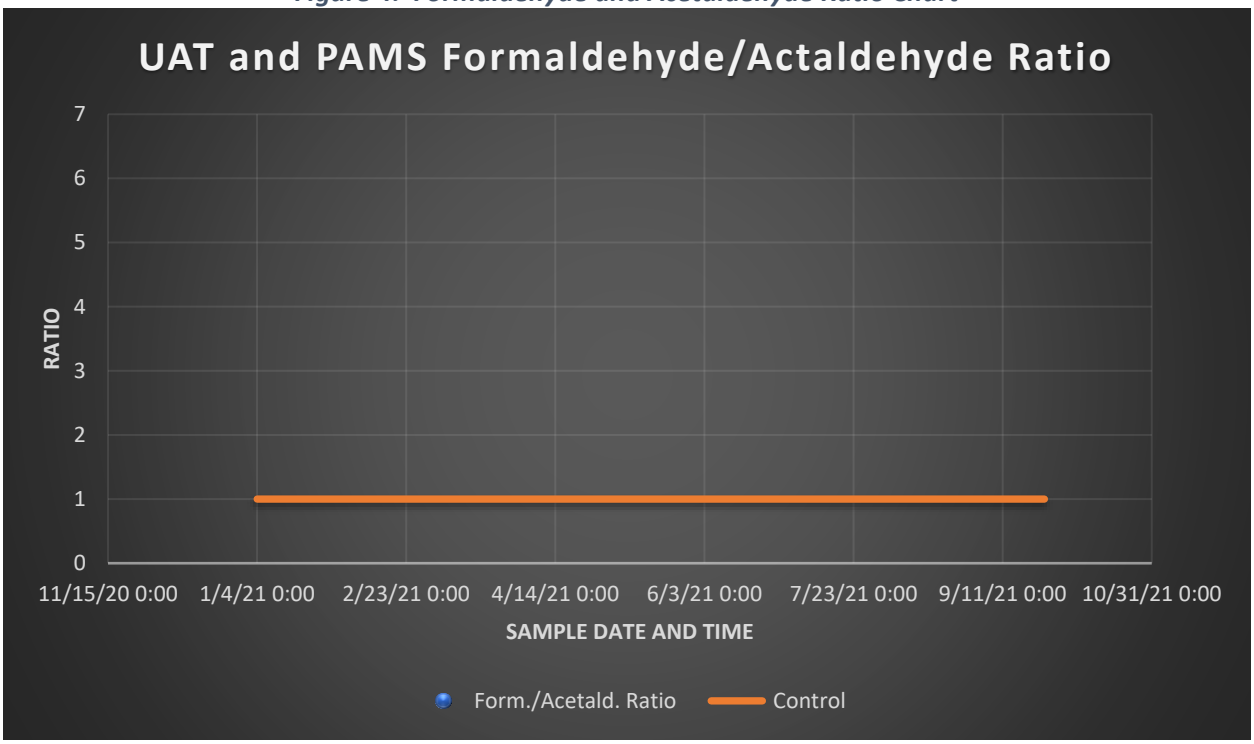
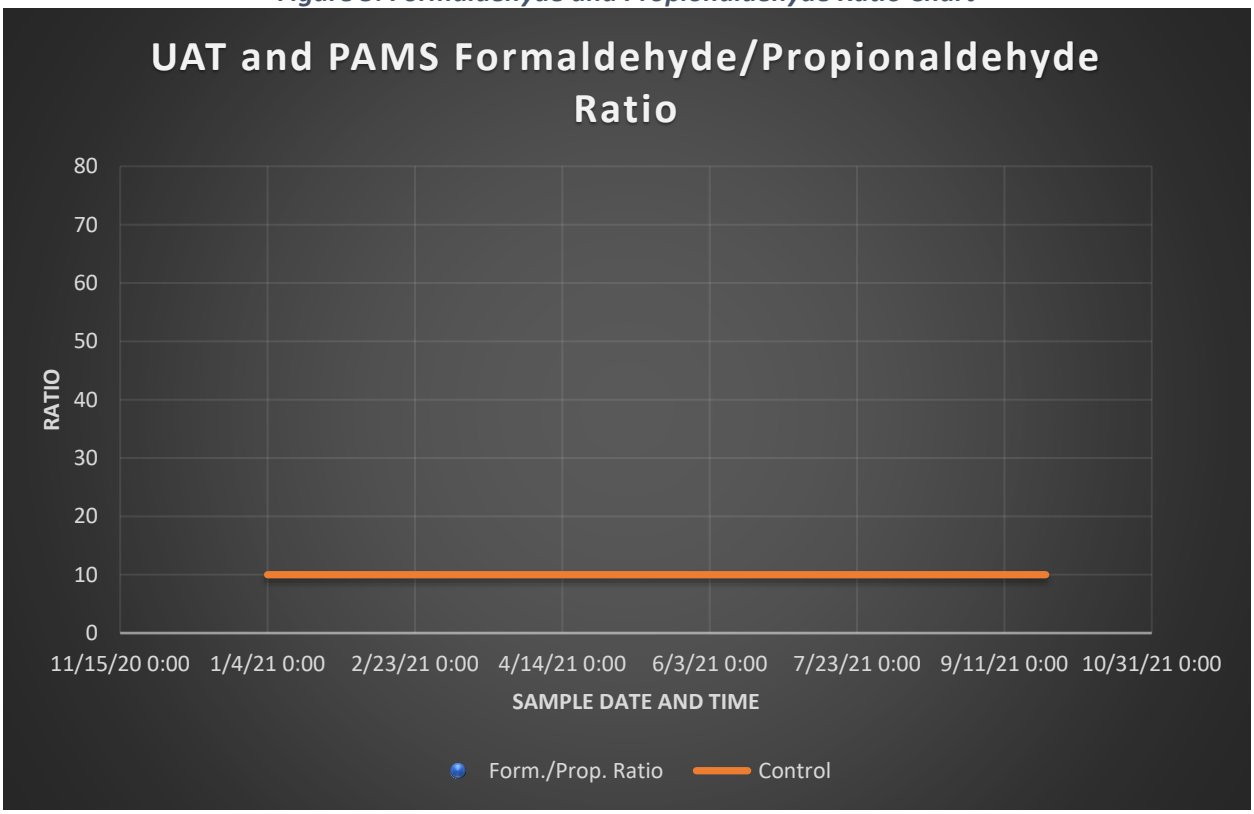


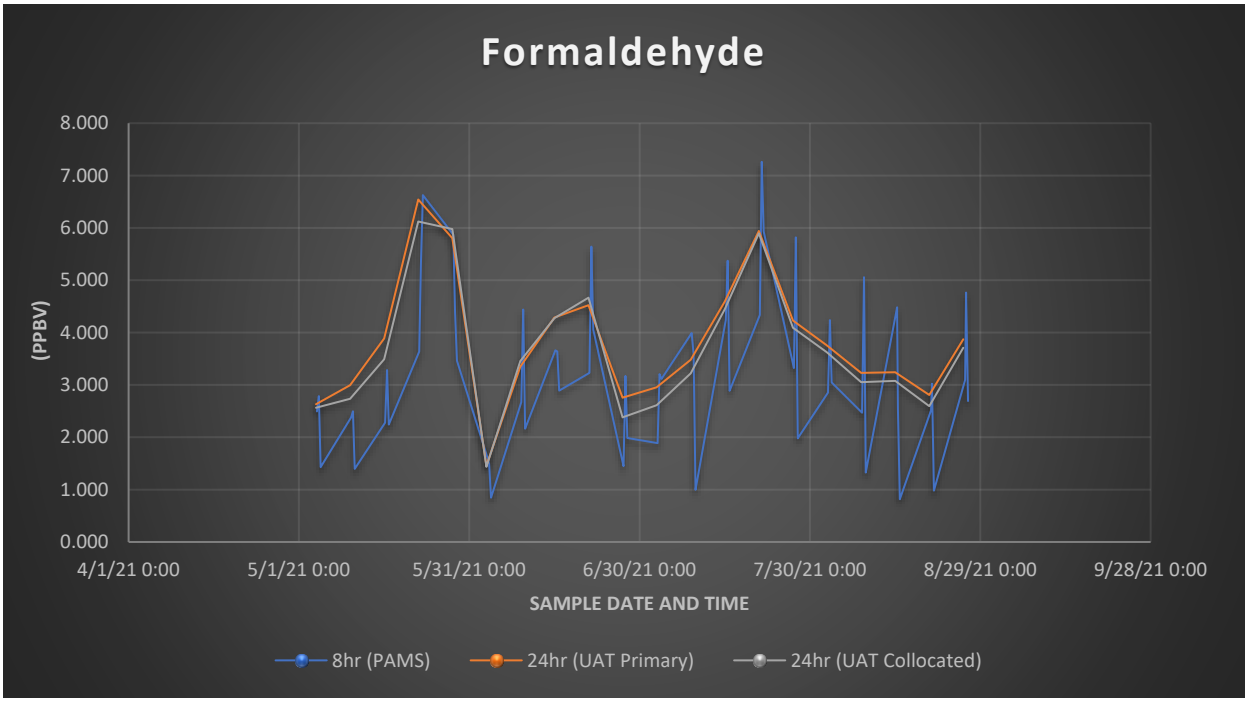
Figure 5: Formaldehyde and Propionaldehyde Ratio Chart



4.2.3 PAMS (8hr) and UAT (24hr) Carbonyl Concentrations

The 24-hour (hr) UAT primary and collocated carbonyl sample results overlayed with 8hr PAMS carbonyl sample results will show a trend where the 24hr results track between the minimum and maximum 8hr values. Also, the 24hr results and 8hr results should rise and fall together indicating matching peaks and valleys. Please see **Figure 6** below for a control chart of 8hr and 24hr formaldehyde concentrations in ppbv.

Figure 6: 8hr and 24hr Formaldehyde Time Series Chart



Extreme deviations between 8hr and 24hr results or separation between the primary and collocated results may indicate sampling or analysis issues.

4.3 Analysis Instrument Acceptance Criteria

QA summary reports, document number **DAQ-03-016**, are generated by the carbonyl analyst and undergo Level 1 and Level 2 review before being released to the Level 3 reviewer.

The QA summary report is generated with each analysis sequence and summarizes the within-run QC checks and displays compounds that fail the QC check including the type of flag that should be applied (null flag or qualifier flag).

Table 2: UAT and PAMS Carbonyl Analysis QC Criteria

Where to look for Flag	QC parameter	Flag Criteria	AQS Flag	How to apply Flag
Validation spreadsheet "Lot blank" workbook tab	Analysis of 3 cartridges from a newly received lot of DNPH cartridges	acetaldehyde ≤ 0.02 µg/mL; formaldehyde ≤ 0.03 µg/mL; acetone ≤ 0.06 µg/mL; all other individual compounds ≤ 0.02 µg/mL	QA qualifier: LB	Apply flag "LB" to failing carbonyls, apply to all DNPH cartridge lot# used to collect ambient samples
QA Summary "General QA" Lab Flag 1a	Solvent Blank	All target carbonyls must be ≤ MDLspk	QA qualifier: LB	Apply flag "LB" to failing carbonyl compounds detected in the analysis sequence
QA Summary "General QA" Lab Flag 2a	Method blank (CART BLK)	All target carbonyls must be ≤ MDL	QA qualifier: LB	Flag failing Carbonyls with Qualifier flag LB
QA Summary "General QA" Lab Flag 2b	Field Blank Cartridge Analysis	Formaldehyde ≤ 0.06 µg/mL Acetone ≤ 0.15 ug/mL; Acetaldehyde ≤ 0.08 ug/mL; Sum of All other ≤ 1.4 ug/mL	QA qualifier: FB	Flag failing Carbonyls with Qualifier flag FB
QA Summary "General QA" Lab Flag 3a	Calibration Curve QA	Linear fit with offset; Correlation Coefficient ≥ 0.999 to pass	Null: AT	Void failing compounds with Null Code AT
QA Summary "Flag3b CAL Curve Relative Error" workbook tab	Calibration Curve QA	Relative Error for each level against calibration curve must be ≤ 20% of nominal	Null: AT	Void failing compounds with Null Code AT
QA Summary "General QA" Lab Flag 3c	Calibration Curve QA	The absolute value of cal. curve offset/slope must be ≤ MDL	Null: AT	Void failing compounds with Null Code AT
QA Summary "General QA" Lab Flag 4	Daily Calibration Check	Relative error for each carbonyl in the check standard is ≤ 15% of nominal	Null: AS	Void failing compounds with Null Code AS
QA Summary "General QA" Lab Flag 5	Replicate Analysis	The RPD of two analyses must be ≤ 10% for all compounds detected > 0.1µg/mL	Null: AX	Void failing Carbonyls with Null Code AX

Table 2: UAT and PAMS Carbonyl Analysis QC Criteria

Where to look for Flag	QC parameter	Flag Criteria	AQS Flag	How to apply Flag
QA Summary "General QA" Lab Flag 6a	Cartridge past hold time limit	Sampled Cartridge hold time must be ≤ 14 days	Null: TS	Void all Carbonyls in failing sample with Null Code TS
QA Summary "General QA" Lab Flag 6b	Extract past hold time limit	Extracted Sample hold time must be ≤ 30 days	Null: TS	Void all Carbonyls in failing sample with Null Code TS
QA Summary "Sample Retention Time Check" workbook tab	Retention time of target carbonyl detected in sample	Retention time must be within limits of the QA Summary Report	Null: BH	Void failing Carbonyls with Null Code BH
Review Checklist	Sample receipt temperature	Carbonyl Cartridge Receiving temperature must be ≤ 4°C	QA qualifier: TT	Flag all Carbonyls with Qualifier Flag TT
Validation spreadsheet "Prim.vsColl._ppbv QAFlag 3" workbook tab	Collocated/Duplicate sample collections	The relative percent difference (RPD) between primary and collocated carbonyl sample collections must be ≤ 20%	QA qualifier: 3	Flag failing Carbonyls with Qualifier Flag 3
QA Summary "DNPH TEST" workbook tab	DNPH peak area analysis	The DNPH peak area found in samples must be ≥ 50% of the average DNPH peak area from lab blanks and cartridge spikes	QA qualifier: DN	Flag failing carbonyls with qualifier flag DN
QA Summary "General QA" Lab Flag QX	Cartridge Spike Recoveries	Cartridge spike recoveries: Formaldehyde = ± 20% All others = ± 30%	QA qualifier: QX	Flag failing carbonyls with qualifier flag QX
QA Summary "General QA" Lab Flag QX	Cartridge Spike/Spike Duplicate Precision	Cartridge spike/spike duplicate RPD must be ≤ 20%	QA qualifier: QX	Flag failing carbonyls with qualifier flag QX
Validation spreadsheet "YYYY UATorPAMS Carbonyls_ppbv+L3 Flags" workbook tab	Sample Concentrations	Reported concentration = 0.000 (from analysis instrument)	QA qualifier: ND	Report 0.000 and apply qualifier flag ND

Table 2: UAT and PAMS Carbonyl Analysis QC Criteria

Where to look for Flag	QC parameter	Flag Criteria	AQS Flag	How to apply Flag
Validation spreadsheet "YYYY UATorPAMS Carbonyls_ppbv+L3 Flags" workbook tab	Sample Concentrations	Reported concentration > 0.000 but < MDL	QA qualifier: MD	Report concentration and apply flag MD
Validation spreadsheet "YYYY UATorPAMS Carbonyls_ppbv+L3 Flags" workbook tab	Sample Concentrations	Reported concentration ≥ MDL and < lowest calibration level	QA qualifier: SQ	Report concentration and apply qualifier flag SQ

Detailed procedures for generation and review of the QA summary reports are found in the carbonyl analysis instrument operator SOP # **DAQ-03-004.2**.

4.4 Sampling Equipment Acceptance Criteria

Carbonyl sampling event results are recorded on carbonyl sampler information forms, document number **DAQ-16-009** and in the current year UAT and PAMS carbonyl master spreadsheet, document number **DAQ-03-012.** Each carbonyl sample cartridge, lab QC cartridge, and field QC cartridge will be accompanied with a filled-in, carbonyl sample information form.

Sampling equipment acceptance criteria are described in SOP # **DAQ-03-002.1** ATEC 2200 UAT carbonyl sampler ECB responsibilities, **DAQ-09-002.1** ATEC 8000 PAMS carbonyl sampler ECB responsibilities, **DAQ-03-002.2** ATEC 2200 UAT carbonyl sampler operator responsibilities, and **DAQ-09-002.2** ATEC 8000 PAMS carbonyl sampler operator responsibilities. See Table 3 for details on sampling equipment acceptance criteria.

Table 3. UAT and PAMS Sampling Method QC Criteria

Where to look for Flag	QC parameter	Flag Criteria	AQS Flag	How to apply Flag
Review Checklist	Pre-Sample Flow Rate Verification and/or Post-Sample Flow Rate Verification	Measured flow must be 0.9-1.1 L/min.	QA Qualifier: W	Apply flag “W” to all carbonyl concentrations detected in sample
Review Checklist	Flow Tolerance and/or Zero Tolerance Error	Sampler operating software detected flow rate that exceeds pre-set limits	QA Qualifier: W	Apply flag W to all carbonyl concentrations detected in sample

Table 3. UAT and PAMS Sampling Method QC Criteria

Where to look for Flag	QC parameter	Flag Criteria	AQS Flag	How to apply Flag
Review Checklist	Sample Volume	UAT Volume (1242 L-1650 L) PAMS Volume (414 L – 550 L)	QA Qualifier: LK or LL	Apply flag LK if volume below limits or apply LL if volume above limits to all carbonyl concentrations detected in sample.
Carbonyl Sampler Information Form	Ozone denuder Temperature Tolerance issue	Sampler operating software detected a KI denuder temperature that exceeds pre-set limits	QA Qualifier: QX	Apply flag QX to all carbonyl concentrations detected in sample

4.5 Sample Date and Duration Criteria

The EPA sets the sample schedule every calendar year. The EPA sampling schedules can be found here:

https://www.epa.gov/amtic/sampling-schedule-calendar.

- UAT Carbonyl sampling occurs 1-in-6 days, January through December. Sample durations must be 24±1-hour periods.
- PAMS Carbonyl sampling occurs June 1 through August 31 on a 1-in-3-day schedule for 8-hour periods with the following start times: 04:00, 12:00, and 20:00.

Sample dates are recorded on the carbonyl sample information form, document number **DAQ-16-009** and in the current year UAT and PAMS carbonyl master spreadsheet, document number **DAQ-03-012.**

4.6 Method Detection Limits and Reportable Limits

Method detection limits (MDLs) are determined minimally once per calendar year, preferably in the 1st calendar quarter. The MDL is statistically determined using the method update rule and guidance in section 4.1 of the National Air Toxics Trends Station (NATTS) Technical Assistance Document (TAD) revision 3.

The MDL is calculated using results from a series of seven or eight MDL blank and MDL spike cartridges. The greater of the two MDLs is used to further flag reported carbonyl concentrations. See **Table 1** for a current list of reportable limits.

- Carbonyl sample concentrations below the lowest calibration level and greater than or equal to the MDL receive qualifier “SQ”.
- Carbonyl sample concentrations greater than 0 but less than the MDL receive qualifier “MD”.

Current carbonyl MDLs are calculated in the UAT and PAMS Carbonyl data validation spreadsheet under the workbook tabs named “MDL SPIKE” and “MDL BLANK”.

5.0 CARBONYL SAMPLING AND ANALYSIS DATA VALIDATION

Validation of the carbonyl data cannot begin until the Level 1 (self) and Level 2 (peer) reviews are complete. The carbonyl analyst prepares data packages that include carbonyl analysis results. Each data package undergoes Level 1 and Level 2 review before being released to the Level 3 reviewer.

5.1 Carbonyl Data Transfer to Validation Spreadsheet

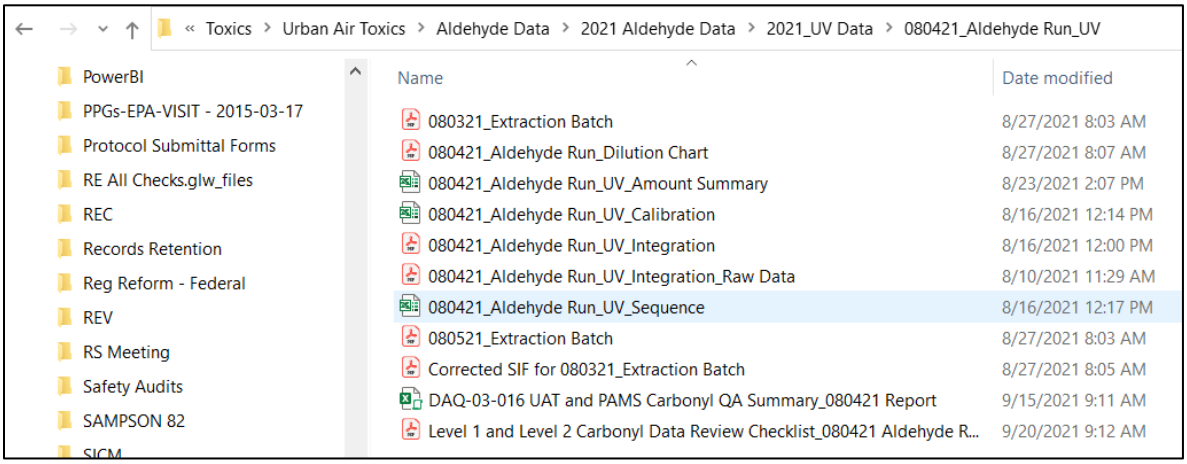
Once a carbonyl data package is complete and gone through the Level 1 and Level 2 data reviews, the Level 3 validator will transfer the approved results from the analysis instrument files and the UAT and PAMS Carbonyl master spreadsheet to the data validation spreadsheet.

The Level 3 reviewer receives communication via email or phone call from the Level 2 reviewer indicating the carbonyl data has been released for final validation.

5.1.1 Field-Collected Carbonyl Data Transfer

1. Open the current year UAT and PAMS Carbonyl data validation spreadsheet located on the p-drive here: **P:\Toxics\Urban Air Toxics\Aldehyde Data\YYYY Aldehyde Data** and open the current year UAT and PAMS carbonyl master spreadsheet (**DAQ-03-012)** also located in the same folder on the p-drive.
2. Open the current run folder under review located on the same internal network drive as listed in step #1 and open the sequence file(s), DAQ-03-016 file, and the review checklist file. See **Figure 7** below showing all files that should be present in the run folder on the p-drive. If one or more files are missing, contact the Level 1 and Level 2 reviewers to correct the issue. *Do not proceed until all files are present.*

Figure 7: Example of Files Present in Carbonyl Analysis Run Folder



3. Transfer the information (Sample #, Lot ID, Field Site, Sample Date, and Extraction Date) for all field-collected samples and QC cartridge samples analyzed in the current data package under review. Transfer the information from the current year UAT and PAMS carbonyl master spreadsheet “extraction log” workbook tab to the current year UAT and PAMS carbonyl data

validation spreadsheet "YYYY Carbonyls_ppbv" workbook tab, where YYYY is the current four-digit year (for example 2022).

4. For all field collected samples and QC cartridge samples analyzed in the current sequence, transfer the analysis date and time from the current year UAT and PAMS carbonyl master spreadsheet "carbonyls-UV ug_mL" workbook tab to the current year data validation spreadsheet "YYYY Carbonyls_ppbv" workbook tab.
5. For all field collected samples and QC samples analyzed in the current sequence, transfer carbonyl concentrations (ppbv) and comments from the current year carbonyl master spreadsheet "carbonyls-UV ppbv" workbook tab to the current year data validation spreadsheet "YYYY Carbonyls_ppbv" workbook tab. Do not transfer Acetone and Acrolein concentrations.
6. Look for QC samples recently transferred to the data validation spreadsheet "YYYY Carbonyls_ppbv" workbook tab.
7. Highlight the rows with sample #'s containing the following text "lot blank, sampler cert, cartridge blank, cartridge spike, cartridge spike duplicate, cartridge mdl spike, IDOC, and PT".
8. Remove/delete these samples from the "YYYY Carbonyls_ppbv" workbook tab in the data validation spreadsheet. Data from these samples will be transferred to other workbook tabs in the data validation spreadsheet, but different units will be required.

5.1.2 DNPH Cartridge Lot Blank Data Transfer

1. Look for QC samples in the current sequence with the words "LOT BLANK" in the injection name. If these QC samples do not exist, continue to 5.1.3.
2. If present, transfer the Sample #, Lot ID, Field Site, Sample Date, and Extraction Date from the current year UAT and PAMS carbonyl master spreadsheet "extraction log" workbook tab to the current year UAT and PAMS carbonyl data validation spreadsheet "LOT BLANK_ug_mL" workbook tab.
3. Transfer the carbonyl concentrations (µg/mL) from the current year UAT and PAMS carbonyl master spreadsheet "carbonyls-UV ug_mL" workbook tab to the current year data validation spreadsheet "LOT BLANK_ug_mL" workbook tab.
4. Check the conditional formatting formulas for all carbonyl parameters in the "LOT BLANK_ug_mL" workbook tab. Parameters with red filled cells indicate a failure of the lot blank acceptance criteria.
5. Close the UAT and PAMS Carbonyl Master Spreadsheet and do not save the changes if prompted to.
6. Click the save icon on the current year UAT and PAMS carbonyl data validation spreadsheet after transferring data from the master spreadsheet to the data validation spreadsheet

5.1.3 MDL_{spk} and MDL_{blk} Cartridge Data Transfer

1. Look for QC samples in the current sequence with the words "MDL SPIKE" and "MDL BLANK" in the injection name. If these samples do not exist, continue to 5.1.4.
2. If present, open the file with "amount summary" in file name (as shown in **Figure 7**).
3. Transfer the MDL SPIKE injection name, injection Date/Time, DNPH (area counts), and carbonyl concentrations (µg/mL) from the "amount summary" file for all MDL spike samples analyzed in the current sequence to the current year UAT and PAMS carbonyl data validation spreadsheet

"MDL SPIKE**"** workbook tab. Include results for **Acetone** and **Acrolein** because these compounds are present in the derivatized standards used to make the MDL spike samples.

4. Transfer the MDL BLANK injection name, injection Date/Time, DNPH (area counts), and carbonyl concentrations (µg/mL) from the "amount summary" file for all MDL blank samples analyzed in the current sequence to the current year UAT and PAMS carbonyl data validation spreadsheet "MDL BLANK" workbook tab. Include results for Acetone and Acrolein because these compounds may be present in detectable amounts on un-sampled DNPH cartridges.
5. When a minimum of seven MDL spike and MDL blank samples have been added to the data validation spreadsheet, the Level 3 reviewer will calculate the MDL according to Section 4.1 of the NATTS TAD Revision 3. The MDL is calculated using the method update rule.
6. Immediately after calculating an updated MDL, the Level 3 reviewer must also update the MDL and MDL spike values used in the QA Summary Report, document # (**DAQ-03-016**).

5.1.4 Cartridge Spike and Cartridge Spike Duplicate Data Transfer

Cartridge spike and cartridge spike duplicate pairs are used to monitor laboratory extraction and analysis precision. The data validation spreadsheet contains calculations and conditional formats embedded within the spreadsheet that will highlight when the coefficient of variation exceeds the limit of ± 15%. When the extraction and analysis coefficient of variation (CV) exceeds the limit, a corrective action report (CAR) must be initiated by the Level 3 validator to uncover the root cause for the out-of-control status.

1. Open the QA Summary Report (**DAQ-03-016**) for the current run being reviewed.
2. Look for the cartridge spike/cartridge spike duplicate data on the "General QA" workbook tab, as shown in **Figure 8** below.

Figure 8: Cartridge Spike/Cartridge Spike Duplicate Data

CARTRIDGE SPIKE ACCURACY AND PRECISION							
CARTRIDGE SPIKE (QX)			CARTRIDGE SPIKE-DUP (QX)			Precision Check (QX)	
Spiking Level->	0.15	ug/mL	Spiking Level ->	0.15	ug/mL		
24 CART SPK 081721	RPD	pass <= 20% (Form); pass<=30% (others)	25 CART SPK DUP 081721	RPD	pass <= 20% (Form); pass<=30% (others)	RPD	Pass <=20%
08.20.21 17:30			08.20.21 18:20				
25.1468			25.2635				
0.1563	4.19%		0.1550	3.36%		0.80	
0.1607	7.16%		0.1592	6.14%		0.96	
0.1760	17.37%		0.1790	19.31%		1.64	
0.1473	1.80%		0.1495	0.32%		1.49	
0.1368	8.79%		0.1350	10.03%		1.36	
0.1537	2.47%		0.1572	4.79%		2.24	
0.1504	0.24%		0.1533	2.18%		1.92	
0.1650	9.97%		0.1623	8.17%		1.65	
0.1376	8.24%		0.1363	9.16%		1.01	
0.1477	1.52%		0.1442	3.84%		2.39	
0.1446	3.57%		0.1419	5.41%		1.93	
0.1411	5.92%		0.1433	4.49%		1.50	
0.1395	6.99%		0.1378	8.14%		1.25	

3. Transfer the cartridge spike and cartridge spike duplicate results to the "LAB Ext._ug_mL (CV)" workbook tab in the UAT and PAMS data validation spreadsheet. Remember to paste special, transpose these values into the data validation spreadsheet.
4. Add the name of the aldehyde run folder to column Q in the "LAB Ext._ug_mL (CV)" workbook tab in the UAT and PAMS data validation spreadsheet.
5. Update the CV calculations on the "LAB Ext._ug_mL (CV)" workbook tab. The CV cannot be calculated until at least two pairs of cartridge spike and cartridge spike duplicate sample results are available.
6. Update the CV calculations by inserting the RPDs of the recently added cartridge spike/spike duplicate samples. If two pairs are added, insert two lines for the new RPD values. See **Figure 9** below for an example of where to insert the recently added RPD values (insert on row #68).

Figure 9: Updating the CV Calculations for Extraction and Analysis Precision Part 1

1	Sample Name	Injection Date/Time	DNPH (area counts)	Formaldehyde (µg/mL)	Acetaldehyde (µg/mL)	Acetone (µg/mL)
41	24 CART SPK 081721	08.20.21 17:30	25.1468	0.1563	0.1607	0.1760
42	25 CART SPK DUP 081721	08.20.21 18:20	25.2635	0.1550	0.1592	0.1790
43	Difference/Average			0.00797059	0.00959322	-0.01638323
44						
45						
46	Difference/Average			#DIV/0!	#DIV/0!	#DIV/0!
47						
48						
49	Difference/Average			#DIV/0!	#DIV/0!	#DIV/0!
50						
51						
52	Difference/Average			#DIV/0!	#DIV/0!	#DIV/0!
53	CV Calculations					
54						
55	Difference/Average			-0.03282544	-0.00698580	0.30435281
56	Difference/Average			-0.03229932	-0.01444453	-0.04182780
57	Difference/Average			-0.00070806	0.00107821	-0.02582379
58	Difference/Average			0.01271692	-0.01227242	-0.00260923
59	Difference/Average			-0.00776063	0.00116346	0.05893494
60	Difference/Average			0.02155034	0.00819350	0.18275102
61	Difference/Average			0.01377833	-0.01093039	-0.07489631
62	Difference/Average			-0.01606605	-0.00997108	-0.03555467
63	Difference/Average			0.00277830	0.01242294	0.00321162
64	Difference/Average			0.01355763	0.01830524	-0.01546831
65	Difference/Average			-0.00087263	0.01645229	-0.00396048
66	Difference/Average			-0.01849823	-0.02583176	-0.03120009
67	Difference/Average			-0.00592961	-0.01118962	-0.05723059
68	Difference/Average			0.00797059	0.00959322	-0.01638323
69						

7. Continue to work down the workbook tab and insert a line as shown in row #86 as shown in **Figure 10** below. Update the calculations in row#86 to be sure they're referencing the correct RPD. In this example, Cell D86 should be referencing D68.

Figure 10: Updating the CV Calculations for Extraction and Analysis Precision Part 2

1	Sample Name	Injection Date/Time	DNPH (area counts)	Formaldehyde (µg/mL)	Acetaldehyde (µg/mL)	Acetone (µg/mL)
65	Difference/Average			-0.00087263	0.01645229	-0.00396048
66	Difference/Average			-0.01849823	-0.02583176	-0.03120009
67	Difference/Average			-0.00592961	-0.01118962	-0.05723059
68	Difference/Average			0.00797059	0.00959322	-0.01638323
69						
70			Number	14	14	14
71			2n =	28	28	28
72						
73	Difference/Average			0.00107751	0.00004880	0.09263063
74	Difference/Average			0.00104325	0.00020864	0.00174956
75	Difference/Average			0.00000050	0.00000116	0.00066687
76	Difference/Average			0.00016172	0.00015061	0.00000681
77	Difference/Average			0.00006023	0.00000135	0.00347333
78	Difference/Average			0.00046442	0.00006713	0.03339793
79	Difference/Average			0.00018984	0.00011947	0.00560946
80	Difference/Average			0.00025812	0.00009942	0.00126413
81	Difference/Average			0.00000772	0.00015433	0.00001031
82	Difference/Average			0.00018381	0.00033508	0.00023927
83	Difference/Average			0.00000076	0.00027068	0.00001569
84	Difference/Average			0.00034218	0.00066728	0.00097345
85	Difference/Average			0.00003516	0.00012521	0.00327534
86	Difference/Average			0.00006353	0.00009203	0.00026841
87						
88			Sum	0.00388875	0.00234121	0.14358119
89			Sum/2n	0.00013888	0.00008361	0.00512790
90			CV	*1.18%*	*0.91%*	*7.16%*
91						

8. Additionally, update the formulas in cells D70 (**Number of pairs**), D71 (**2n**), D88 (**Sum**), and D89 (**Sum/2n**).
9. The CV automatically updates and represents the ongoing extraction and analysis precision for all previous RPDs determined added to rows #55 to #68.
10. This CV calculation is used to monitor ongoing precision for PAMS carbonyl results. UAT precision is calculated in the same manner but uses primary and collocated UAT sample collection results for the CV calculations.

5.1.5 Separate the UAT and PAMS Carbonyl Data

1. The UAT and PAMS Carbonyl data recently transferred to the "YYYY Carbonyls_ppbv" workbook tab must be separated into their respective workbook tabs: "YYYY UAT carbonyls_ppbv+L3 flag" and "YYYY PAM carbonyls_ppbv+L3 flags"

2. UAT and PAMS data are reported in units of ppbv so there are two sets of calibration limits and two sets of MDL limits to apply to the measured carbonyl concentration data (due to the different sample volumes).
3. Using the filtering function on the "YYYY Carbonyls_ppbv" workbook tab will allow the user to only look for recently added PAMS or UAT carbonyl samples.
4. Filter by analysis date/time to show only recently added samples
5. Then filter by field site, only selecting "Millbrook" "Candor" and "Millbrook D" to display only the UAT carbonyl results.
6. Count the number of rows and remember this number.
7. On the "YYYY UAT carbonyls_ppbv+L3 flag" workbook tab, go to the last entry and insert the same number of rows counted in step #6. The last entry should be pushed to bottom of list.
8. Copy the last entry and paste it so that it's moved to the top of the blank rows recently inserted.
9. Transfer all UAT carbonyl rows from the "YYYY Carbonyls_ppbv" workbook tab to the blank rows on the "YYYY UAT carbonyls_ppbv+L3 flag" workbook tab.
10. Repeat Steps #4-9 but this time filter the field sites to only show recently added samples for "Millbrook CH1 P-1" "Millbrook CH1 P-2" and "Millbrook CH1 P-3" and transfer this data to the "YYYY PAM carbonyls_ppbv+L3 flags" workbook tab.
11. Update the Time in the sample date (column D). The default is 0:00 and this value must be updated to reflect the time the sample started collecting.
12. For example, P-1 samples start collecting at the 04:00 hour. P-2 samples start collecting at the 12:00 hour, and the P-3 samples start collecting at the 20:00 hour. Deviations to the P-1 = 04:00; P-2 = 12:00; and P-3 = 20:00 are possible and will be documented in the Level 1 and Level 2 data review checklist.
13. Review the data review checklist for comments that indicate the port number or start time deviates from those listed in step #12 above.
14. Save the data validation spreadsheet.

5.1.6 Transfer of Duplicate Injection Data

Duplicate injections are performed with each carbonyl analysis run. The duplicate injection assesses precision of the analytical instrument. The Level 3 reviewer monitors ongoing analysis instrument precision by calculating a CV. The Level 3 reviewer transfers the duplicate injection results from the QA Summary report, "General QA" workbook tab generated for the current run under review to the data validation spreadsheet's "LAB Dup. Inj._ug_mL (CV)" workbook tab.

1. Open the QA Summary report and the "General QA" workbook tab for the current run under review.
2. Look for the "Flag Code 5" and "Replicate Analysis" fields as shown in **Figure 11** below.

Figure 11: Duplicate Injection Data

40		Flag Code 5					
41		Replicate Analysis					
42	Sample name--->	22 PC080521M1	23 PC080521M1S			RPD	pass ≤ 10%
43	Injection Date Time --->	08.18.21 18:30	08.18.21 19:21				
44	DNPH (area counts)	19.8253	19.6375				
45	Formaldehyde (µg/mL)	0.293	0.291			0.68%	
46	Acetaldehyde (µg/mL)	0.096	0.096				
47	Acetone (µg/mL)	0.386	0.381			1.29%	
48	Acrolein (µg/mL)	0.000	0.000				
49	Propionaldehyde (µg/mL)	0.016	0.017				
50	Crotonaldehyde (µg/mL)	0.000	0.000				
51	2-Butanone (ug/mL)	0.029	0.027				
52	Methacrolein (ug/mL)	0.021	0.021				
53	Butyraldehyde (µg/mL)	0.008	0.008				
54	Benzaldehyde (µg/mL)	0.007	0.006				
55	Valeraldehyde (µg/mL)	0.000	0.000				
56	m-Tolualdehyde (µg/mL)	0.000	0.000				
57	Hexaldehyde (µg/mL)	0.010	0.012				

3. Transfer the Duplicate injection results (highlighted in **Figure 11**) to the "LAB Dup. Inj._ug_mL (CV)" workbook tab in the carbonyl data validation spreadsheet.
4. Add the file name of the aldehyde run folder where the duplicate injection data came from to column Q of the "LAB Dup. Inj._ug_mL (CV)" workbook tab.
5. The "LAB Dup. Inj._ug_mL (CV)" workbook tab is designed just like the LAB Ext._ug_mL (CV)" workbook tab.
6. The Level 3 reviewer must update the CV calculations. Follow steps 5-10 in section 5.1.4 to update the CV calculations monitoring analysis instrument precision.

5.2 Application of Null Codes and Qualifier Flags Due to Sampling and Analysis Issues

Once all carbonyl data has been split up into its respective collection method (UAT or PAMS) workbook tab the application of the null codes and qualifier flags can begin. Null codes and qualifier flags are applied to the "YYYY UAT carbonyls_ppbv+L3 flag" workbook tab and the "**YYYY PAM carbonyls_ppbv+L3 flags**" workbook tab. Null codes and qualifier flags ***should not*** be applied to the "**YYYY Carbonyls_ppbv**" workbook tab. See Table D2-1 in the UAT Network QAPP (DAQ-01-008) for a Table of null codes and qualifier codes that can be applied to the UAT and PAMS carbonyl concentration value.

5.2.1 Application of Qualifier Flags to Carbonyl Concentrations Near the MDL

1. Apply the "ND, MD, SQ and EH" qualifier flags based on the conditional format color of the carbonyl concentration. Yellow concentrations that are also 0.000 receive an "ND" qualifier flag. Yellow colored concentrations > 0.000 receive an "MD" qualifier flag. Orange colored concentrations receive an "SQ" flag. Bold font and red carbonyl concentrations receive "EH" flag. Apply the ND, MD, SQ, and EH flags to the flag column next to the concentration displaying the out-of-control status.
2. Do not apply an "ND, MD, SQ, or EH" flag if the cell value is > 0.000 and contains no color.

5.2.2 Application of Qualifier Flags for Lot Blank Results

1. Look over the "lot blank analysis" workbook tab in the carbonyl data validation spreadsheet for carbonyls concentrations with red filled cells. Red filled cells indicate a failure of lot blank acceptance criteria.
2. Apply the LB flag in the flag column of the failing carbonyls in both workbook tabs titled "YYYY UAT carbonyls_ppbv+L3 flag" and "YYYY PAM carbonyls_ppbv+L3 flags" and continue to apply the same flag to failing parameters of all field-collected samples collected using the contaminated lot.
3. If an "ND" flag is already present, do not apply the LB flag, keep the ND flag in place.
4. If a qualifier flag is already present in the flag column, apply the LB flag in the same cell with the previous flag, separated by a comma. For example. If MD is present in the flag column, apply the LB flag as shown: "MD,LB"
5. Multiple qualifier flags can be applied to the same carbonyl concentration.

5.2.3 Application of Null Codes for Calibration Results

1. Open the QA summary report to review the within-run QC checks and associated LAB flags.
2. Click the "**general QA**" workbook tab.
3. Look for calibration curve QC failures first. (LAB flags: 3a and 3c). Failures are formatted to display "FAIL" and color the cell. See **Figure 12** below showing no QC failures for 3a or 3c.

Figure 12: Example of QA Summary Report Calibration Curve Flags (No Failures)

20		Flag code 3a		Flag code 3c			
21		Calibration Curve QA		Calibration Curve QA			
22	Sample name--->	(R^2 %)	pass ≥ 99.9%	Offset (mAU*min)	Slope	Offset/Slope	pass ≤ MDL_{spk}
23	Injection Date Time --->						
24	DNPH (area counts)	n.a.		n.a.	n.a.		
25	Formaldehyde (µg/mL)	100.000		0.0016	2.2079	0.0007	
26	Acetaldehyde (µg/mL)	99.999		-0.0002	1.6614	0.0001	
27	Acetone (µg/mL)	100.000		0.0030	1.1984	0.0025	
28	Acrolein (µg/mL)	99.999		-0.0016	1.3734	0.0012	
29	Propionaldehyde (µg/mL)	100.000		-0.0001	1.2377	0.0001	
30	Crotonaldehyde (µg/mL)	99.999		-0.0027	1.0765	0.0025	
31	2-Butanone (ug/mL)	99.999		0.0010	0.9549	0.0011	
32	Methacrolein (ug/mL)	100.000		-0.0019	1.1419	0.0017	
33	Butyraldehyde (µg/mL)	99.999		0.0014	1.0258	0.0013	
34	Benzaldehyde (µg/mL)	99.999		-0.0007	0.7192	0.0010	
35	Valeraldehyde (µg/mL)	99.999		-0.0009	0.8533	0.0011	
36	m-Tolualdehyde (µg/mL)	99.996		-0.0017	0.6088	0.0027	
37	Hexaldehyde (µg/mL)	99.998		0.0004	0.7441	0.0005	

4. If a failing condition exists, as shown in **Figure 13** below, the Level 3 reviewer will apply null code "AT" to the flag column of the failing carbonyl compound in the validation spreadsheet workbooks "YYYY UAT carbonyls_ppbv+L3 flags" and "YYYY PAM carbonyls_ppbv+L3 flags" and continue applying the same AT flag for all samples analyzed in the sequence.

Figure 13: Example of QA Summary Report Calibration Curve Flags (With Failures)

		Flag code 3a		Flag code 3c			
		Calibration Curve QA		Calibration Curve QA			
	Sample name--->	(R^2 %)	pass ≥ 99.9%	Offset (mAU*min)	Slope	Offset/Slope	pass ≤ MDL_{spk}
	Injection Date Time --->						
	DNPH (area counts)	n.a.		n.a.	n.a.		
	Formaldehyde (µg/mL)	100.000		-0.0007	2.1813	0.0003	
	Acetaldehyde (µg/mL)	99.999		-0.0052	1.6398	0.0031	
	Acetone (µg/mL)	99.999		-0.0069	1.1789	0.0059	
	Acrolein (µg/mL)	99.998		-0.0119	1.3438	0.0088	FAIL
	Propionaldehyde (µg/mL)	99.999		-0.0010	1.2242	0.0008	
	Crotonaldehyde (µg/mL)	99.959		-0.0259	0.9474	0.0273	FAIL
	2-Butanone (ug/mL)	100.000		-0.0015	0.9437	0.0016	
	Methacrolein (ug/mL)	99.999		-0.0082	1.1177	0.0073	FAIL
	Butyraldehyde (µg/mL)	99.997		-0.0007	1.0107	0.0007	
	Benzaldehyde (µg/mL)	100.000		-0.0021	0.7030	0.0030	
	Valeraldehyde (µg/mL)	99.999		-0.0022	0.8428	0.0027	
	m-Tolualdehyde (µg/mL)	99.988		-0.0086	0.5886	0.0147	FAIL
	Hexaldehyde (µg/mL)	99.998		0.0004	0.7378	0.0006	

5. Apply flag **AT** to carbonyls failing LAB flags 3a and 3c. See **Figure 14** below showing where to apply the "AT" flag. Acrolein is not shown because it is not reported to AQS.
6. If a qualifier flag(s) has already been applied, overwrite the qualifier flag with the "AT" null code. Null codes supersede qualifier flags.

Figure 14: Example of Adding Flags to Data Validation Spreadsheet

1	Sample #	Lot ID	Field Site	Sample Date	Extraction Date	CART Hold Time (Extraction - Sample Dates)	Cartridge Hold Time Flag 6a	EXTR. Hold Time (Analysis - Extraction Date	Extract Hold Time Flag 6b	Analysis Date and Time	Crotonaldehyde	flag	Methacrolein	flag	m-tolualdehyde	Flag
93	C061521M	008631019A	Millbrook	6/15/21 0:00	6/28/2021	13		2		6/30/21	0.000	AT	0.287	AT	0.000	AT
94	C061521MD	008631019A	Millbrook D	6/15/21 0:00	6/28/2021	13		2		6/30/21	0.000	AT	0.303	AT	0.000	AT
95	C061521C	008631019A	Candor	6/15/21 0:00	6/28/2021	13		2		6/30/21	0.000	AT	0.203	AT	0.000	AT
96	C062121M	008631019A	Millbrook	6/21/21 0:00	6/28/2021	7		3		6/30/21	0.000	AT	0.383	AT	0.000	AT
97	C062121MD	008631019A	Millbrook D	6/21/21 0:00	6/28/2021	7		3		6/30/21	0.000	AT	0.463	AT	0.000	AT
98	C062121C	008631019A	Candor	6/21/21 0:00	6/28/2021	7		3		6/30/21	0.000	AT	0.273	AT	0.000	AT
99	C062721M	008631019A	Millbrook	6/27/21 0:00	6/30/2021	3		1		7/1/21	0.000	AT	0.183	AT	0.000	AT
100	C062721MD	008631019A	Millbrook D	6/27/21 0:00	6/30/2021	3		1		7/1/21	0.000	AT	0.186	AT	0.000	AT
101	C062721C	008631019A	Candor	6/27/21 0:00	6/30/2021	3		1		7/1/21	0.000	AT	0.113	AT	0.000	AT

7. Click the "Flag3b CAL Curve Relative Error" workbook tab in the QA Summary report for the current sequence under review.
8. Look for failing compounds as shown in **Figure 15** below. Failures will be highlighted "pink" and a "3b" flag will also be displayed.

Figure 15: QA Summary Report Calibration Curve Accuracy Flag

	Relative Error						Assigned Flag 3b					
							Level-1	Level-2	Level-3	Level-4	Level-5	Level-6
Formaldehyde (µg/mL)	1.9%	0.6%	2.5%	0.4%	0.5%	0.0%	OK	OK	OK	OK	OK	OK
Acetaldehyde (µg/mL)	1.7%	3.4%	0.4%	0.8%	0.6%	0.1%	OK	OK	OK	OK	OK	OK
Acetone (µg/mL)	4.8%	3.8%	1.4%	0.4%	0.5%	0.0%	OK	OK	OK	OK	OK	OK
Acrolein (µg/mL)	6.4%	7.7%	1.1%	0.5%	0.8%	0.1%	OK	OK	OK	OK	OK	OK
Propionaldehyde (µg/mL)	8.4%	2.5%	2.8%	0.4%	0.0%	0.0%	OK	OK	OK	OK	OK	OK
Crotonaldehyde (µg/mL)	7.7%	3.2%	4.8%	0.8%	0.8%	0.1%	OK	OK	OK	OK	OK	OK
2-Butanone (ug/mL)	8.9%	2.5%	4.0%	0.3%	0.4%	0.0%	OK	OK	OK	OK	OK	OK
Methacrolein (ug/mL)	8.3%	2.1%	0.1%	0.3%	0.4%	0.0%	OK	OK	OK	OK	OK	OK
Butyraldehyde (µg/mL)	30.0%	3.2%	3.1%	1.1%	0.6%	0.1%	3b	OK	OK	OK	OK	OK
Benzaldehyde (µg/mL)	#VALUE!	7.8%	0.0%	1.6%	0.3%	0.0%	#VALUE!	OK	OK	OK	OK	OK
Valeraldehyde (µg/mL)	#VALUE!	6.2%	0.4%	0.5%	0.5%	0.1%	#VALUE!	OK	OK	OK	OK	OK
m-Tolualdehyde	#VALUE!	11.0%	3.0%	1.2%	1.4%	0.1%	#VALUE!	OK	OK	OK	OK	OK
Hexaldehyde (µg/mL)	#VALUE!	8.4%	0.3%	1.6%	1.0%	0.1%	#VALUE!	OK	OK	OK	OK	OK

9. Apply "AT" flag to the flag column of the failing carbonyl compound in the validation spreadsheet workbooks "**YYYY UAT carbonyls_ppbv+L3 flags**" and "**YYYY PAM carbonyls_ppbv+L3 flags**" and continue applying the same AT flag for all samples analyzed in the current sequence under review.
10. If a null code is already applied, do not overwrite. The original null code takes precedent over a second null code should that condition exist.
11. If a qualifier flag(s) has already been applied, overwrite the qualifier flag with the null code. Null codes supersede qualifier flags.

5.2.4 Application of Null Codes for Calibration Check Standard Results

1. On the QA Summary report, general QA workbook tab, look for "Flag Code 4" and "Daily Calibration Check" fields.
2. Failing conditions will be highlighted with green filled cells with "fail" written in bold, red font. Please see **Figure 16** below.

Figure 16: Daily Calibration Check Failure Indicator on the QA Summary Report

Flag Code 4											
Daily Calibration Check											
18 HL QA (0.90ug/mL)_ Restek	RPD	pass ≤ 15%	32 HL QA (0.90ug/mL)_R estek	RPD	pass ≤ 15%	46 HL QA (0.90ug/mL)_R estek	RPD	pass ≤ 15%	18 HL QA (0.90ug/mL)_R estek	RPD	pass ≤ 15%
08.18.21 15:09			08.19.21 02:54			08.19.21 14:39			08.20.21 12:28		
0.0000			0.0000			0.0000			0.0000		
0.9196	2.18%		0.6000	33.33%	FAIL	0.9198	2.20%		0.9124	1.38%	
0.8992	0.09%		0.8960	0.45%		0.9009	0.10%		0.9066	0.74%	
0.9082	0.91%		0.8999	0.01%		0.9150	1.66%		0.9013	0.15%	
0.9074	0.82%		0.8993	0.08%		0.9121	1.34%		0.9003	0.03%	
0.9147	1.63%		0.9005	0.05%		0.9182	2.02%		0.9100	1.11%	
0.9069	0.77%		0.9007	0.08%		0.9121	1.34%		0.9093	1.04%	
0.9045	0.50%		0.9043	0.48%		0.8985	0.17%		0.9009	0.10%	
0.9013	0.15%		0.9119	1.33%		0.9049	0.54%		0.9060	0.67%	
0.8941	0.66%		0.9073	0.81%		0.8955	0.50%		0.9066	0.74%	
0.8946	0.60%		0.8961	0.43%		0.8956	0.49%		0.8976	0.26%	
0.9086	0.95%		0.9080	0.89%		0.9239	2.66%		0.8979	0.23%	
0.8943	0.63%		0.8901	1.10%		0.9077	0.86%		0.9159	1.77%	
0.9134	1.49%		0.9075	0.83%		0.9193	2.15%		0.9043	0.48%	

3. Using the example in **Figure 16**, Apply the "AS" null code to the flag column for the failing parameter. Apply this flag to all samples analyzed between 8/18/2021 15:09 to 8/19/2021 14:39 (injection date/time indicated in the orange-colored cell in **Figure 16**.
4. Reference the sequence file to confirm which field-collected samples receive the "AS" null code for the failing carbonyl compound.
5. If a null code has already been applied, do not apply the AS null code. Keep the original null code.
6. If a qualifier flag(s) has already been applied, overwrite the qualifier flag(s) with the AS null code.

5.2.5 Application of Null Codes for Duplicate Injection Results

Each analysis run contains a duplicate injection of a field collected sample to assess instrument precision. The QA Summary report, "General QA" workbook tab contains the duplicate injection results. Please see **Figure 17** below showing the duplicate injection results with failures.

Figure 17: QA Summary Report Duplicate Injection Results (with failures)

40		Flag Code 5					
41		Replicate Analysis					
42	Sample name--->	22 PC080521M1	23 PC080521M1S			RPD	pass ≤ 10%
43	Injection Date Time --->	08.18.21 18:30	08.18.21 19:21				
44	DNPH (area counts)	19.8253	19.6375				
45	Formaldehyde (µg/mL)	0.250	0.291			15.07%	FAIL
46	Acetaldehyde (µg/mL)	0.096	0.096				
47	Acetone (µg/mL)	0.386	0.381			1.29%	
48	Acrolein (µg/mL)	0.000	0.000				
49	Propionaldehyde (µg/mL)	0.016	0.017				
50	Crotonaldehyde (µg/mL)	0.000	0.000				
51	2-Butanone (ug/mL)	0.029	0.027				
52	Methacrolein (ug/mL)	0.021	0.021				
53	Butyraldehyde (µg/mL)	0.008	0.008				
54	Benzaldehyde (µg/mL)	0.007	0.006				
55	Valeraldehyde (µg/mL)	0.000	0.000				
56	m-Tolualdehyde (µg/mL)	0.000	0.000				
57	Hexaldehyde (µg/mL)	0.010	0.012				

1. Open the QA Summary report and go to the "General QA" workbook tab and locate the "Flag 5" and "Replicate Analysis" fields. Please see **Figure 17**.
2. Please note the failing condition in **Figure 17.** The formaldehyde failed the duplicate injection precision.
3. Apply null code "AX" to all formaldehyde concentrations detected in the UAT and PAMS field collected samples that were also analyzed in the current run under review. Apply the AX null code to the flag column next to the formaldehyde concentration as shown in **Figure 18** below.

Figure 18: Applying Null Code AX to the Data Validation Spreadsheet

	A	B	C	D	E	F	G	H	I	J	K	L
1	Sample #	Lot ID	Field Site	Sample Date	Extraction Date	CART Hold Time (Extraction - Sample Dates)	Cartridge Hold Time Flag 6a	EXTR. Hold Time (Analysis - Extraction Date	Extract Hold Time Flag	Analysis Date and Time	Formaldehyde	flag
121	C080221C	008631019A	Candor	8/2/21 0:00	8/5/2021	3		1		8/6/21	2.922	
122	C080721C	008631019A	Candor	8/7/21 0:00	8/17/2021	10		2		8/18/21	1.322	AX
123	C080821M	008631019A	Millbrook	8/8/21 0:00	8/17/2021	9		2		8/18/21	3.231	AX
124	C080821MD	008631019A	Millbrook D	8/8/21 0:00	8/17/2021	9		2		8/18/21	3.054	AX
125	C081021C	008631019A	Candor	8/10/21 0:00	8/17/2021	7		2		8/19/21	1.483	AX
126	C081421M	008631019A	Millbrook	8/14/21 0:00	8/17/2021	3		2		8/19/21	3.243	AX
127	C081421MD	008631019A	Millbrook D	8/14/21 0:00	8/17/2021	3		2		8/19/21	3.079	AX
128	C081421C	008631019A	Candor	8/14/21 0:00	8/17/2021	3		4		8/20/21	0.005	AN

4. If a null code has already been applied, do not apply the new null code, keep the original null code.
5. If a qualifier flag(s) has already been applied, overwrite the qualifier flag(s) with the AX null code.

5.2.6 Application of Null Codes Due to Holding Time Issues

Holding times are assessed in two ways. Sampled cartridge must be extracted within 14 days of the sample date and extracted samples must be analyzed within 30 days of the extraction date. Holding time tests are applied in the QA Summary Report for the current run under review.

1. Open the QA Summary report and look for the "Flag Code 6a" and "Cartridge Past Hold Time" fields on the "General QA" workbook tab as shown in **Figure 19** below.

Figure 19: QA Summary Report Sampled Cartridge and Extract Holding Times

Flag Code 6a					Flag Code 6b				
Cartridge Past Hold Time					Extract Past Hold Time				
Sample ID	Sample Date	Extraction Date	Cartridge Hold Time (days)	pass ≤ 14 days	Sample ID	Extraction Date	Analysis Date	Extract Hold Time (Days)	pass ≤ 30 days
C072121M	7/21/2021	8/5/2021	15	FAIL	C072121M	8/3/2021	9/5/2021	33	FAIL
C072121MD	7/21/2021	8/3/2021	13		C072121MD	8/3/2021	8/4/2021	2	
C072121C	7/21/2021	8/3/2021	13		C072121C	8/3/2021	8/4/2021	2	
PC072121M1	7/21/2021	8/3/2021	13		PC072121M1	8/3/2021	8/4/2021	2	
PC072121M2	7/21/2021	8/3/2021	13		PC072121M2	8/3/2021	8/4/2021	2	
PC072121M3	7/21/2021	8/3/2021	13		PC072121M3	8/3/2021	8/4/2021	2	
PC072421M1	7/24/2021	8/3/2021	10		PC072421M1	8/3/2021	8/5/2021	2	
PC072421M2	7/24/2021	8/3/2021	10		PC072421M2	8/3/2021	8/5/2021	2	
PC072421M3	7/24/2021	8/3/2021	10		PC072421M3	8/3/2021	8/5/2021	2	
C072721M	7/27/2021	8/3/2021	7		C072721M	8/3/2021	8/5/2021	2	
C072721MD	7/27/2021	8/3/2021	7		C072721MD	8/3/2021	8/5/2021	2	

2. Apply Null Code "TS" to all carbonyl parameters if the sampled cartridge hold time exceeds 14 days. If the extract hold time exceeds 30 days, apply null code "TS" to all carbonyl parameters detected in the failing sample.
3. **Figure 19** shows how the failing condition is displayed in the QA Summary Report for sampled cartridge holding times and extract holding times.
4. Apply the null code TS in the flag column of the data validation spreadsheet, in either "YYYY UAT carbonyls_ppbv+L3 flags" or the "YYYY PAM carbonyls_ppbv+L3 flags" depending on which method contains the failing holding time status.
5. Using the example in **Figure 19**, the null code "TS" is applied to all carbonyl parameters detected in sample # C072121M (UAT Millbrook carbonyl sample collected on 7/21/2021).
6. If a null code has already been applied, do not apply the TS null code. Keep the original null code.
7. If a qualifier flag(s) has already been applied, overwrite the reported value with the TS null code and remove any applied qualifier flag(s).

5.2.7 Application of Non-detects Due to Retention Time Issues

1. Open the QA Summary Report for the current run under review and click the "sample retention time check" workbook tab.
2. Examine the retention time data for gray colored cells that also contain a non-zero numerical value.
3. Gray colored cells with a number > 0.000 indicate a retention time shift. All carbonyls detected in field-collected samples with retention times that fall outside the upper control limit (UCL) and lower control limit (LCL), must be qualifier flagged "ND" and 0.000 reported as the concentration prior to AQS upload.
4. If a null code has already been applied, keep the original null code, and do not apply the ND qualifier flag.
5. If a qualifier flag has already been applied, remove the original qualifier flag, and apply the ND qualifier flag and report 0.000 for the concentration.

5.2.8 Application of Qualifier Flags Due to Solvent Blank, Method Blank, and Field Blank Issues

1. Open the QA summary report for the current run under review and click the "General QA" workbook tab.
2. Look for the blank results as shown in **Figure 20** below.

Figure 20: QA Summary Blank Results

	Flag Code 1a		Flag Code 1a		Flag Code 2a		Flag Code 2b	
	ACN Blank (solvent blank)		ACN Blank (solvent blank)		Method Blank (CART BLK)		Field Blank	
Sample name--->	17 ACN BLANK	pass ≤ MDL_{spk}	17 ACN BLANK	pass ≤ MDL_{spk}	21 CART BLK 081721	pass ≤ MDL	35 PC081821MFb	Formaldehyde ≤ 0.06 µg/mL Acetone ≤ 0.15 ug/mL; Acetaldehyde ≤ 0.08 ug/mL; Sum of All other ≤ 1.4 ug/mL
Injection Date Time --->	8/18/2021 14:18		8/20/2021 11:37		08.18.21 17:40		08.21.21 02:44	
DNPH (area counts)	0.0000		0.0000		21.8398		25.3105	
Formaldehyde (µg/mL)	0.000		0.000		0.001		0.001	
Acetaldehyde (µg/mL)	0.050	FAIL	0.050	FAIL	0.090	FAIL	0.092	FAIL
Acetone (µg/mL)	0.000		0.000		0.039		0.021	
Acrolein (µg/mL)	0.000		0.000		0.000		0.000	
Propionaldehyde (µg/mL)	0.000		0.000		0.000		0.000	
Crotonaldehyde (µg/mL)	0.000		0.000		0.000		0.000	
2-Butanone (ug/mL)	0.000		0.000		0.000		0.000	
Methacrolein (ug/mL)	0.000		0.000		0.000		0.000	
Butyraldehyde (µg/mL)	0.000		0.000		0.000		0.000	
Benzaldehyde (µg/mL)	0.000		0.000		0.000		0.000	
Valeraldehyde (µg/mL)	0.000		0.000		0.000		0.000	
m-Tolualdehyde (µg/mL)	0.000		0.000		0.000		0.000	
Hexaldehyde (µg/mL)	0.000		0.000		0.000		0.000	

3. Using the example in **Figure 20**, apply an LB flag for the solvent blank and method blank failures.
4. Apply the LB flag to the failing carbonyl and continue applying to all field collected samples analyzed in the current run under review.
5. If a null code or "ND" flag has already been applied, do not apply the LB flag. Keep the original null code or ND flag.
6. If a qualifier flag(s) has already been applied, add the LB flag to the existing qualifier flag(s) and use a comma to separate them as shown here: "SQ,LB."
7. Using the example in **Figure 20**, apply an FB flag for the field blank failure.
8. Repeat steps 4-6 but use FB instead of LB. Using the previous example in step #6 "SQ,LB." should now be "SQ,LB,FB".
9. Multiple (up to 10) qualifier flags can be reported for the same carbonyl concentration.

5.2.8 Application of Qualifier Flags Due to Cartridge Spike/Cartridge Spike Duplicate Recovery and Precision Issues

1. Open the QA Summary Report for the current run under review and click on the "General QA" workbook tab.
2. Look for the "Cartridge Spike Accuracy and Precision" fields as shown in **Figure 21** below.

Figure 21: QA Summary Cartridge Spike Accuracy and Precision Fields

CARTRIDGE SPIKE ACCURACY AND PRECISION							
CARTRIDGE SPIKE (QX)			CARTRIDGE SPIKE-DUP (QX)			Precision Check (QX)	
Spiking Level->	0.15	ug/mL	Spiking Level ->	0.15	ug/mL		
52 CART SPK 090221	RPD	pass <= 20% (Form); pass<=30% (others)	53 CART SPK DUP 090221	RPD	pass <= 20% (Form); pass<=30% (others)	RPD	Pass <=20%
09.09.21 19:37			09.09.21 20:27				
24.2190			23.5704				
0.1100	26.67%	FAIL	0.1100	26.67%	FAIL	0.00	
0.1502	0.14%		0.1483	1.16%		1.30	
0.1636	9.05%		0.1610	7.33%		1.59	
0.1429	4.73%		0.1000	33.33%	FAIL	35.33	FAIL
0.1364	9.04%		0.1312	12.54%		3.92	
0.1445	3.66%		0.1426	4.96%		1.36	
0.1391	7.28%		0.1344	10.38%		3.40	
0.1432	4.52%		0.1407	6.18%		1.75	
0.1175	21.66%		0.1221	18.60%		3.83	
0.1481	1.27%		0.1463	2.46%		1.21	
0.1254	16.40%		0.1222	18.55%		2.61	
0.1463	2.45%		0.1415	5.66%		3.34	
0.1365	8.97%		0.1316	12.29%		3.71	

3. The failing condition will appear as an orange-colored cell with “FAIL” written in the cell. The failing condition will appear next to the RPD.
4. Apply the qualifier flag “QX” to all failing carbonyls detected in field-collected samples analyzed in the current run under review.
5. If a null code or ND flag has already been applied do not apply the qualifier flag. Keep the original null code or ND flag.
6. If a qualifier flag(s) has already been applied, add the “QX” flag to the previously applied qualifier flag and separate the QX flag with a comma as shown: “MD,LB,QX”

5.2.9 Application of Qualifier Flags Due to Excess DNPH Issues

1. Open the QA Summary Report for the current run under review and click on the “DNPH TEST” workbook tab.
2. Examine this workbook for sample names that have failed this criterion.
3. The failing condition will appear as shown in lower right corner of **Figure 22** below.

Figure 22: QA Summary Excess DNPH Test

Excess DNPH TEST

Blanks and Spiked Cartridges

Cartridge Lot Number 008631019A

Sample Name	Injection Date/Time	DNPH area counts	AVG DNPH area counts
21 CART BLK 090221	08/09/21 17:36	21.379	23.456
22 C083021 PT BLK	08/09/21 18:26	22.012	
23 C083021 PT SPK 54030-77-13	08/09/21 19:16	21.826	
51 CART MDL SPK Test 090221	09/09/21 18:47	23.930	
52 CART SPK 090221	09/09/21 19:37	24.219	
53 CART SPK DUP 090221	09/09/21 20:27	23.570	
55 CART BLK 090921	09/09/21 22:08	24.535	
58 C090221CFb	10/09/21 00:39	24.684	
66 CART SPK 090921	10/09/21 07:22	24.954	

Samples

Cartridge Lot Number 008631019A

Sample Name	Injection Date/Time	DNPH area counts	Pass/Fail
24 C082021M	08/09/21 20:07	12.169	PASS
25 C082021MD	08/09/21 20:57	13.958	PASS
26 C082021C	08/09/21 21:47	9.642	FAIL
27 C082021CS	08/09/21 22:38	9.854	FAIL
28 PC082021M1	08/09/21 23:28	11.580	FAIL
29 PC082021M2	09/09/21 00:19	6.670	FAIL

4. Apply the qualifier flag “DN” to all carbonyls detected in the field collected samples.
5. If a null code or “ND” flag has already been applied, do not add the DN flag. Keep the original null code or ND flag in place
6. If a qualifier flag(s) has already been applied, add the DN flag to the flag column and separate the DN flag from other qualifier flags with a comma as shown: “LB,DN.”

5.2.10 Application of Qualifier Flags Due to Sample Transport Temperature Issues

1. Open the current year’s UAT and PAMS Carbonyl Data Master Spreadsheet (**DAQ-03-012**) and click on the “extraction log” workbook tab.
2. Open the files in the current run folder under review with “extraction batch” listed in the file name. Make a note of the extraction dates.
3. Filter the master spreadsheet by the extraction dates noted by the user so that samples extracted in the current run folder under review are displayed.
4. Check column N for any cells that are colored pink and have a bold, red font value. These samples were received with temperatures outside the acceptable limits.
5. Apply the qualifier flag “TT” to all carbonyls that were detected in the sample that was received above temperature requirements.

6. If a null code or "ND" flag has already been applied, do not apply the TT flag. Keep the original null code or ND flag in place
7. If a qualifier flag(s) has already been applied, add the TT flag to the same column and separate the TT flag from other qualifier flags with a comma as shown: "LB,TT"

5.2.11 Application of Null Codes and Qualifier Flags Due to Carbonyl Sampler Collection Issues

1. Sample collection issues are recorded on the cartridge sample information form, and through the review process, additionally noted in the comments section of the carbonyl data master spreadsheet and the data review checklist.
2. Open the data review check list for the current run under review and scan the file for sample#(s) listed in the comment section as shown in blue ink in **Figure 23** below.

Figure 23: Review Checklist: Locating Suspect Sample Collections

DAQ-03-013 Level 1 and Level 2 Data Review Checklist
Revision 0
Effective: 06/01/2021

Are there site or lab comments? If yes, list sample # in comment	✓		✓		Entered into Carbonyl Master Spreadsheet 08/14/21 C071521MD C072021MFD

General QA/QC Review and Verification:

Questions	Level 1 Review YES	Level 1 Review NO	Level 2 Review YES	Level 2 Review NO	Comment
Does the Sample #'s entered in the QA Summary worksheet match the sample #'s recorded on the Carbonyl Sampler Information Forms and Sequence Report?	✓		✓		
Does the calibration curve meet acceptance criteria?	✓		✓		
Do the detected compounds in the sample extracts meet retention time criteria?	✓		✓		
Level 2 Reviewer: Are the calculations embedded in the QA Summary Report performing the correct mathematics and referencing the correct cells?			✓		

3. Using the example in **Figure 23**, open the extraction batch files containing sampler information forms for sample# 071521MD.
4. The sampler information form indicated the following comment "zero tolerance…" as shown in **Figure 24** below.

Figure 24: Field Comment on Carbonyl Sampler Information Form

Field Comments: Zero Tol error upon arrival 7/16/21

5. A zero-tolerance error alone does not require a flag. Instead, the zero-tolerance error must also be accompanied with a total volume outside acceptable limit and/or failing flow verifications. Apply qualifier flag "W" to the flag column in the data validation spreadsheet to

all carbonyls detected in the affected sample. If the total volume and flow checks are acceptable, do not apply the qualifier flag.

6. If a null code or ND flag has already been applied, do not apply the qualifier flag. Keep the original null code or ND flag in place
7. If a qualifier flag(s) has already been applied, add the "W" flag to the flag column with the other qualifier flags and separate the flags using a comma as shown here: "MD,W"
8. Add a comment to the data validation spreadsheet indicating the action taken, initial and date the comment.
9. Additional sampler collection issues detected by the sampler software are "temp. tolerance" errors. If a "temp. tolerance" error is detected it should also be noted on the sampler information form, flag the detected carbonyls in the affected sample "QX". Temp tolerance errors indicate a problem with the KI denuder during the sampling period.
10. Add a comment to the data validation spreadsheet indicating the action taken, initial and date the comment.
11. If a null code or an ND flag has already been applied, do not apply QX. Keep the original null code or the ND code in place.
12. If a qualifier flag(s) has already been applied, add the QX qualifier to the flag column and separate the qualifier flag using a comma as shown here: "MD,LB,QX"
13. Additional sample collection issues detected by the sampler software are "flow tolerance" errors.
14. Flow tolerance errors alone do not require a qualifier flag to be applied to the results. Instead, "flow tolerance" errors must also be accompanied with flow verification failure and/or total sample volume failure. Apply qualifier flag W to all carbonyls detected in the affected sample.
15. If a null code or an ND flag has been applied, do not apply W. Keep the original null code or the ND code in place.
16. If a qualifier flag(s) has been applied, add the W flag to the other qualifier flag and separate using a comma as shown here: "MD,LB,QX,W"
17. Additional sample collection issues involve the recorded flow checks and the recorded total volume on the sampler information forms. If the flow checks or the volume fall outside acceptable limits, apply qualifier flag W to all carbonyls detected in the affected sample.
18. Add a comment to the data validation spreadsheet indicating the action taken, initial and date the comment added to the carbonyl data validation spreadsheet.
19. If a power outage occurred, the duration of the power outage should be noted on the sampler information form.
20. If the duration of the power outage is not included, contact the site operator to determine the length of the power outage or review the electronic sampling data download file (if one is available) to determine how long the power outage lasted.
21. If the power outage lasts for 1 hour or less (UAT samples) or 20 minutes or less (PAMS samples) out of the total sampling period, do not apply the null code "AZ."
22. If the power outage lasts for more than 1-hour (UAT samples) or more than 20 minutes (PAMS samples) out of the total sample collection period, apply null code "AZ" to all carbonyls detected in the affected sample (if the affected sample was analyzed).

23. If the affected sample was not analyzed due to the power outage and the affected sample date is an EPA-Nationally Scheduled Sample date, the AZ null code must be reported for all carbonyls.
24. If the affected sample was analyzed and a null code has already been applied, overwrite the null code with AZ. Sample collection null codes supersede null codes applied for analysis issues such as: AT,AS,AX, and HT.
25. If the affected sample was analyzed and a qualifier code has already been applied, overwrite the qualifier flag with AZ.

5.2.12 Comparing Field-Collected Carbonyl Samples Against the EPA National Sampling Schedule

1. All field-collected sample dates must be compared to the EPA national sampling schedule for the current calendar year and according to the method sampling frequency: 1-in-6 day (UAT) or 1-in-3 day (PAMS). UAT samples are collected all calendar year. PAMS carbonyl samples are collected from June 1 – August 31.
2. Field-collected samples can be missed from time to time. To find these instances, look for the words “make up sample” in the comment column in the data validation spreadsheet.
3. The sample date of the field-collected samples with this type of comment are not collected on an EPA nationally scheduled sample date. Therefore, the original EPA nationally scheduled sample date was missed for some reason.
4. The reason for missing the EPA nationally scheduled sample date should be recorded on the sample information form assigned to the designated make up sample.
5. If the reason for the missed sample is not recorded, contact the site operator to determine why the scheduled sample was missed.
6. Insert the missing sample in chronological order by sample date into the data validation spreadsheet UAT or PAMS workbook tabs (depending on which method contains the missing sample).
7. Leave the sample #, Lot ID, Extraction Date, and Analysis Date and Time cells blank on the data validation spreadsheet.
8. Add the field site where the missing sample was supposed to be collected “Candor, Millbrook, or Millbrook D” for the missed UAT sample.
9. Add the field site “Millbrook CH1 P-1, Millbrook CH1 P-2, Millbrook CH1 P-3” for the missed PAMS sample.
10. Add the missed EPA nationally scheduled sample to the sample date column. Also add the time: 0:00 for UAT; 04:00 for Millbrook CH1 P-1; 12:00 for Millbrook CH1 P-2; and 20:00 for Millbrook CH1 P-3
11. Apply the null code that best describes the missed sample in the flag column to all carbonyls of the missed sample.
12. Add a comment to the data validation spreadsheet briefly explaining the null code applied. Initial and date the comment.

5.2.13 Application of Qualifier Flags for Primary and Collocated Sample Precision Issues (UAT only)

1. Once all null codes and qualifier flags have been applied due to sampling and analysis issues, the last flag to be applied to the carbonyl data involves an evaluation of the primary and collocated sample collection pairs.
2. Open the carbonyl data validation spreadsheet for the current calendar year and click on the "YYYY UAT carbonyls_ppbv+L3 flags" workbook tab.
3. Transfer the rows containing M and MD in the sample# to the "UAT Prim.vsColl._ppbv_QAflag3" workbook tab in the carbonyl data validation spreadsheet.
4. In the "UAT Prim.vsColl._ppbv_QAflag3" workbook tab, the RPD is calculated automatically as the rows are added. The calculated RPD appears in the cell below the MD carbonyl concentration.
5. If the RPD between the primary and collocated carbonyl concentration is outside the limit of ±25%, apply qualifier flag "3" to the failing carbonyl concentrations detected in the primary and collocated sample.
6. If a null code or ND flag has already been applied, do not apply the "3" flag. Keep the original null code or ND flag.
7. If a qualifier flag(s) has already been applied, add the "3" flag to the existing qualifier flag(s) and separate using a comma as shown here: "LB,3".
8. Also, add the null code or qualifier flag to the cell right next to the calculated RPD

5.3 Generating Time Series Charts Ratio Charts

Time series charts are generated to visualize urban and rural formaldehyde concentrations. These charts are not used to apply null codes or qualifier flags but are instead used to find data points that require a second look. The second look may require the analyst to reprocess the data package that contains the "suspect data point."

Ratio charts are used to compare compounds detected in the sampled cartridge. Compounds that fail the control limits of the ratios are not necessarily null coded or qualified, but instead require a second look that may require the analyst to reprocess the data package containing the "suspect data point." In most cases of failing ratios, the detected compounds and/or the sample is qualified or null coded for failing sampling and/or analysis measurement quality objectives.

5.3.1 Urban vs. Rural Formaldehyde Time Series Charts

This chart applies to UAT carbonyl samples collected at the primary Millbrook (urban) and Candor (rural) sites. These charts should be generated immediately following the application of the final qualifier flags to the carbonyl data.

1. Open the carbonyl data validation spreadsheet and click the "YYYY UAT carbonyls_ppbv+L3 flags" workbook tab.
2. Count the number of Candor samples recently transferred to this workbook tab. Remember this number.
3. Click on the "UAT Carbonyls Urban vs Rural" workbook tab.

4. Go to the last data point in the “Rural” column. Click the row number to highlight the entire row, right click and insert the same number of rows determined in Step #2.
5. Click on the last row and copy and paste this row to the top blank row recently inserted in step #4.
6. Click on the “YYYY UAT carbonyls_ppbv+L3 flags” workbook tab and transfer the information from column A through column L to the recently inserted rows in the “UAT Carbonyls Urban vs Rural” workbook tab. Use the “ctrl” key to include multiple selections.
7. Check the chart to ensure the added data are included in the chart. If the chart did not update with the new data, highlight the data in the chart and click “select data” to adjust the data ranges in the chart so the recently added data are included.
8. Repeat steps 1-7 but this time count the Millbrook samples recently added and go to the last data point in the “Urban” column of the “UAT Carbonyls Urban vs Rural” workbook tab to insert the recently added Millbrook data.
9. Once the control charts have been updated, the charts should be examined to be sure the following trends hold true: Urban formaldehyde values are > Rural formaldehyde values.
10. If a deviation is detected, examine the “UAT Carbonyls Urban vs Rural” workbook tab for null codes or qualifier flags applied to the data point displaying the deviation.
11. If a null code or qualifier flag has been applied, no further steps are necessary to investigate the cause of the suspect data point.
12. If a null code or qualifier flag was not previously applied, open the sampler information form to look for field or lab comments that may have been overlooked and may help explain the anomaly.
13. If the comment is not present. Open the analysis chromatogram and look for integration and/or baseline issues that may help explain the anomaly.
14. Contact the lab analyst to see if the data point in question can be corrected by reprocessing the data point.
15. If reprocessing is not possible, apply a qualifier flag “QX” to all carbonyls detected in the urban and rural data point in question on the UAT carbonyls workbook tab in the carbonyl data validation spreadsheet
16. Add a comment briefly explaining the qualifier flag. Initial and date the comment

5.3.2 PAMS 8hr vs. UAT 24hr Carbonyl Concentrations Time Series Charts

This control chart only applies during the PAMS season. During the PAMS season the carbonyl concentrations detected in the PAMS and UAT samples collected at the Millbrook site can be compared. This chart typically requires a calendar quarters’ worth of data to effectively monitor the typical trend between the two collection methods.

1. Open the carbonyl data validation spreadsheet and click the “YYYY PAM carbonyls_ppbv+L3 flags” workbook tab.
2. Count the number of Millbrook PAMS carbonyl samples recently transferred to the workbook tab. Remember this number.
3. Click the “PAMS 8hr vs UAT 24hr_ppbv” workbook tab.

4. Go to the last row of the entries made to the PAMS 8hr data and click the number of the last row to highlight the entire row. Right click and insert the same number of rows counted in step #2.
5. Click on the last row and copy and paste this row to the top blank row inserted in step #4.
6. Click on the "**YYYY** PAM carbonyls_ppbv+L3 flags" workbook tab and transfer the information from column A through column L to the recently inserted rows in the "PAMS 8hr vs UAT 24hr_ppbv" workbook tab. Use the "ctrl" key to include multiple selections.
7. Check the chart to ensure the added data are included in the chart. If the chart did not update with the new data, highlight the data in the chart and click "select data" to adjust the data ranges in the chart so the recently added data are included.
8. Repeat steps 1-7 but this time separately count the UAT samples (Millbrook and Millbrook D) recently transferred and go to the last data point in the "24-hour UAT Primary" column and the "24-hour UAT Collocated" column of the "PAMS 8hr vs UAT 24hr_ppbv" workbook tab to insert the recently added UAT data to the chart.
9. This process should update the time series charts for all the carbonyls reported to AQS.
10. Once the charts have been updated, the time series charts should be examined to be sure the following trends hold true: 8hr carbonyl concentrations line will appear noisy (sharp increases and decreases in concentrations) from sample to sample while the 24hr carbonyl concentration line will appear smoother from sample to sample. Additionally, the graph lines should show the primary and collocated UAT samples overlap, rising and falling together from sample to sample. The 24hr UAT values should also be trending with the 8hr PAMS values.
11. If a deviation is detected examine the ""PAMS 8hr vs UAT 24hr_ppbv" workbook tab for null codes or qualifier flags applied to the data point displaying the deviation.
12. If a null code or qualifier flag has been applied, no further steps are necessary to investigate the cause of the suspect data point.
13. If a null code or qualifier flag has not been applied, open the sampler information form to look for field or lab comments that may have been overlooked and may help explain the anomaly.
14. If the comment is not present. Open the analysis chromatogram and look for integration and/or baseline issues that may help explain the anomaly.
15. Contact the lab analyst to see if the data point in question can be corrected by reprocessing the data point.
16. If reprocessing is not possible, apply a qualifier flag "QX" to the 8hr and 24hr carbonyl concentration data point in question in the UAT and PAMS workbook tab of the carbonyl data validation spreadsheet.
17. Add a comment briefly explaining the qualifier flag. Initial and date the comment.

5.3.3 Generating Ratio Charts

Ratio charts are used to compare formaldehyde, acetaldehyde, and propionaldehyde concentrations detected in ambient samples only. Carbonyls detected in blank and spiked cartridges will not follow typical ratio trends and should not be included in the ratio chart. Ratio charts must be generated using only carbonyls detected in ambient samples. Samples and carbonyls null coded due to sampling or

analysis method quality objective (MQO) failures cannot be included in the ratio chart. Samples and carbonyls with qualifier flags applied should be included in the ratio chart.

1. Open the carbonyl data validation spreadsheet and click the "YYYY UAT Carbonyls_ppbv+L3Flags" workbook tab.
2. Count the number of Millbrook, Millbrook D, and Candor samples recently added to the validation spreadsheet. Remember this number.
3. Click the "UAT and PAMS Carbonyl Ratios" workbook tab and go to the last data point entered and insert the same number of lines as counted in step #2 above.
4. Copy and paste the last row to the first blank row previously inserted.
5. Click on the "YYYY UAT Carbonyls_ppbv+L3Flags" workbook tab and transfer the information from column A to column P to the inserted rows in the "UAT and PAMS Carbonyl Ratios" workbook tab.
6. Repeat steps 1-5 for the recently added PAMS carbonyl samples.
7. Once the control chart data has been added, update the ratio calculations in columns R and T and ensure the calculations are referencing the correct cells
8. Update the control limits in columns S and U. column S is always 1 and column U is always 10.
9. Click on the control charts and select the data ranges to be sure the charts are displaying the updated data recently added.
10. Once the control charts are shown to be accurate, examine the control chart for points that fall below the acceptable limit line.
11. Data points that fall outside the ratio may indicate a sampling or analysis issue.
12. In most cases data points that fall below the control limits have already been qualified for sampling or analysis MQO failures.
13. If a data point falls below the control limit line and was not already qualified, review the COC form for field comments that may have been missed during the Level 1 and Level 2 reviews.
14. If a comment is not found, open the analysis chromatogram, and examine the integration of the suspect data point.
15. If an issue is observed in the analysis chromatogram, contact the primary analyst to re-process the suspected data point and provide updated results.
16. If reprocessing is not possible, ask the primary analyst to re-analyze the sample.
17. If re-analysis is not possible, flag the suspect sample and carbonyl "QX" prior to AQS upload. Include a brief comment explaining the reason for the QX flag.
18. Record the comment in the "YYYY UAT Carbonyls_ppbv+L3Flags" workbook tab or "YYYY PAM Carbonyls_ppbv+L3Flags" workbook tab, depending on which sampling method contains the suspect data point. Also, initial and date the comment.

6.0 INDEPENDENT ACCURACY AUDITS

Independent accuracy audits consist of proficiency testing (PT) and instrument performance audits (IPA). These assessments are also used to evaluate and control the bias of the UAT and PAMS carbonyl analysis and sampling methods.

6.1 Carbonyl Laboratory Analysis Proficiency Testing (PT)

Proficiency testing (PT) samples are used to assess bias in the UAT and PAMS carbonyl analysis method. The DAQ LAB participates in the NATTS PT program. The DAQ LAB receives PT samples from an EPA approved contractor, extracts and analyzes the sample, and submits the results to the EPA contractor.

At a minimum, two times per calendar year (actual frequency depends on availability of EPA contractor supplies) the DAQ LAB ships out an unsampled DNPH cartridge to an approved EPA contractor to spike the blank DAQ cartridge with carbonyl compounds. The spiked cartridge is returned to the DAQ LAB, and the carbonyl analyst extracts and analyzes the PT sample(s) alongside routine, field collected UAT and PAMS carbonyl samples.

The results of the PT sample are reported to the EPA contractor by the Level 3 reviewer and a report is generated by the EPA contractor comparing reported results against designated NATTS laboratory average results, the referee laboratory average results, and the nominal carbonyl concentration spiked on the PT sample.

6.2 Instrument Performance Audit (IPA)

Carbonyl sampler (ATEC 2200 and ATEC 8000) MFC's are calibrated by the LAB electronics technician prior to field deployment using a National Institute of Standards and Technology (NIST) traceable flow standard. Flow rate verifications are performed by the site operator before and after each sample event using a different NIST traceable flow standard. The results of pre and post sample flow verifications are recorded on the carbonyl cartridge sampler information forms.

In addition to the routine calibration and verification check performed by the electronics technician and site operators, twice per calendar year and at least once every 182 days, the Level 3 reviewer or designee performs an IPA using a NIST traceable flow standard that is different from the flow standards used for routine sampler flow verifications and carbonyl sampler MFC calibrations.

The result of the IPA is recorded in the site logbook. The IPA should be performed while the site operator is present so the auditor and site operator results can be compared.

7.0 PRECISION CHECK DATA

Carbonyl precision is measured in three ways. The first precision measurement is derived from repeat analysis of a field-collected sample during an analysis sequence (also known as duplicate injection analysis). The results of the duplicate injections are reported to AQS.

The second precision measurement is derived from the cartridge spike and cartridge spike duplicate sample results (also known as extraction and analysis precision). DAQ does not currently report these results to AQS but maintains the results in the QA Summary reports and the data validation spreadsheet.

The third precision measurement is derived from the primary and collocated sample pairs collected in the UAT carbonyl network (also known as overall method precision). Carbonyl concentrations detected in the primary sample are reported to AQS using POC **3** and the carbonyl concentrations detected in the collocated sample are reported to AQS as POC **4**.

Please see **Figure 25** below for the precision equation. The CV must be ≤ 15%.

Figure 25: Formula for Calculating CV

$$CV = \sqrt{\frac{\sum_{i}^{n}\left[\frac{(p-r)}{0.5 * (p+r)}\right]^2}{2n}}$$

p = primary value
r = replicate, repeated or collocated value
n = number of pairs and n must be ≥ 2

When a single pair of precision data are being evaluated, the RPD is calculated using part of the formula bracketed in **Figure 25**. This equation is simply defined as the **difference/average** and the RPD must be ± 25%. The equation is as follows: ***RPD = [(p-r)/(0.5*(p+r))]*100***

Within 30 days of the conclusion of the calendar quarter, the Level 3 reviewer prepares and sends a "UAT and PAMS Carbonyl Precision Summary Report" to DAQ management and staff directly involved in the UAT operations. This report includes CVs calculated from the beginning of the calendar year to the end of the most recent calendar quarter. The CV is calculated using primary and collocated sample collection pair RPDs, cartridge spike and cartridge spike duplicate pair RPDs, and duplicate injection pair RPDs.

8.0 AIR QUALITY SYSTEM TRANSACTION FILE GENERATION

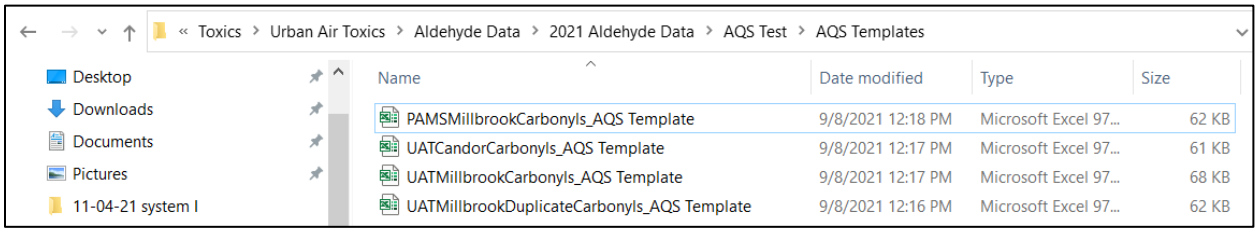
The Level 3 reviewer generates pipe delimited transaction files which are used to upload UAT and PAMS carbonyl concentration data, blank and precision data, and NATTS PT sample results.

8.1 Raw Data Transaction File Generation and Reporting

The Level 3 reviewer generates pipe delimited text files that are derived from AQS templates populated with validated carbonyl concentration data. This process occurs every calendar quarter. Validated data from the carbonyl data validation spreadsheet is transferred into AQS templates and the AQS templates are converted into pipe delimited text files. These pipe files are manually uploaded to AQS within 90 days from the end of the calendar quarter.

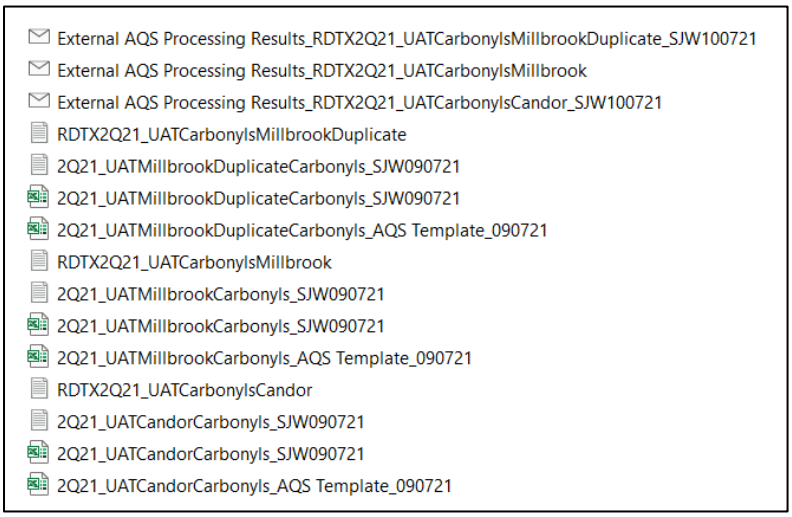
1. Open the AQS template located here that pertains to the method (UAT or PAMS) and site: **P:\Toxics\Urban Air Toxics\Aldehyde Data\YYYY Aldehyde Data\AQS Test\AQS Templates**. The file names are shown in **Figure 26** below. In this example, we'll use UAT carbonyls from second quarter of 2021.

Figure 26: AQS Template File Location



2. Create storage folders for the calendar quarter's worth of data. The naming conventions are shown in **Figure 27** below. The storage location should be here: **P:\Toxics\Urban Air Toxics\Aldehyde Data\2021 Aldehyde Data\AQS Test\UAT-Carbonyls\2021\2Q**.

Figure 27: AQS File Naming Conventions



3. Save the AQS template as "2Q21_UATCandorCarbonyls_AQS Template_MMDDYY" where the MMDDYY is the current date the file is created.
4. Repeat this process for the remaining UAT carbonyl sites (Millbrook and MillbrookDuplicate).
5. Save the files using the naming convention in step 3 but replace "Candor" with "Millbrook" and "MillbrookDuplicate".
6. Open the data validation spreadsheet and transfer carbonyl sample dates, carbonyl concentrations, null code(s), and qualifier flag(s) to the AQS template.
7. Once data has been added to the AQS template, delete the top row (containing header names) and save the file using the naming convention in step 3 but replace "AQS Template_" with the initials (3 letters) of person creating the file
8. Also save the file using the same name as shown in step 7 but save the file as a text, tab delimited file.
9. Open the tab delimited text file.
10. Highlight the space between "RD and I" and press "ctrl C" to copy the space
11. Click edit, replace.
12. In the "find what" field paste the space recently copied
13. In the "replace with" field place the pipe character. Click replace all.
14. Next, in the "find what" field enter "end"
15. In the "replace with" field keep this space blank. Click replace all.
16. This file is now a formatted and ready for AQS upload.
17. Using second quarter 2021 Candor carbonyl data as the example, save the file as "RDTX2Q21_UATCarbonylsCandor." The quarter number and two-digit year will change depending on the quarter and calendar year the data are being transcribed into AQS pipe delimited text files.
18. Repeat steps 1-17 for each UAT carbonyl site and or other quarters. Remember each quarter is saved in a unique folder.
19. Once all RDTX files have been made, copy the files to the following location: **P:\Ambient\PUB\RegOffices.NC\AQS\Manual Upload Files.**
20. Send an email to the data base manager indicating pipe delimited text files are in the manual upload folder and are ready for upload to AQS.
21. Upon completion of the data upload, the data base manager emails the AQS transaction details to the Level 3 reviewer.
22. Using the 2nd quarter 2021 Candor carbonyl data as the example, the AQS transaction detail file is saved using the naming convention shown in the first 3 files listed in **Figure 27**.
23. The Level 3 reviewer then examines the AQS transaction details for transactions that were rejected by AQS. Rejected transactions must be corrected and re-uploaded to AQS.
24. Changes to the files require the file to be saved using the same naming conventions with the addition of a version number added to the end of the file name.

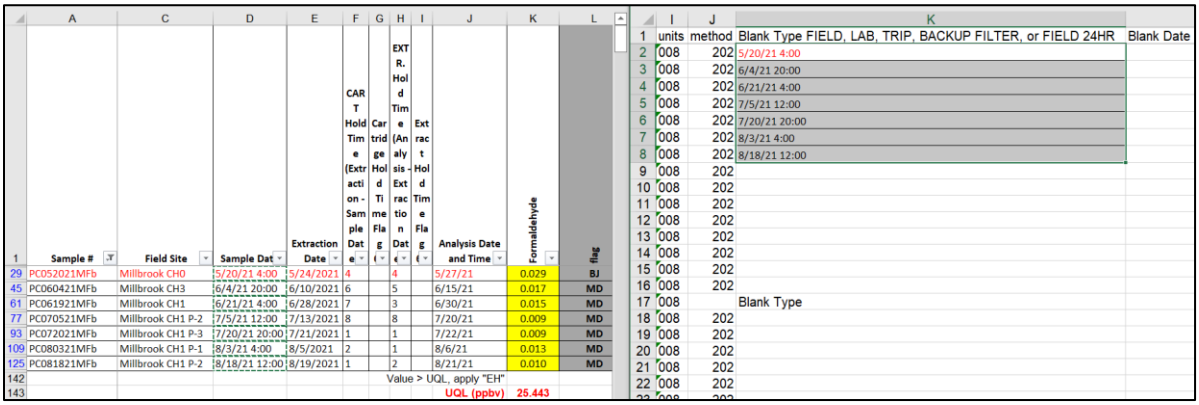
8.2 Quality Control Transaction File Generation and Reporting

This section describes creation and transformation of the QC transaction files for PAMS and UAT field blank results, and PAMS and UAT replicate (duplicate injection) results.

8.2.1 PAMS and UAT Carbonyl Field Blank Transaction Files

1. Open the file named **PAMS_FieldBlanks_MillbrookCarbonyls_AQS Template**. This file is located on the p-drive here: **P:\Toxics\Urban Air Toxics\Aldehyde Data\YYYY Aldehyde Data\AQS Test\AQS Templates**. The four-digit calendar year "YYYY" will change depending on the calendar year the field blanks were sampled and reported to AQS.
2. Save the AQS template using the following naming convention: **YYYY_PAMS_FB_MillbrookCarbonyls** with YYYY denoting the calendar year the field blanks were collected. Save the file on the p-drive here: **P:\Toxics\Urban Air Toxics\Aldehyde Data\YYYY Aldehyde Data\AQS Test\PAMS-Carbonyls\YYYY**
3. Open the current year carbonyl data validation workbook and click the "YYYY PAM Carbonyls_ppbv+L3Flags" workbook tab.
4. Click the custom filter dropdown menu for column A.
5. Uncheck the select all box and then check all sample #'s that contain "Fb" in the sample # name.
6. Transfer the information in column D of the data validation spreadsheet into column K of the AQS template for field blanks. This is only temporary to ensure the proper dates and times are reported. See **Figure 28** below (left side of figure is data validation spreadsheet and right side of figure is the AQS FB template.

Figure 28: Transferring PAMS FB Data



	A	C	D	E	F	G	H	I	J	K	L
1	Sample #	Field Site	Sample Dat	Extraction Date	CART Hold Time (Extraction - Sample Date)	Cartridge Holded Time Flag	EXT R. Hold Time (Analysis - Extraction Dat	Extract Holded Time Flag	Analysis Date and Time	Formaldehyde	flag
29	PC052021MFb	Millbrook CH0	5/20/21 4:00	5/24/2021	4		4		5/27/21	0.029	BJ
45	PC060421MFb	Millbrook CH3	6/4/21 20:00	6/10/2021	6		5		6/15/21	0.017	MD
61	PC061921MFb	Millbrook CH1	6/21/21 4:00	6/28/2021	7		3		6/30/21	0.015	MD
77	PC070521MFb	Millbrook CH1 P-2	7/5/21 12:00	7/13/2021	8		8		7/20/21	0.009	MD
93	PC072021MFb	Millbrook CH1 P-3	7/20/21 20:00	7/21/2021	1		1		7/22/21	0.009	MD
109	PC080321MFb	Millbrook CH1 P-1	8/3/21 4:00	8/5/2021	2		1		8/6/21	0.013	MD
125	PC081821MFb	Millbrook CH1 P-2	8/18/21 12:00	8/19/2021	1		2		8/21/21	0.010	MD
142							Value > UQL, apply "EH"				
143									UQL (ppbv)	25.443	

	I	J	K	L
1	units	method	Blank Type FIELD, LAB, TRIP, BACKUP FILTER, or FIELD 24HR	Blank Date
2	008	202	5/20/21 4:00	
3	008	202	6/4/21 20:00	
4	008	202	6/21/21 4:00	
5	008	202	7/5/21 12:00	
6	008	202	7/20/21 20:00	
7	008	202	8/3/21 4:00	
8	008	202	8/18/21 12:00	
9	008	202		
10	008	202		
11	008	202		
12	008	202		
13	008	202		
14	008	202		
15	008	202		
16	008	202		
17	008		Blank Type	
18	008	202		
19	008	202		
20	008	202		
21	008	202		
22	008	202		

7. In the AQS FB template, split the dates and times recently entered in column L using this format YYYYMMDD, where YYYY is the four-digit year, MM is the two-digit month, and DD is the two-digit day and enter the time in column M using this format HH:MM, where HH is the two-digit hour and MM is the two-digit minutes.
8. Replace the dates and times recently entered in column K with "FIELD"
9. Copy and paste the data in columns K, L, and M (only rows 2-8) into the same columns but into rows 18-24 and repeat for all parameters listed in the file.
10. Delete the rows with a blank value in column K. Using **Figure 28** as an example, delete rows 9-16 and repeat this process for each parameter. The next parameter starts on row 18 in the right side of **Figure 28**.
11. Transfer the information (measured concentration) in column K of the data validation spreadsheet to column N on the AQS FB template for the first parameter.

12. Transfer the information in column L of the data validation spreadsheet (flags) to column O of the AQS template. Null codes will stay in column O and a null concentration should be reported in column N. If qualifier flags are present, keep the concentration value and the flag must be moved from column O to column P of the AQS template. If multiple qualifier flags are applied (separated by a comma) separate the qualifier codes into column Q, R or S depending on how many qualifier codes have been applied.
13. Information from column M of the data validation spreadsheet also goes into column N on the AQS FB template but for the next parameter (starting on row 18 when using **Figure 28** as an example). Repeat until all concentrations from the data validation spreadsheet are transferred to the AQS template.
14. Repeat the transfer of null codes and qualifier codes for each parameter in the AQS template. See step #12 above.
15. Transform the AQS template by deleting row #1 and all rows that start with a # sign. Unfreeze the panes. The AQS template should now look like **Figure 29** below.

Figure 29: Transformed AQS Template

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB
1	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210520	04:00		BJ													end
2	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210604	20:00	0.017		MD												end
3	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210621	04:00	0.015		MD												end
4	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210705	12:00	0.009		MD												end
5	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210720	20:00	0.009		MD												end
6	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210803	04:00	0.013		MD												end
7	RB	I	37	183	0014	43502	2	5	008	202	FIELD	20210818	12:00	0.010		MD												end
8	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210520	04:00		BJ													end
9	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210604	20:00	0.015		MD												end
10	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210621	04:00	0.038		MD												end
11	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210705	12:00	0.028		MD												end
12	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210720	20:00	0.021		MD												end
13	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210803	04:00	0.028		MD												end
14	RB	I	37	183	0014	43503	2	5	008	202	FIELD	20210818	12:00	0.027		MD												end
15	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210520	04:00		BJ													end
16	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210604	20:00	0.000		ND												end
17	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210621	04:00	0.000		ND												end
18	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210705	12:00	0.000		ND												end
19	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210720	20:00	0.000		ND												end
20	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210803	04:00	0.000		ND												end
21	RB	I	37	183	0014	43504	2	5	008	202	FIELD	20210818	12:00	0.000		ND												end

16. Save the transformed AQS template as an Excel workbook and then save the template again as a text (tab delimited) file.
17. Open the text file and highlight the space between RB and I, right click and select copy.
18. Click the edit replace and paste the copied space in the “find what” field.
19. Enter a pipe character in the “replace with” field and select replace all.
20. Enter the text “end” into the “find what” field and leave the “replace with” field blank and select replace all.
21. Scroll to the bottom of the file and delete the pipes that show up below the last row of numerical data.
22. Save this text file using the following naming convention “RBTXYYYY_PAMS_FB_MillbrookCarbonyls” where YYYY is the four-digit year. The file will now look like Figure 30 below.

Figure 30: PAMS FB Pipe Delimited File

```
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210520|04:00||BJ|||||||||||||
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210604|20:00|0.017||MD|||||||||||
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210621|04:00|0.015||MD|||||||||||
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210705|12:00|0.009||MD|||||||||||
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210720|20:00|0.009||MD|||||||||||
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210803|04:00|0.013||MD|||||||||||
RB|I|37|183|0014|43502|2|5|008|202|FIELD |20210818|12:00|0.010||MD|||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210520|04:00||BJ|||||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210604|20:00|0.015||MD|||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210621|04:00|0.038||MD|||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210705|12:00|0.028||MD|||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210720|20:00|0.021||MD|||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210803|04:00|0.028||MD|||||||||||
RB|I|37|183|0014|43503|2|5|008|202|FIELD |20210818|12:00|0.027||MD|||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210520|04:00||BJ|||||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210604|20:00|0.000||ND|||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210621|04:00|0.000||ND|||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210705|12:00|0.000||ND|||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210720|20:00|0.000||ND|||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210803|04:00|0.000||ND|||||||||||
RB|I|37|183|0014|43504|2|5|008|202|FIELD |20210818|12:00|0.000||ND|||||||||||
```

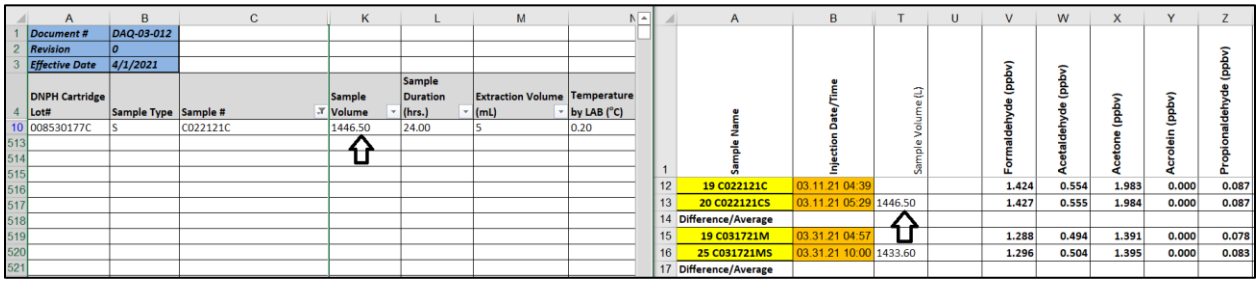
23. Place a copy of the RBTX file in the manual upload folder on the p-drive and notify the data base manager that data are ready for AQS upload.
24. Repeat Steps 1-23 for UAT FB results. Replace the terms “PAMS or PAM” with “UAT” in the naming conventions and storage locations of the generated files and replace “Millbrook” with “MillbrookDuplicate” and “Candor” (additional UAT sites). There are AQS templates for each UAT site and PAMS site.

8.2.2 UAT and PAMS Carbonyl Replicate Transaction Files

1. Open the file named **PAMS_Replicates(duplicate injection)_MillbrookCarbonyls_AQS Template.** This file is located here: **P:\Toxics\Urban Air Toxics\Aldehyde Data\YYYY Aldehyde Data\AQS Test\AQS Templates**. The four-digit calendar year “YYYY” will change depending on the calendar year the replicates were collected.
2. Save the AQS template using the following naming convention: **YYYY_PAMS_Replicates(duplicate injection)_MillbrookCarbonyls** with YYYY denoting the calendar year the replicates were collected. Save the file on the p-drive here: **P:\Toxics\Urban Air Toxics\Aldehyde Data\YYYY Aldehyde Data\AQS Test\PAMS-Carbonyls\YYYY**
3. Open the current year carbonyl data validation workbook and click the “LAB Dup. Inj._ug_mL (CV)” workbook tab.
4. Duplicate injection precision calculations and flagging of the data based on precision issues is performed using the units of the analysis instrument. The initial and duplicate injection values are reported to AQS in the units of ppbv. The duplicate injection data is transferred to the data validation spreadsheet according to steps in section 5.1.6 of this document.
5. These values must be converted to ppbv then transferred to the AQS replicate template.
6. Open the current year PAMS and UAT carbonyl master spreadsheet and click on the “extraction log” workbook tab.

7. Click the filter drop down for column C and locate the sample # that matches the same sample listed in column A of the data validation spreadsheet "LAB Dup. Inj._ug_mL (CV)" workbook tab.
8. Transfer the volume from column K of the master spreadsheet to column T of the data validation spreadsheet "LAB Dup. Inj._ug_mL (CV)" workbook tab. Make sure the volume is in column T but also on the same row as the sample with the letter "S" at end of sample name.
9. Once the volume is entered into the correct column, the duplicate injection values transferred in section 5.1.6 will be automatically converted to ppbv as shown in figure 31 below.

Figure 31: Volume Transfer for Replicates

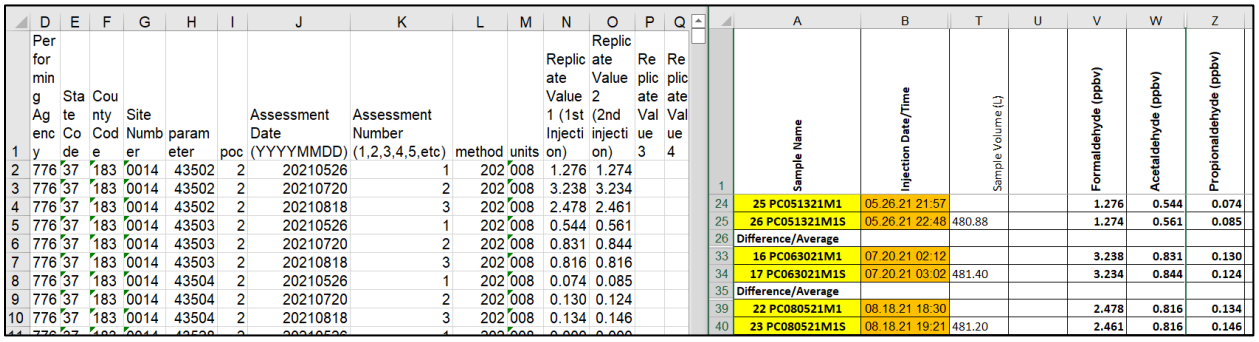


	A	B	C	K	L	M	N
1	Document #	DAQ-03-012					
2	Revision	0					
3	Effective Date	4/1/2021					
4	DNPH Cartridge Lot#	Sample Type	Sample #	Sample Volume	Sample Duration (hrs.)	Extraction Volume (mL)	Temperature by LAB (°C)
10	008530177C	S	C022121C	1446.50	24.00	5	0.20
513							
514							
515							
516							
517							
518							
519							
520							
521							

	A	B	T	U	V	W	X	Y	Z
1	Sample Name	Injection Date/Time	Sample Volume (L)		Formaldehyde (ppbv)	Acetaldehyde (ppbv)	Acetone (ppbv)	Acrolein (ppbv)	Propionaldehyde (ppbv)
12	19 C022121C	03.11.21 04:39			1.424	0.554	1.983	0.000	0.087
13	20 C022121CS	03.11.21 05:29	1446.50		1.427	0.555	1.984	0.000	0.087
14	Difference/Average								
15	19 C031721M	03.31.21 04:57			1.288	0.494	1.391	0.000	0.078
16	25 C031721MS	03.31.21 10:00	1433.60		1.296	0.504	1.395	0.000	0.083
17	Difference/Average								

10. The assessment date is the same date as in column B row 12 in **Figure 31** above and must be transformed to YYYMMDD format when entered in the AQS replicate template.
11. Transfer the value in ppbv (columns V-AH) of the data validation spreadsheet (right side Figure 31) into recently saved AQS replicate template.
12. The AQS replicate file with three PAMS replicate assessments for the 2021 PAMS carbonyl season is shown in the left side of **Figure 32** below. The right side shows the replicate values and assessment dates being transferred from the data validation spreadsheet to the AQS replicate template.

Figure 32: Filled out AQS Replicate File



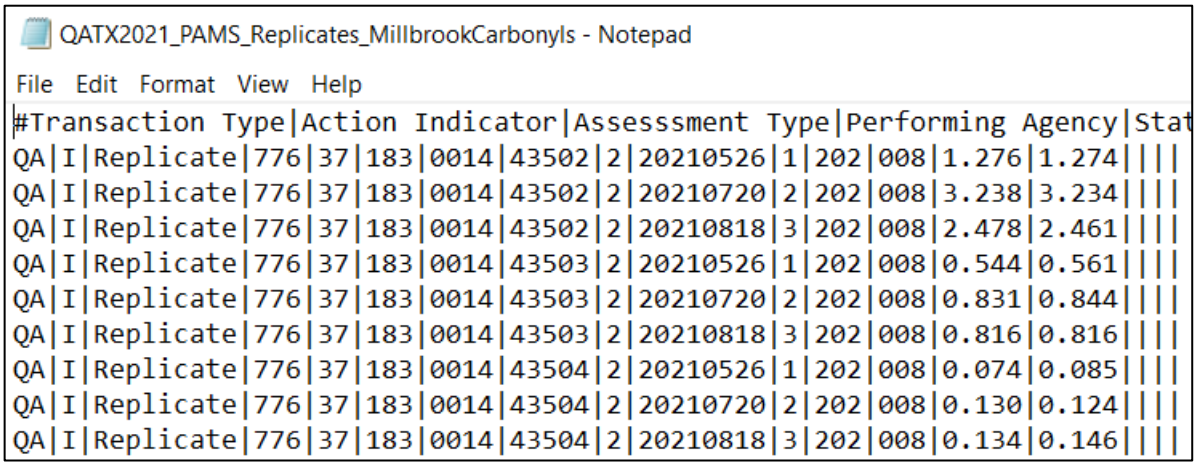
	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	Performing Agency	State Code	County Code	Site Number	parameter	poc	Assessment Date (YYYYMMDD)	Assessment Number (1,2,3,4,5,etc)	method	units	Replicate Value 1 (1st Injection)	Replicate Value 2 (2nd injection)	Replicate Value 3	Replicate Value 4
2	776	37	183	0014	43502	2	20210526	1	202	008	1.276	1.274		
3	776	37	183	0014	43502	2	20210720	2	202	008	3.238	3.234		
4	776	37	183	0014	43502	2	20210818	3	202	008	2.478	2.461		
5	776	37	183	0014	43503	2	20210526	1	202	008	0.544	0.561		
6	776	37	183	0014	43503	2	20210720	2	202	008	0.831	0.844		
7	776	37	183	0014	43503	2	20210818	3	202	008	0.816	0.816		
8	776	37	183	0014	43504	2	20210526	1	202	008	0.074	0.085		
9	776	37	183	0014	43504	2	20210720	2	202	008	0.130	0.124		
10	776	37	183	0014	43504	2	20210818	3	202	008	0.134	0.146		

	A	B	T	U	V	W	Z
1	Sample Name	Injection Date/Time	Sample Volume (L)		Formaldehyde (ppbv)	Acetaldehyde (ppbv)	Propionaldehyde (ppbv)
24	25 PC051321M1	05.26.21 21:57			1.276	0.544	0.074
25	26 PC051321M1S	05.26.21 22:48	480.88		1.274	0.561	0.085
26	Difference/Average						
33	16 PC063021M1	07.20.21 02:12			3.238	0.831	0.130
34	17 PC063021M1S	07.20.21 03:02	481.40		3.234	0.844	0.124
35	Difference/Average						
39	22 PC080521M1	08.18.21 18:30			2.478	0.816	0.134
40	23 PC080521M1S	08.18.21 19:21	481.20		2.461	0.816	0.146

13. Save the AQS replicate file once all values have been transferred from the data validation spreadsheet.
14. Save the AQS replicate file as a text, tab delimited file.
15. Open the text file and make sure the top row contains a # sign. AQS will ignore rows that start with # sign. Add a # sign to the top row if it's missing.
16. Highlight the space between QA and I, right-mouse click, and select copy

17. Left click the “edit” menu at top of text file and select “replace”
18. Paste the recently copied space in the “find what” field and enter a pipe character in the “replace with” field. Select replace all.
19. Enter “end” into the “find what” field and leave the “replace with” field blank with no characters or spaces.
20. The AQS replicate text file should look like **Figure 33** below

Figure 33: Pipe Delimited AQS Replicate File



21. Save this file using the following convention: “QATXYYYY_PAMS_Replicates_MillbrookCarbonyls” where YYYY denotes the current calendar year the replicate assessments were analyzed.
22. Place a copy of the QATX file in the manual upload folder on the p-drive and notify the data base manager that data are ready for AQS upload.
23. Repeat Steps 1-22 for UAT Carbonyl Replicate results. Replace the terms “PAMS or PAM” with “UAT” in the naming conventions and storage locations of the generated files and replace “Millbrook” with “MillbrookDuplicate” and “Candor” (additional UAT sites). There are AQS templates for each UAT site and PAMS site.

9.0 TROUBLESHOOTING AND CORRECTIVE ACTIONS

Routine troubleshooting and corrective actions are described in this section.

9.1 Data Validation Issues

During data validation the Level 3 reviewer may discover errors in the sampling and analysis records originally data review records.

9.1.1 Level 1 and Level 2 Reviews

During data validation, the Level 3 reviewer may discover issues from the Level 1 and Level 2 data reviews. The level 3 reviewer contacts the Level 1 and Level 2 reviewer for issue correction. Reports or checklists that may be edited/changed/altered during this process must be saved in a manner that the original documentation, record, report, or checklist is preserved along with the corrected documentation. This is typically achieved by adding a "version #" or "update #" to the end of the original file name.

9.1.2 Correcting Data Uploaded to AQS

If AQS errors are discovered, corrections must be made by the Level 3 reviewer. The documentation of the data corrections is recorded in the "AQS Audit Report and Data Update Form 9.0". Contact the PPB chemist responsible for this form and request and blank copy. Fill in all fields of the form where applicable to the correction. See Appendix **11.2** for an example of this form and some of the fields.

The best practice is to find the excel template version of the transaction files that contains the error and resave the file with "updates1" added to the file name.

9.2 NATTS PT Issues

Carbonyl compounds reported between two consecutive failing PT sample assessment dates must be qualified "QX,4" in AQS. This action may require data already reported to AQS to be updated with the "QX,4" qualifier flags. Follow guidance in section 9.1.2 to update AQS data. Carbonyl concentrations reported between the two failing PT samples must have the results qualified "QX,4" in AQS. Additionally, the qualifier flags must remain on the data until the failing carbonyl compound passes the next PT sample or passes the next In-house PT sample.

Immediately following the NATTS PT failure, the Level 3 reviewer prepares an "In-house" PT sample. The Level 3 reviewer spikes a blank, unsampled carbonyl cartridge with a known amount of derivatized or underivatized carbonyl compounds that are traceable to NIST. The Level 3 reviewer may spike a mixture of several carbonyl compounds but at a minimum must include the same compounds as in the original NATTs PT sample.

The in-house PT sample is handed directly to the carbonyl analyst to be extracted and analyzed. The Level 3 reviewer generates and sends an "In-house PT Sample Results Report" to DAQ management and staff directly involved in carbonyl analysis that summarizes the results of the "in-house PT" and provides "pass/fail" indicator for each carbonyl spiked in the PT sample.

9.3 Instrument Performance Audit Issues

In the event a failing IPA occurs, the level 3 reviewer will locate a second NIST flow standard and fresh, unsampled DNPH cartridge from the DAQ LAB and perform the IPA again. If the failing status is confirmed, the sampler must be removed from the field for recalibration of the MFC and recertified as clean prior to returning to the field site.

Additionally, the Level 3 reviewer must qualify all carbonyls detected in the affected samples "QX,W". The affected samples include all samples analyzed prior to the last passing IPA.

The cartridges are typically the cause of failing flow verifications, IPAs, and sampler software warnings of flow rate issues during sampling events. Because pre and post flow verifications are NOT performed on the DNPH cartridge used for sample collection, it's possible to have sampler software errors for flow rates while the pre and post sample flow verifications pass.

9.4 Primary and Collocated Sample Collection Pair RPD Issues

When three consecutive carbonyls detected in sufficient quantities from primary and collocated sample collection pairs fails the RPD acceptable limits (± 25); application of qualifier codes for affected carbonyls must occur, but also a CAR must be generated to determine the root cause of the systemic failure. The CAR is generated according to **SOP# DAQ-15-002**.

10.0 REVISION HISTORY

1. Revision 0, SJW 02/08/2022

11.0 APPENDICES

11.1 UAT and PAMS Carbonyl Precision Summary Report

UAT and PAMS Carbonyl Precision Summary Report

Overall UAT Precision (Primary VS Collocated)

Carbonyl	CV	PASS/FAIL	Comment
Formaldehyde	6.04%	PASS	
Acetaldehyde	7.64%	PASS	
Propionaldehyde	6.71%	PASS	
Crotonaldehyde	#DIV/0!	#DIV/0!	could not be calculated because all field-collected samples are ND
2-Butanone (MEK)	3.21%	PASS	
Methacrolein	3.64%	PASS	
Butyraldehyde	6.90%	PASS	
Benzaldehyde	7.62%	PASS	
Valeraldehyde	6.50%	PASS	
m-tolualdehyde	#DIV/0!	#DIV/0!	could not be calculated because all field-collected samples are ND
Hexaldehyde	7.94%	PASS	

UAT and PAMS Extraction Precision (Cartridge Spike VS Cartridge Spike Duplicate)

Carbonyl	CV	PASS/FAIL	Comment
Formaldehyde	1.18%	PASS	
Acetaldehyde	0.91%	PASS	
Propionaldehyde	1.12%	PASS	
Crotonaldehyde	1.73%	PASS	
2-Butanone (MEK)	1.55%	PASS	
Methacrolein	1.26%	PASS	
Butyraldehyde	1.46%	PASS	
Benzaldehyde	1.05%	PASS	
Valeraldehyde	1.93%	PASS	
m-tolualdehyde	1.58%	PASS	
Hexaldehyde	0.87%	PASS	

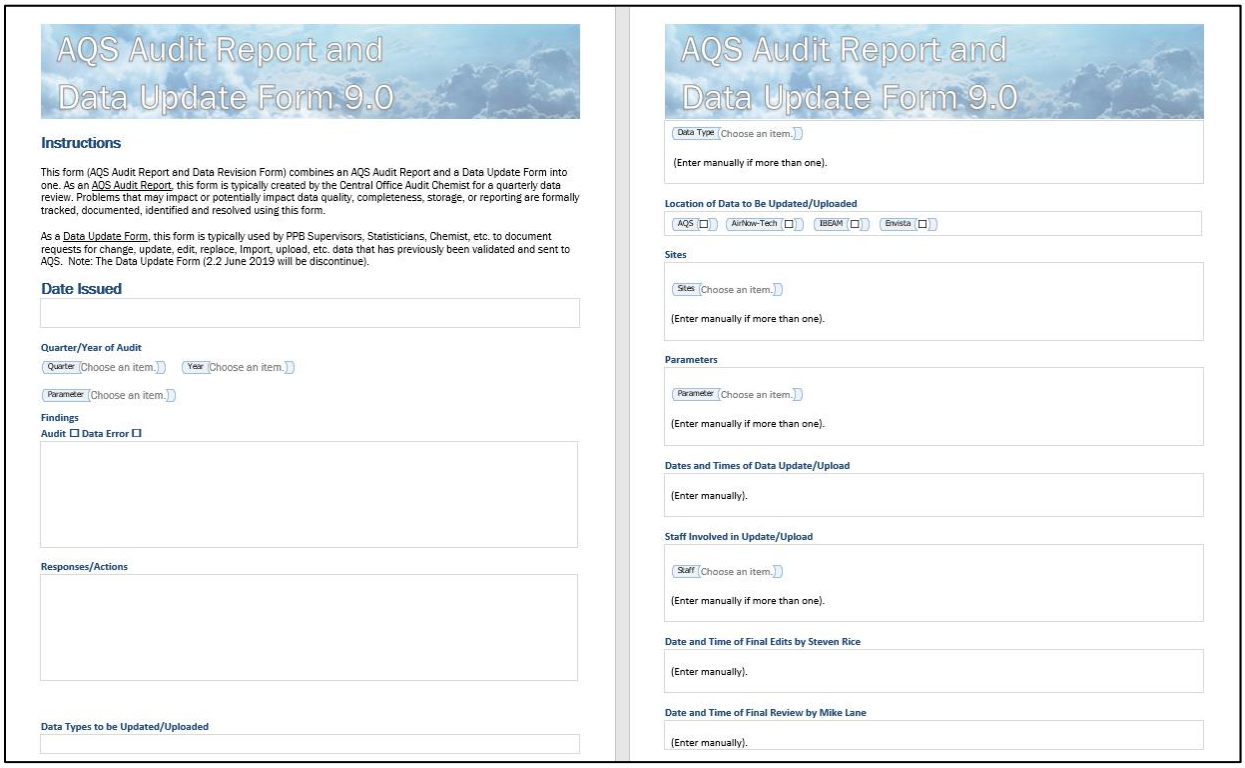
UAT and PAMS Duplicate Injection Precision (First Injection VS Second Injection of Field Sample)

Carbonyl	CV	PASS/FAIL	Comment
Formaldehyde	0.22%	PASS	
Acetaldehyde	0.87%	PASS	
Propionaldehyde	4.70%	PASS	
Crotonaldehyde	#DIV/0!	#DIV/0!	could not be calculated because all field-collected samples are ND
2-Butanone (MEK)	4.34%	PASS	
Methacrolein	0.76%	PASS	
Butyraldehyde	6.87%	PASS	
Benzaldehyde	7.85%	PASS	
Valeraldehyde	7.22%	PASS	
m-tolualdehyde	#DIV/0!	#DIV/0!	could not be calculated because all field-collected samples are ND
Hexaldehyde	5.77%	PASS	

Time Period Covered by Report
1-1-2021 to 6-31-2021

Prepared by:	Date Prepared:
Steven Walters (level 3 reviewer)	7/15/2021

11.2 AQS Audit and Data Update Form



AQS Audit Report and Data Update Form 9.0

Instructions

This form (AQS Audit Report and Data Revision Form) combines an AQS Audit Report and a Data Update Form into one. As an AQS Audit Report, this form is typically created by the Central Office Audit Chemist for a quarterly data review. Problems that may impact or potentially impact data quality, completeness, storage, or reporting are formally tracked, documented, identified and resolved using this form.

As a Data Update Form, this form is typically used by PPB Supervisors, Statisticians, Chemist, etc. to document requests for change, update, edit, replace, Import, upload, etc. data that has previously been validated and sent to AQS. Note: The Data Update Form (2.2 June 2019 will be discontinue).

Date Issued

Quarter/Year of Audit

Quarter Choose an item. Year Choose an item.

Parameter Choose an item.

Findings

Audit ☐ Data Error ☐

Responses/Actions

Data Types to be Updated/Uploaded

AQS Audit Report and Data Update Form 9.0

Data Type Choose an item.

(Enter manually if more than one).

Location of Data to Be Updated/Uploaded

AQS ☐ AirNow-Tech ☐ IBEAM ☐ Envista ☐

Sites

Sites Choose an item.

(Enter manually if more than one).

Parameters

Parameter Choose an item.

(Enter manually if more than one).

Dates and Times of Data Update/Upload

(Enter manually).

Staff Involved in Update/Upload

Staff Choose an item.

(Enter manually if more than one).

Date and Time of Final Edits by Steven Rice

(Enter manually).

Date and Time of Final Review by Mike Lane

(Enter manually).

12.0 REFERENCES

1. EPA Compendium Method TO-11A, second addition, January 1999: https://www.epa.gov/sites/default/files/2019-11/documents/to-11ar.pdf
2. National Air Toxics Trends Station, Technical Assistance Document, Revision 3, October 2016: https://www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf
3. Technical Assistance Document for Sampling and Analysis of Ozone Precursors for PAMS, Revision 2, April 2019: https://www.epa.gov/sites/default/files/2019-11/documents/pams_technical_assistance_document_revision_2_april_2019.pdf