

**STATE OF VERMONT
AIR QUALITY & CLIMATE DIVISION
QUALITY ASSURANCE PROJECT PLAN
FOR THE AIR TOXICS MONITORING AND
NATIONAL AIR TOXICS TRENDS STATIONS NETWORK**

1.0 Title and Approval Sheet

Title: *State of Vermont Air Quality & Climate Division Quality Assurance Project Plan for the Air Toxics Monitoring and National Air Toxic Trends Stations (NATTS) Networks*

As signed and accepted by the people below, the following Quality Assurance Project Plan (QAPP) commits the Vermont Department of Environmental Conservation, Air Quality & Climate Division to the operations described within.

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2.3 List of Acronyms and Abbreviations

AMTIC – Ambient Monitoring Technical Information Center
AQCD – (Vermont) Air Quality and Climate Division
APTI – Air Pollution Training Institute
AQS – Air Quality System
CAA – Clean Air Act
CFR – Code of Federal Regulations
CSA – consolidated statistical area
CV – coefficient of variance
DAS – data acquisition system
DCO – Document Control Officer
DD – Division Director
DEC – (Vermont) Department of Environmental Conservation
DNPH – dinitrophenylhydrazine
DQA – data quality assessment
DQO – data quality objective
EDO – environmental data operation
EPA – Environmental Protection Agency
ESC – Environmental Systems Corporation
FEM – Federal Equivalent Method
FRM – Federal Reference Method
GC – gas chromatography
GC/MS – gas chromatography/mass spectrometry
GIS – geographical information systems
GLP – good laboratory practice
GPS – global positioning system
HAP – hazardous air pollutants
HPLC – high performance liquid chromatography
ICP/MS – inductively coupled plasma/mass spectrometry
ID – identification
IMPROVE – Interagency Monitoring of Protected Visual Environments
IO – Inorganic
IT – information technology
LAN – local area network
LIMS – laboratory information management system
MDL – method detection limit
MFC – mass flow controller
MQAG – Monitoring and Quality Assurance Group
MQOs – measurement quality objectives
MPA – monitoring planning area
MSA – metropolitan statistical area
MSR – management system review
NAAQS – National Ambient Air Quality Standards
NAMS – National Air Monitoring Station
NATTS- National Air Toxics Trends Stations
NECMSA – New England county metropolitan statistical area

NESHAP – National Emission Standards for Hazardous Air Pollutants
NIST – National Institute of Standards and Technology
NPAP – National Performance Audit Program
NSPS – New Source Performance Standard
OAQPS – Office of Air Quality Planning and Standards
OARM – Office of Administration and Resources Management
OIRM – Office of Information Resources Management
OMB – Office of Management and Budget
ORD – Office of Research and Development
PAMS – Photochemical Assessment Monitoring Stations
P&A – precision and accuracy
PC – personal computer
PE – performance evaluation
PM_{2.5} – particulate matter (2.5 microns)
PM₁₀ – particulate matter (10 microns)
PMSA – primary metropolitan statistical area
QA – quality assurance
QA/QC – quality assurance/quality control
QAARWP – quality assurance annual report and work plan
QAD EPA – Quality Assurance Division
QAM – quality assurance manager
QAO – quality assurance officer
QAPP – quality assurance project plan
QA Redbook – most recent revision of EPA’s Quality Assurance Handbook for Air Pollution Measurement Systems (this multi-volume guidance document was once provided in red binders).
QMP – quality management plan
RH – relative humidity
RPD – relative percent difference
SIPS – State Implementation Plans
SLAMS – state and local monitoring stations
SOP – standard operating procedure
SPMS – special purpose monitoring stations
TO – Toxic Organic
TSA – technical system audit
TSP – total suspended particulate
UATMP – Urban Air Toxics Monitoring Program
VAEL – Vermont Agriculture and Environmental Laboratory
VOC – volatile organic compound

3.0 Distribution List

Table 3.1 Distribution List

Name	Position	Division/Branch
Vermont Air Quality & Climate Division		
Heidi Hales, Ph.D.	Director	VT DEC Air Quality & Climate Division
Robert Lacaillade	Monitoring Supervisor/Project Manager	VT DEC AQCD Monitoring Section
Renee Miller	Environmental Analyst	VT DEC AQCD Monitoring Section
Jenny Berschling	Monitoring QA Coordinator	VT DEC AQCD Monitoring Section
Ben DiLauro	Environmental Technician	VT DEC AQCD Monitoring Section
Jean Woodward	Environmental Analyst	VT DEC AQCD Monitoring Section
Jessie Motard-Cote	Environmental Analyst	VT DEC AQCD Planning Section
Vacant	Laboratory Supervisor	VAEL Chemistry Laboratory
David Crosby	Environmental Scientist	VAEL Chemistry Laboratory
Matt Millard	Environmental Scientist	VAEL Chemistry Laboratory
Anne Charbonneau	Environmental Scientist	VAEL Chemistry Laboratory
EPA – New England		
Alysha Lynch	EPA – New England Contact	EPA – New England
Robert Judge	ECA Air Team Leader	EPA – New England

4.0 Project Organization

4.1 Roles and Responsibilities

The roles and responsibilities identified below for the Vermont Air Toxics and NATTS Monitoring program are based on guidelines in EPA's *Quality Management Plan for the National Air Toxics Trends Station Monitoring Program*, EPA-454/R-02-006.

4.1.1 Office of Air Quality Planning and Standards (OAQPS)

OAQPS is the organization charged under the authority of the Clean Air Act (CAA) to protect and enhance the quality of the nation's air resources. OAQPS sets standards for pollutants considered harmful to public health or welfare and, in cooperation with EPA's Regional Offices and the States, enforces compliance with the standards through state implementation plans (SIPs) and regulations controlling emissions from stationary sources. The OAQPS evaluates the need to regulate potential air pollutants, especially air toxics and develops national standards; works with State and local agencies to develop plans for meeting these standards; monitors national air quality trends and maintains a database of information on air toxics and controls; provides technical guidance and training on air pollution control strategies; and monitors compliance with air pollution standards.

Within the OAQPS Emissions Monitoring and Analysis Division (EMAD), the Monitoring and Quality Assurance Group (MQAG) is responsible for the oversight of the Ambient Air Quality Monitoring Network. MQAG has the following responsibilities:

- ▶ ensuring that the methods and procedures used in making air pollution measurements are adequate to meet the programs objectives and that the resulting data are of satisfactory quality
- ▶ operating the National Performance Audit Program (NPAP);
- ▶ evaluating the performance, through technical systems audits and management systems reviews, of organizations making air pollution measurements of importance to the regulatory process;
- ▶ implementing satisfactory quality assurance programs over EPA's Ambient Air Quality Monitoring Network;
- ▶ ensuring that national regional laboratories are available to support toxics and QA programs;
- ▶ ensuring that guidance pertaining to the quality assurance aspects of the Ambient Air Program are written and revised as necessary;
- ▶ Rendering technical assistance to the EPA Regional Offices and air pollution monitoring community.

4.1.2 EPA New England Office

The EPA Regional Offices will address environmental issues related to the States within their jurisdiction and to administer and oversee regulatory and congressionally mandated programs. The major quality assurance responsibilities of EPA's Regional Offices, in regards to the Ambient Air Quality Program, are the coordination of quality assurance matters at the Regional

levels with the State and local agencies. This is accomplished by the designation of EPA Regional Project Officers who are responsible for the technical aspects of the program including:

- ▶ reviewing QAPPs by Regional QA Coordinators who are delegated the authority by the Regional Administrator to review and approve QAPPs for the Agency;
- ▶ supporting the air toxics audit evaluation program;
- ▶ Coordinate quarterly split-sample quality assessment program for Region 1 Labs (when available)
- ▶ evaluating quality system performance, through technical systems audits and network reviews whose frequency is addressed in the Code of Federal Regulations and Section 20;
- ▶ acting as a liaison by making available the technical and quality assurance information developed by EPA Headquarters and the Region to the State and local agencies, and making EPA Headquarters aware of the unmet quality assurance needs of the State and local agencies.

The State of Vermont will direct all technical and QA questions to EPA – New England Office through the Regional EPA – New England contact.

4.1.3 State of Vermont Roles and Responsibilities

The major responsibility of the State of Vermont Air Quality & Climate Division is the implementation of a satisfactory monitoring program, which includes sample collection and analysis with an appropriate quality assurance program. Figure 4.1 represents the organizational structure of the areas of the Vermont AQCD that are responsible for the activities of the Air Toxics Monitoring Program and the National Air Toxics Trends Station (NATTS). The following section lists the specific responsibilities of each individual.

4.1.3.1 AQCD Director – Heidi Hales, Ph.D.

The AQCD Director has the overall responsibility for the functioning of the division, including decision-making authority on budgetary matters.

4.1.3.2 AQCD Monitoring Supervisor/Project Manager– Robert Lacaillade

The Monitoring Supervisor oversees all aspects of air toxics monitoring for the State of Vermont AQCD and our participation in the NATTS. This position is also the Project Manager for VOC, Carbonyl, Metals and Semi-volatiles monitoring programs. The project manager is responsible for the technical operation of the program on a day-to-day basis. He coordinates with the analytical lab and field staff to ensure adequate scheduling, equipment, and procedures are in place to properly complete the project requirements. He is responsible for coordinating the resolution of any technical issues, needs or conflicts that may arise. He is responsible for ensuring that samples are collected on schedule, analyzed in a timely manner and valid results are properly reported and that the QAPP is adhered to. He assists with the development of the QAPP and related SOPs and performs QA activities for the sampling and data validation portions of the project.

4.1.3.3 AQCD Quality Assurance Coordinator– Jenny Berschling

This position is responsible for review of the QAPP and related SOPs and performing and/or participating in technical system audits of all field operations. The QA Coordinator will also review assessment reports and reports to management to be able to verify the validation status and quality of project data. This position reports directly to the Monitoring Supervisor. This position is also responsible for data submittal into AQS

4.1.3.4 AQCD Environmental Analyst and Technician –Renee Miller, Ben DiLauro

These positions are responsible for operating and maintaining field equipment and collecting samples for VOC, carbonyls, trace metals and semi-volatiles as well as performing performance audits and routine maintenance activities. Ben DiLauro performs review, validation and reporting of VOC results under the Supervisor’s oversight.

4.1.3.5 AQCD Environmental Analyst- Field Operations Center – Jean Woodward

This position is the responsible for filter logistics and sample handling for the trace metals monitoring program including pre and post sample filter receiving/preparation and coordination with the gravimetric lab. This position also performs PM10 gravimetric data review/ validation prior to submittal for metals analysis. This position also prepares the PM10 filters for delivery to VAEL for analysis after completing the lab’s pre-registration form and coordinates their delivery to VAEL. This position also performs review, validation and reporting of Carbonyl results under the Supervisor’s oversight and serves as a backup for field activities in 4.1.3.4.

4.1.3.6 VAEL Director– Guy Roberts

The Lab Director is ultimately responsible for all the analytical laboratory activities associated with VOC, carbonyl and metal analyses. He oversees and ensures proper validation and reporting of VOC, Carbonyl and Metals results to the AQCD which meet established data quality objectives. He also serves as a point of contact to address any program/data issues.

4.1.3.7 VAEL QA Officer – Vacant

The Lab QA Coordinator is responsible for conducting an independent review and validation of the analytical results following the established data quality objectives in the QAPP. This position is current vacant and is under recruitment. While vacant these responsibilities will be performed by various designated staff.

4.1.3.8 VAEL Organic Chemistry: Technical Director- David Crosby; Chemist– Matt Millard; Chemist-- Candice Barber

Matt Millard is primary staff responsible for VOC and carbonyl analysis. This includes the cleaning and certification of 6L canisters to meet sampling requirements and ensuring verified DNPH cartridges are available for the field staff to meet sampling requirements. David Crosby provides backup and peer review for VOC analyses while Candice Barber provides backup and peer review for carbonyl analyses.

4.1.3.9 VAEL Metals Center: Technical Director Anne Charbonneau; Chemist Rachel Markey

Anne Charbonneau is primary staff responsible for trace metal sample extraction and analysis. Rachel Markey provides backup and peer review for trace metal analyses.

4.1.4 Eastern Research Group (ERG) Roles and Responsibilities

4.1.4.1 As EPA's support Laboratory for Air Toxics and NATTS, ERG in Morrisville, NC is responsible for:

- ▶ Backup VOC, Carbonyl and Metals sample analyses and associated canister preparation/certification (as needed).
- ▶ Underhill Semi-volatile sample prep and analyses, method and SOP development
- ▶ Report analytical results to VT AQCD, EPA New England and upload to AQS as needed

Figure 4.1 Vermont DEC Air Toxic Monitoring Organizational Chart

DEC-AQCD Air Toxics Monitoring Organization

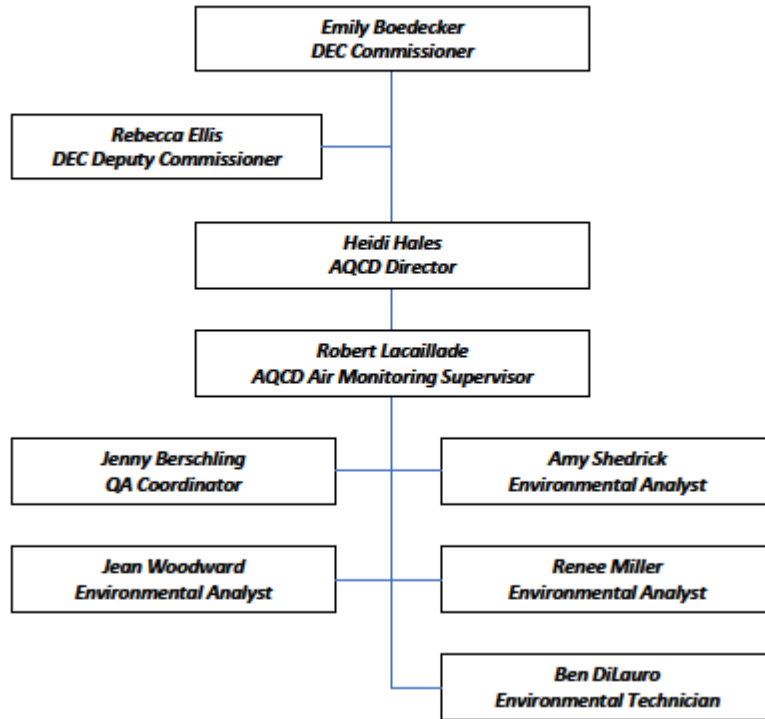
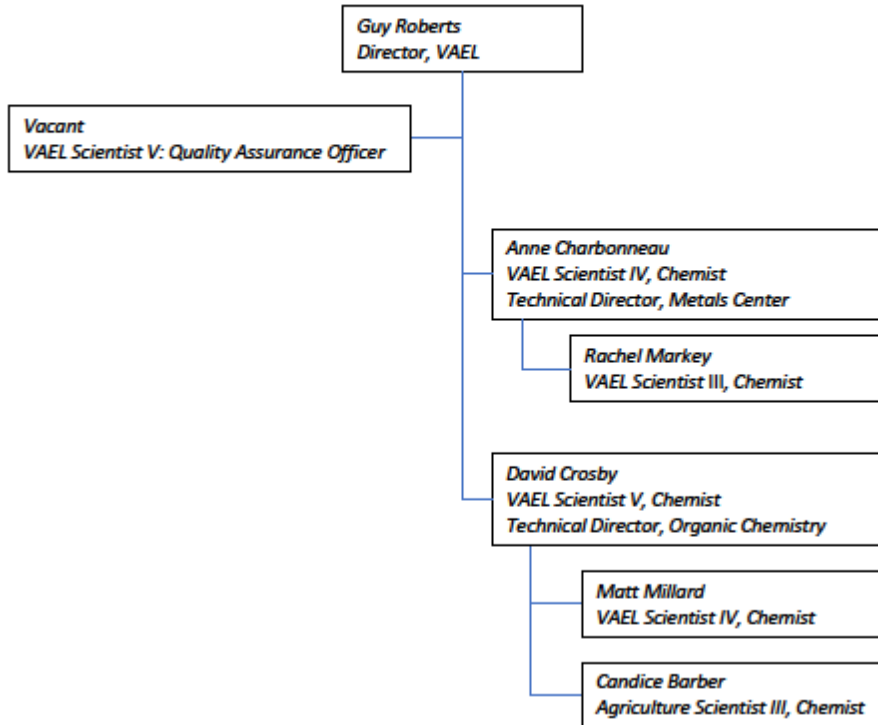


Figure 4.2 Vermont Agriculture and Environmental Laboratory Air Toxics Organization Chart

VAEL Air Toxics Organization



5.0 Problem Definition/Background

Considering the lack of ambient monitoring data for air toxics, the Vermont Legislature mandated in 1993 (Act 92) that an air toxics monitoring program be conducted by the Agency of Natural Resources under the guidance of the Hazardous Air Contaminant Advisory Committee. This mandate directed the Agency to measure the presence of hazardous air contaminants in ambient air and gather sufficient data to allow the Secretary to establish appropriate standards. One portion of the monitoring program to meet this goal is collecting ambient air samples at multiple sites around the state and analyzing them for volatile organic compounds (VOC) such as benzene and 1,3 butadiene, as well as carbonyl compounds such as formaldehyde and acetone. Vermont began operating four (4) sites in the Vermont Air Toxics Monitoring Network measuring VOCs, carbonyls. From 1993-1997, the VOC/Carbonyl portion of the network was conducted through participation in EPA's Urban Air Toxics Monitoring Program (UATMP). The UATMP program is a year-round sampling program, collecting 24-hour integrated ambient air samples at urban sites in the contiguous United States every 12 days. After 1998 the VOC/Carbonyl portion of the Vermont Air Toxics Monitoring Network was conducted using a combination of contractor and in-house samplers and laboratory analyses. Beginning in 2003, all sampling and analyses for VOC/Carbonyls was conducted completely in-house. In 2004 the Underhill site began participation in the EPA's National Air Toxics Trends Station (NATTS) monitoring program. NATTS required semi-volatiles, trace metals and hexavalent chromium at Underhill, the analysis for which is done through an ERG contract with EPA. In 2008, the Brattleboro site was terminated and in January of 2009, the VOC analyst position at the DEC Lab was eliminated due to a State reduction in force process. At that time the AQCD was forced to contract with ERG for VOC analytical services through March 31, 2010. At that point ERG continued to provide VOC analytical services via the EPA National Contract through 2013. On August 28, 2011 flooding caused by tropical storm Irene destroyed the DEC Lab building in Waterbury, Vermont and the AQCD was forced to use the EPA Region 1 Laboratory for Carbonyl analytical services for samples collected through June 30, 2012. Samples collected after that date were analyzed by ERG through the EPA National Contract through January 2013 for Burlington and Rutland samples and June 30, 2013 for Underhill samples. Hexavalent Chromium sampling/analysis was suspended at the Underhill NATTS site on July 1, 2013. The DEC Lab was relocated to the Hills Building on the UVM Campus in Burlington. TO-11A capability was restored in February 2013, TO-15 capability was restored on January 1, 2014 and Metals analyses capability was restored on January 1, 2015. In July 2015, the DEC Lab officially merged with the Agency of Agriculture, Food & Markets Lab to become the Vermont Agriculture and Environmental Lab (VAEL). In 2017, the VAEL hired a new organic chemist for VOC and carbonyl analyses and the AQCD began submitting Rutland PM10 filters for metals analyses. In 2018 the AQCD began submitting Burlington PM10 filters for metals analyses.

The two (2) other current sites are located in Burlington and Rutland. A list of pollutants to be measured is presented in Tables 5.1, 5.2 and 5.3. The NATTS site (Underhill) is located in a rural area and is considered a background site in the NATTS network. The Burlington and Rutland sites are considered population based/neighborhood scale.

The NATTS network is an effort by EPA to characterize national air toxics exposures and trends using air toxics monitoring data.

Table 5.1 Volatile Organic Compounds Measured at Vermont Air Toxic Sites

1,1,1-Trichloroethane	Carbon Tetrachloride	Methyl Methacrylate
1,1,2,2-Tetrachloroethane	Chlorobenzene	METHYL tert-BUTYL ETHER
1,1,2-Trichloroethane	Chloroethane	Methylene Chloride
1,1-Dichloroethane	Chloroform	n-Octane
1,1-Dichloroethene	Chloromethane	o-DICHLOROBENZENE
1,2,4-Trichlorobenzene	CHLOROPRENE	o-Xylene
1,2,4-Trimethylbenzene	cis-1,2-DICHLOROETHYLENE	p-DICHLOROBENZENE
1,2-Dibromoethane	cis-1,3-Dichloropropene	Styrene
1,2-Dichloroethane	Dibromochloromethane	tert-AMYL METHYL ETHER
1,2-Dichloropropane	Dichlorodifluoromethane	TETRACHLOROETHYLENE
1,3,5-Trimethylbenzene	DICHLOROTETRAFLUROETHANE	Toluene
1,3-Butadiene	Ethyl Acrylate	trans-1,2-DICHLOROETHYLENE
3-Chloropropene	Ethyl tert-Butyl Ether	trans-1,3-Dichloropropene
Acrolein	Ethylbenzene	TRICHLOROETHYLENE
Acrylonitrile	HEXACHLORO-1,3-BUTADIENE	Trichlorofluoromethane
Benzene	m,p-XYLENE	TRICHLOROTRIFLUOROETHANE
Bromochloromethane	m-DICHLOROBENZENE	Vinyl Chloride
Bromodichloromethane	Methyl Isobutyl Ketone	
Bromoform		
Bromomethane		

Table 5.2 Carbonyl compounds measured at Vermont Air Toxic Sites

Formaldehyde	Benzaldehyde	2,5-Dimethylbenzaldehyde
Acetaldehyde	Isovaleraldehyde	
Acetone	Valeraldehyde	
Propionaldehyde	Tolualdehydes	
Butyraldehyde	Hexanaldehyde	

Table 5.3 Trace Metals (DEC)and Semivolatiles (ERG)

Trace Metals	Semi-volatiles	Semi-volatiles
Antimony	Naphthalene	Acenaphthylene
Arsenic	Acenaphthene	Fluorene
Barium	9-Fluorenone	Fluoranthene
Beryllium	Pyrene	Phenanthrene
Cadmium	Anthracene	Retene
Chromium	Benz(a)anthracene	Cyclopenta(c,d)pyrene
Cobalt	Chrysene	Benzo(b)fluoranthene
Lead	Benzo(k)fluoranthene	Benzo(e)pyrene
Manganese	Benzo(a)pyrene	Perylene
Molybdenum	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene
Nickel	Benzo(g,h,i)perylene	Coronene
Selenium		
Silver		
Strontium		
Vanadium		

6.0 Project/Task Description

6.1 Description of Work to be Performed

The four types of measurements used to quantify the compounds identified in Tables 5.1, 5.2 and 5.3 are:

- ▶ VOCs, collected in RESTEK Silcosteel-treated stainless steel canisters, following EPA Method TO-15.
- ▶ Carbonyls, collected on dinitrophenylhydrazine (DNPH)-Waters SepPAK® cartridges, using EPA Method TO-11A.
- ▶ Trace metals, collected by the low-volume PM10 method on calendar year Teflon® filters using EPA Method IO-3.1 and IO-3.5.
- ▶ Semi-volatiles, collected using a 104 mm quartz filter and glass thimble containing PUF/XAD sandwich and analyzed following ERG-MOR-049, EPA Method TO-13A and ASTM D6209 (Underhill site only).

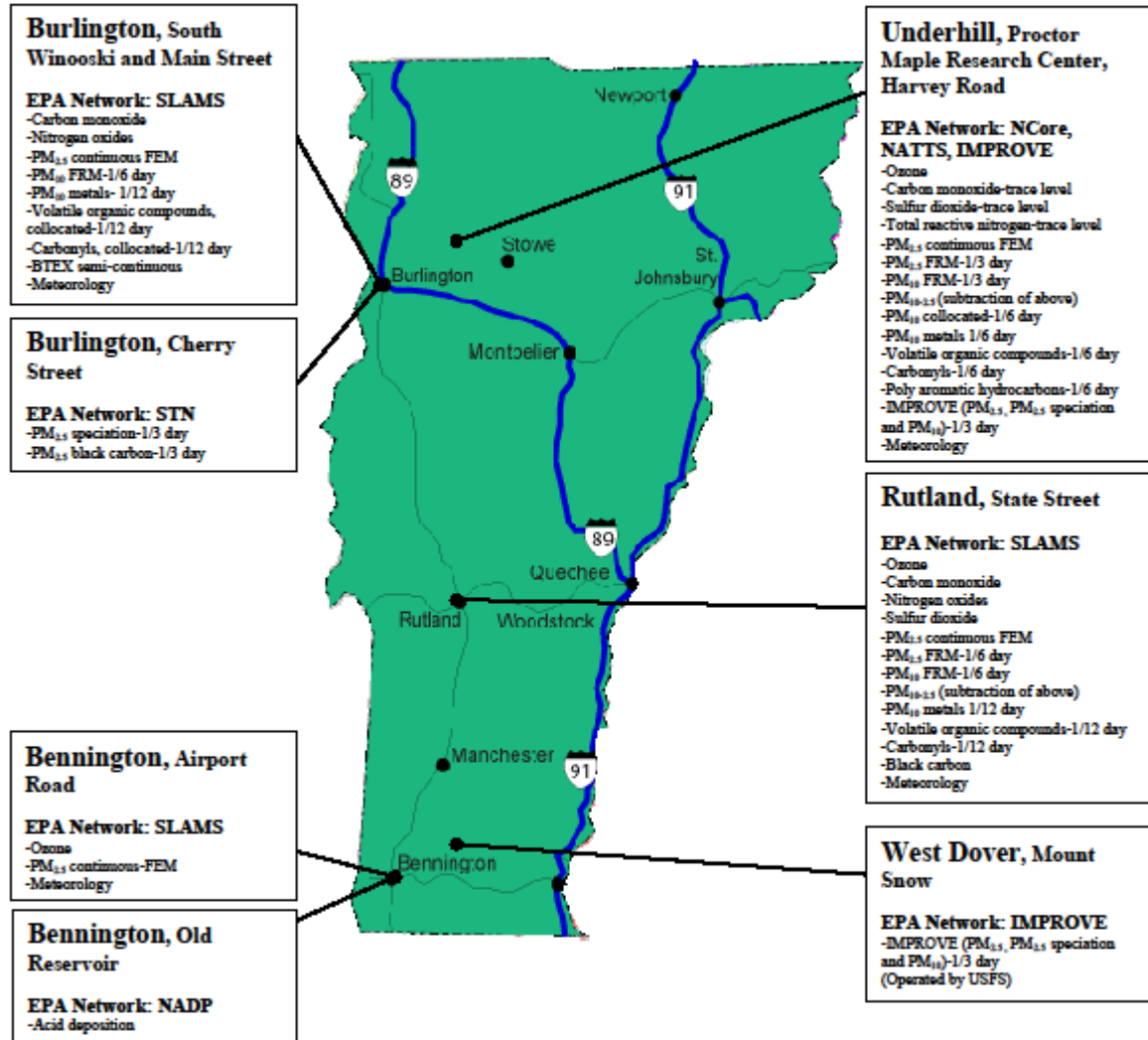
These measurements will be made at the following sites:

- ▶ Underhill (NATTS site) (VOC, Carbonyl, semi-volatile and trace metals)
- ▶ Burlington (VOC and Carbonyl and trace metals)
- ▶ Rutland (VOC and Carbonyl and trace metals)

See Figure 6.1 for the complete ambient air-monitoring network map for the State of Vermont.

Figure 6.1 State of Vermont Ambient Air Monitoring Network Map (2018)

2018 Vermont Ambient Air Monitoring Network



The following sections will describe the measurements required for the routine field and laboratory activities for the network. Details on the sampling and analytical methods are provided in Sections 11 and 13.

6.2 Field Activities

The following parameters will be monitored at AQCD sites as indicated in Section 6.1.

VOCs: Sub-atmospheric whole-air samples are collected in specially treated, stainless steel, six (6) liter canisters using automated samplers. VOC samples are collected over a 24-hour period from midnight to midnight. Underhill will collect samples on the published EPA one-in-six day (1/6) sampling schedule and Burlington and Rutland will collect samples on the EPA one-in-twelve day (1/12) sampling schedule. Co-located VOC samples will be collected at the Burlington site on the 1/12 schedule. After each sampling period, field staff downloads pertinent information from the samplers on a thumb drive (which is emailed to Supervisor), print a chain of custody label (which is adhered to the field data sheet) complete the proper documentation for the sample on the field data sheet and then transport it to the Barre, VT AQCD facility where it is processed and delivered to the VAEL at UVM (Burlington, VT) Samplers undergo periodic maintenance, performance verification and biennial certification.

Carbonyls: Integrated ambient air samples are collected in cartridges containing DNPH-coated silica gel using automated samplers. Carbonyl samples are collected over a 24-hour period from midnight to midnight. Underhill will collect samples on the published EPA one-in-six day (1/6) sampling schedule and Burlington and Rutland will collect samples on the EPA one-in-twelve day (1/12) sampling schedule. Co-located carbonyl samplers will be collected at the Burlington site on the 1/12 schedule. After each sampling period, field staff downloads pertinent information from the samplers on a thumb drive (which is emailed to Supervisor), print a chain of custody label (which is adhered to the field data sheet) complete the proper documentation for the sample on the field data sheet and then transport it in a cooler (with ice packs) to the Barre, VT AQCD facility where it is refrigerated until transport to the VAEL at UVM (Burlington, VT) for analysis in batches. Samplers undergo periodic maintenance, performance verification and annual certification.

Trace Metals: Integrated, 24-hour low-volume PM₁₀ samples will be collected on the published EPA one-in-six day (1/6) schedule on Teflon® filters at the Underhill (NATTS) and one-in-twelve (1/12) schedule at the Burlington and Rutland sites. PM₁₀ samples are collected over a 24-hour period from midnight to midnight. After each sampling period, Field staff downloads pertinent information from the samplers, complete the proper documentation for the sample and then transport it to the Barre, VT AQCD facility where samples are placed into plastic holders. Labeled and shipped to Connecticut DEEP for processing, and post weighing. Post weighed filters are shipped back to the Barre, VT AQCD facility in coolers with ice packs ($\leq 4^{\circ}\text{C}$) where they are placed in labeled Hot Block polypropylene digestion tubes and delivered to VAEL for analysis. Samplers undergo periodic maintenance and performance verification.

Semi-volatiles: Integrated, 24-hour semi-volatile samples will be collected on the published EPA one-in-six day (1/6) schedule at the Underhill Site using a sampling assembly that includes a quartz filter and glass sleeve containing a PUF/XAD sandwich. Samples are collected over a 24-hour period from midnight to midnight. A field blank will be collected on normal sampling

days at a frequency specified in ERG's SOP. After each sampling period, field staff record pertinent information from the samplers, complete the proper documentation for the sample and then transport it to the Barre, VT AQCD facility in coolers with blue ice ($\leq 4^{\circ}\text{C}$). Samples are stored in a dedicated freezer until they are processed and then shipped to the ERG Lab in coolers with blue ice. All analysis is done at the ERG laboratory. Samplers undergo periodic maintenance and performance verification.

6.3 Laboratory Activities

The laboratory activities include three general phases:

Pre-Sampling

- ▶ Receiving filters, PUF/XAD glass sleeves and quartz filter, VOC canisters and DNPH cartridges from the vendors, CT DEEP, VAEL and ERG;
- ▶ Checking sample integrity;
- ▶ Verifying DNPH cartridge background levels;
- ▶ Conditioning PM₁₀ Teflon filters under controlled conditions and pre-weighing them @ CT DEEP
- ▶ Storing canisters at room temperature
- ▶ Storing pre-weighed filters prior to field use;
- ▶ Storing DNPH cartridges at $\leq 4^{\circ}\text{C}$ prior to field use;
- ▶ Cleaning and certifying canisters;
- ▶ Preparing filters, canisters, PUF sampling assembly and cartridges for field use;
- ▶ Associated QA/QC activities, such as canister certification;
- ▶ Maintaining microbalance and analytical equipment at specified environmental conditions (CT DEEP);
- ▶ Analytical and microbalance equipment maintenance and calibrations (CT DEEP).
- ▶ Pre-registering VOC, Carbonyl and Metals samples with VAEL Staff for their subsequent LIMS login when samples delivered to the VAEL.

Shipping/Receiving

- ▶ Receiving, canisters and cartridges from the field and logging into the laboratory information management system and related AQCD database(s);
- ▶ Receiving pre-weighed Teflon filters from the CT DEEP for field sampling and processing them after sampling for shipment to CT DEEP then receiving post weighed sample filters for subsequent metals analysis.
- ▶ Storing filters, canisters and cartridges as appropriate prior to analyses;
- ▶ Delivering and/or shipping filters, canisters, cartridges and PUF glass sleeves and quartz filters to VAEL or ERG, as applicable.

Post-Sampling

- ▶ Checking filter, cartridge, PUF sleeve/filter and canister integrity;
- ▶ Disassemble PUF sample assembly
- ▶ Stabilizing and post-weighing filters after conditioning under controlled conditions (CT DEEP);
- ▶ Extraction of metals from Teflon filter;
- ▶ Extraction of carbonyl-hydrazone compounds from the DNPH cartridge;

- ▶ Proper storing of DNPH extract (if applicable);
- ▶ Storing DNPH cartridges $\leq 4^{\circ}\text{C}$ after sampling;
- ▶ Shipping PUF sleeves to ERG in coolers with blue ice; Transport canisters, cartridges and Teflon filters to UVM via state vehicle and logging in the VAEL LIMS
- ▶ Analytical equipment maintenance and calibrations;
- ▶ Analysis of extracted samples;
- ▶ Storing filters/archiving;
- ▶ Associated QA/QC activities and Data review.

6.4 Final Data Processing Activities

The Supervisor performs final validation, which is then verified by the AQCD Quality Assurance Officer. The Supervisor and/or QA Coordinator are then responsible for creating and uploading data file for AQS. The Supervisor(s) perform summaries of the data and generate associated reports.

6.5 Project Assessment Techniques

The quality assessments that will be implemented as part of Air Toxics Monitoring and NATTS network are presented in Tables 6.1-6.4

Table 6.1 Assessment Schedule for VOC and Carbonyl

Assessment Type	Assessment Agency	Frequency
Performance Evaluation Audit/Round Robin (NATTS)	EPA NATTS Contract Lab	Biannual for TO-15 and TO-11A
Performance Evaluation Audit	ERG or AQCD (NATTS and/or contract lab as available)	Biannual
Technical Systems Audits/Network Review (NATTS)	EPA New England Region	Every 3 years
Technical Systems Audits/Network Review (NATTS)	OAQPS-EMAD	As necessary
Technical Systems Audits/Network Review	AQCD (QA Coordinator)	Annual
Performance Audits (field)	AQCD	Biannual
Spit Sample Quality Assurance	EPA New England Region	When available
Second Source Standard	ERG or VAEL (internal)	Every Batch run
Precision (Co-located and analytical replicate samples)	AQCD or contract lab	Every 1/12 sample and each batch run
Field Sampler Certification	AQCD or contract lab	Every 2 years or after a major, non-routine repair or maintenance or if the sample results suggest sampler is contaminated.

Table 6.2 Assessment Schedule for Trace Metals

Assessment Type	Assessment Agency	Frequency
Performance Evaluation Audit	EPA NATTS Contract Lab	Biannual for IO-3.5
Technical Systems Audits/Network Review (NATTS)	EPA New England Region	Every 3 years
Technical Systems Audits/Network Review (NATTS)	OAQPS-EMAD	As necessary
Technical Systems Audits/Network Review	AQCD (QA Coordinator)	Annual

Performance Audits (field)	AQCD	Quarterly
Performance Audits (lab)	VAEL	Every batch run
Analytical QA/QC verification	VAEL	Every batch run
PM10 collection method precision (Co-located samples)	AQCD	Every 1/12 sample for gravimetric, for metals analyses every other month
Analytical precision (replicate sample analysis)	AQCD	Every batch run

Table 6.3 Assessment Schedule for Semi-volatiles

Assessment Type	Assessment Agency	Frequency
Performance Evaluation Audit	EPA NATTS Contract Lab	Biannual (to ERG)
Technical Systems Audits/Network Review (NATTS)	EPA New England Region	Every 3 years
Technical Systems Audits/Network Review (NATTS)	OAQPS-EMAD	As necessary
Technical Systems Audits/Network Review	AQCD (QA Coordinator)	Annual
Performance Audits (field)	AQCD	Quarterly
Performance Audits (lab)	ERG Laboratory	Every batch run
Analytical QA/QC verification	ERG Laboratory	Every batch run
Analytical precision (replicate sample analysis)	ERG	Every batch run

6.6 Project Schedule

VOC, carbonyl, semi-volatile compounds, and trace metals sampling is performed on EPA’s published 1/6 day schedule at the Underhill. VOC, carbonyl and trace metals sampling is performed on EPA’s published 1/12 day schedule at Burlington and Rutland sites.

7.0 Quality Objectives and Criteria for Measurement Data

7.1 Data Quality Objectives (DQOs)

EPA-OAQPS has developed the DQO’s for the NATTS urban and rural sites, following EPA’s QA/G-4 procedures and using input from results from the Pilot Study. The details of this process can be found in EPA’s *Quality Assurance Guidance Document, Model Quality Assurance Project Plan for the National Air Toxics Trends Stations*, EPA-454/R-02-007. The NATTS objective or goal was for the network sites to be able to detect a 15% change in ambient concentrations of core compounds between successive 3-year periods. Through this process, EPA has determined for the following core NATTS compounds, Benzene, 1,3-Butadiene, arsenic, chromium, acrolein and formaldehyde that the NATTS DQO’s will be met at rural sites that satisfy the goals of one-in-six day sampling, 85% completeness and 15% measurement CV. The Underhill site is considered a rural site in the NATTS network.

The Measurement Quality Objectives and Measurement Quality Control Procedures (to assure they are met) for Vermont Air Toxics Monitoring Network are identified in Section 7.2 and 14.0,

respectively. In theory, if these MQOs are met at Underhill site, the measurement uncertainty is controlled to the levels required by the NATTS DQO's and the data can be used for NATTS trends assessments. The associated specific NATTS Measurement/Data Quality Objective Quality Control Procedures are described in the reference *National Air Toxics Trends Stations Monitoring Program Measurement Quality Objectives, Final Draft Version 1.2, 2/1/05*.

7.2 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) are designed to evaluate and control various phases (sampling, preparation, analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the DQOs. MQOs can be defined in terms of the following data quality indicators:

Precision - a measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error. Precision is estimated by various statistical techniques using some derivation of the standard deviation.

Bias - the systematic or persistent distortion of a measurement process, which causes error in one direction. Bias will be determined by estimating the positive and negative deviation from the true value as a percentage of the true value.

Representativeness - a measure of the degree which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Detectability- The determination of the low range critical value of a characteristic that a method specific procedure can reliably discern (MDL assessed following *40 CFR Part 136, Appendix B* as updated in the 8/28/17 MUR and the *EPA NATTS TAD, Revision 3*, as applicable).

Completeness - a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions.

Comparability - a measure of confidence with which one data set can be compared to another.

Accuracy has been a term frequently used to represent closeness to "truth" and includes a combination of precision and bias error components. If possible, the AQCD will attempt to distinguish measurement uncertainties into precision and bias components. For each of these attributes, acceptance criteria can be developed for various phases of the environmental data operation. In theory, if these MQOs are met, measurement uncertainty should be controlled to the levels required by the DQO. Table 7.1 lists the MQOs for pollutants to be measured in our air toxic program. More detailed descriptions of these MQOs and related DQO's and how they will be used to control and assess measurement uncertainty are described in detail in Section 14 (Table 14.1,-14.3 and Sections 14.3, 14.4 as well as Table 4 and Appendix 2 of the TO-15 and TO-11A SOPs and Table 23.3 of the Metals SOP, respectively which are located in Appendix A of this document. To meet the Completeness criteria, the policy of the Vermont Air Toxics Monitoring program is to make up any missed sample collection events as soon as is practical.

Table 7.1 Measurement Quality Objectives – VOCs, Carbonyls, Trace Metals and Semi-volatiles

Compound Class	Reporting Units	Precision (co-located samples)	Accuracy/Bias	Representativeness	Comparability/Method Selection	Completeness	Minimum Detection Limits
VOCs	ppbv/ μg/m ³ *	25% RPD, 15% CV	± 25%	See Table 10.1.	GC/MS (TO15)	> 85%	See Table 7.2
Carbonyls	μg/m ³	20% RPD 15% CV	± 20%	See Table 10.1.	HPLC (TO11A)	> 85%	See Table 7.3
Trace Metals	ng/m ³	20% RPD 15% CV	± 20%	See Table 10.1.	ICP-MS (6020A/IO3.5)	> 85%	See Table 7.4
Semi-volatiles	ng/m ³	20% RPD 15% CV	± 30%	See Table 10.1.	GC/MS;TO13A	> 85%	See Table 7.5

*: VAEL reports results in ppbv which VT AQCD converts to μg/m³ for reporting to AQS

Table 7.2 VOC TO-15 MDLs (VAEL 2017)

Compound	MDL (ppbv)	Compound	MDL (ppbv)
1,1,1-Trichloroethane	0.003	Dibromochloromethane	0.003
1,1,2,2-Tetrachloroethane	0.005	Dichlorodifluoromethane	0.003
1,1,2-Trichloroethane	0.003	Dichlorotetrafluoroethane	0.002
1,1-Dichloroethane	0.003	Ethyl Acrylate	0.003
1,1-Dichloroethene	0.002	Ethyl tert-Butyl Ether	0.001
1,2,4-Trichlorobenzene	0.009	Ethylbenzene	0.003
1,2,4-Trimethylbenzene	0.007	HEXACHLORO-1,3-BUTADIENE	0.006
1,2-Dibromoethane	0.004	m,p-XYLENE	0.003
1,2-Dichloroethane	0.003	m-DICHLOROBENZENE	0.007
1,2-Dichloropropane	0.003	Methyl Isobutyl Ketone	0.003
1,3,5-Trimethylbenzene	0.006	Methyl Methacrylate	0.003
1,3-Butadiene	0.002	METHYL tert-BUTYL ETHER	0.001
3-Chloropropene	0.002	Methylene Chloride	0.004
Acrolein	0.015	n-Octane	0.002
Acrylonitrile	0.006	o-DICHLOROBENZENE	0.012
Benzene	0.003	o-Xylene	0.003
Bromochloromethane	0.003	p-DICHLOROBENZENE	0.007
Bromodichloromethane	0.003	Styrene	0.004
Bromoform	0.005	tert-AMYL METHYL ETHER	0.002
Bromomethane	0.003	TETRACHLOROETHYLENE	0.003
Carbon Tetrachloride	0.003	Toluene	0.001
Chlorobenzene	0.003	trans-1,2-DICHLOROETHYLENE	0.003
Chloroethane	0.004	trans-1,3-Dichloropropene	0.004
Chloroform	0.002	TRICHLOROETHYLENE	0.003
Chloromethane	0.006	Trichlorofluoromethane	0.002
CHLOROPRENE	0.002	TRICHLOROTRIFLUOROETHANE	0.001
cis-1,2-DICHLOROETHYLENE	0.003	Vinyl Chloride	0.002
cis-1,3-Dichloropropene	0.004		

Table 7.3 Carbonyl MDLs (VAEL-2018)

Compound	MDL ($\mu\text{g}/\text{m}^3$)*	Compound	*MDL ($\mu\text{g}/\text{m}^3$)
Formaldehyde	0.007	Valeraldehyde	0.028
Acetaldehyde	0.010	Tolualdehydes	0.028
Acetone	0.061	Hexanaldehyde	0.008
Propionaldehyde	0.018	2,5-Dimethylbenzaldehyde	0.008
Butyraldehyde	0.022		
Benzaldehyde	0.012		
Isovaleraldehyde	0.011		

*Based on sample volume=1.30m³ (at EPA Standard conditions 25oC; 760 mm Hg) (0.9 slpm average flow rate for 1440 minute sample period)

Table 7.4 Trace Metal (low volume PM₁₀) MDLs (VAEL-2018)

Metal	MDL (ng/m³)	Metal	MDL (ng/m³)
Antimony*	0.073	Nickel**	0.340
Arsenic*	0.054	Selenium*	0.111
Barium*	0.136	Silver**	0.169
Beryllium*	0.063	Strontium*	0.151
Cadmium*	0.060	Vanadium*	0.052
Chromium*	2.869		
Cobalt*	0.054		
Lead*	0.108		
Manganese**	0.148		
Molybdenum*	0.048		

Based on nominal sample volume of 24 m³ *: Based on 100 ppt spike on 7 blank filters **= Based on CY2017 blank filters no spike

Table 7.5 Semi-volatile MDLs (ERG 2018)

compound	MDL (ng/m³)	Compound	MDL (ng/m³)
9-Fluorenone	0.0793	Coronene	0.0061
Acenaphthene	0.097	Cyclopenta[cd]pyrene	0.00928
Acenaphthylene	0.0192	Dibenz (a,h)anthracene	0.0196
Anthracene	0.0175	Fluoranthene	0.0324
Benzo (a) anthracene	0.0136	Fluorene	0.0905
Benzo (a) pyrene	0.0138	Indeno(1,2,3-cd)pyrene	0.0174
Benzo (b) fluoranthene	0.0278	Naphthalene	2.38
Benzo (e) pyrene	0.0137	Perylene	0.0121
Benzo (g,h,i) perylene	0.017	Phenanthrene	0.163
Benzo (k) fluoranthene	0.0151	Pyrene	0.0165
Chrysene	0.0105	Retene	0.0806

NOTE: Assumes a 300 m³ (std) sample volume.

8.0 Special Training Requirements/Certification

Given the specialized, program specific and regulated nature of the work, special job-specific training is necessary.

The Monitoring Supervisor and QA Coordinator will design and direct training programs with input from staff. Training can come from a variety of individuals and sources including the Monitoring Supervisor/Project Manager(s), QA Coordinator, EPA and/or NESCAUM training courses, equipment manufacturer manuals and training, EPA Guidance/Technical Assistance Documents and college course work.

Staff members must have specific training and be qualified on QAPPs and SOPs including related monitoring method and equipment theory. Successful completion of a training program by a staff member will be judged by the Monitoring Supervisor/Project Manager and the staff member. No staff member will be responsible for an SOP until the above-named individuals agree the staff member is qualified to do the work and has observed it in the field. The Monitoring Supervisor will maintain an Excel workbook and ACCESS database of training records. The training records table of this database will include individual specific training records. Records in this table will include a field to indicate successful completion of training, supervisor/trainer initials and a field for comments where training observations will be documented. This latter field will be used to elaborate on unsuccessful training actions.

Training will be provided with the goal of creating highly skilled staff.

An individualized training program will be created for each new employee. Training will initially focus on providing an overall understanding of operations, regulations, monitoring method and equipment theory. The training will involve the intensive involvement of the Monitoring Supervisor/Project Manager and QA Coordinator.

Staff members are encouraged to pursue training through APTI and NESCAUM. Work time will be provided for participation in this program.

9.0 Documentation and Records

9.1 Types of Documentation

9.1.1 Sampling and Analytical Documentation

- ▶ All maintenance and field performance audits are documented with field data sheets.
- ▶ Each VOC, Carbonyl, Semi-volatile and particulate sample is documented using a field data sheet (see respective SOP's in Appendix A for copies of AQCD sheets and ERG's SOPs for semi-volatile sheets).
- ▶ Field data sheets contain information supplied by the field staff who installs and recovers samples and operates the sampling equipment and also provides space for chain of custody self-adhesive label printed by the sampler, documenting observations, problems, non-conformances and corrective actions.
- ▶ For the VAEL analyses, VOC, carbonyl and trace metal samples are pre-registered with VAEL staff approximately one week prior to sample delivery. Upon delivery, the VAEL staff logs the samples in the laboratory information system (LIMS). This process generates a unique laboratory ID number for each sample. The LIMS generates a chain of custody verification report with the unique Lab ID numbers. This report is saved electronically in a folder on the Y-drive. VAEL staff applies a self-adhesive label on each sample based on the original pre-registration provided prior to sample delivery.
- ▶ Information from the above field sheets is stored in the dedicated ACCESS databases (on network Y drive see 9.1.2 below) and the field data sheets are stored by the Supervisor in dedicated notebooks.
- ▶ Analytical results from the VAEL (VOC, carbonyl and trace metals) analyses are downloaded electronically from the (LIMS) as Excel files and imported into the respective ACCESS databases for storage, review, processing, validation and reporting.
- ▶ Analytical QA/QC batch summaries are provided to the Supervisor and/or staff by the VAEL staff in electronic or hardcopy format.
- ▶ Analytical calibration results and other QC checks will be stored electronically and/or in hardcopy by the laboratory. These are available upon request.
- ▶ The analytical systems performance and maintenance are also documented in logbooks and/or written checklists (see the specific Analytical SOPs in Appendix A for details).
- ▶ Performance Evaluation sample results are provided by NATTS and/or the contract lab electronically in PDF format.
- ▶ Sampler certification results are provided by the VAEL or Contract Lab in electronic and hardcopy format.
- ▶ ERG results (Semi-volatile compounds) are provided electronically (via email) in excel and PDF formats.

9.1.2 Concentration Data

The analytical data will go through various stages of transformation and validation, mostly in electronic form, both in Excel spreadsheets and ACCESS databases. Validated data will accumulate and be permanently stored in the following dedicated ACCESS databases on the Agency's Network Y drive:

VOC-(Y:/ AP_Monitoring/Database/VOC Database New.mdb)

Carbonyl-(Y:/ AP_Monitoring/Database/Carbonyl Database New.mdb)
Metals-(Y:/ AP_Monitoring/Database/MetalsDECNATTS.mdb)
Semi-Volatiles-(Y:/ AP_Monitoring/SEMIVOL.mdb)

Valid sample and co-located concentration results will be submitted to EPA's AQS database for permanent storage.

9.1.3 Summary Reports

Quarterly Data Reports are generated by the Monitoring Supervisor and QA Coordinator. These reports contain minimum, maximum and average concentrations, data capture, applicable QA/QC data and identification of nonconformance sample data. Historic minimum, maximum and average concentrations will be reported as well to compare with quarterly concentrations.

Reports summarizing compound concentrations and associated QA/QC results will be prepared annually, with statistical analyses and any appropriate conclusions that may be drawn. Annual reports consist of the Annual Network Review, Annual SLAMS Data Certification, Annual Air Quality Report and Technical Systems Audits. These documents will be produced electronically and hardcopy as necessary and will be made available upon request.

See Table 21.1 Reports to Management, for a complete list of reports generated.

9.1.4 Quality Assurance Project Plan (QAPP)

The Supervisor and/or QA Coordinator develops the QAPP and is responsible for revising it as necessary. The QA Coordinator and Supervisor will review and approve the QAPP and any modifications to it. The Supervisor will ensure that document control headers are properly maintained when the QAPP is modified and that everyone on the distribution list has the most current approved version. Old versions will be removed from circulation and discarded/recycled consistent with State Records Management Procedure identified below.

At a minimum, the QAAP will be reviewed annually and updated as necessary. EPA-New England will be provided a written notification of the results and a summary of any proposed changes.

9.2 Document Holding Times

Consistent with the *Vermont DEC Records Management Procedure for Monitoring General Records Schedule (GRS1000.1063) 8/28/12 (revised 1/27/2015)*, and the *EPA NATTS TAD*, Air Monitoring paper and electronic data records will be held for a minimum period of 6 years or until the associated project or grant agreement has expired. The QAPP, associated SOPs, work plans and generated reports will be retained consistent with the EPA Grant requirements (minimum 6 years) and for 3 years after revised or superseded.

10.0 Sampling Design

10.1 Monitoring Site Selection

Beginning in 2004, Vermont operated a total of four (4) sites in the Vermont Air Toxics Monitoring Network measuring VOCs, carbonyls at all sites and trace metals at Underhill only. In 2008, the Brattleboro site was discontinued. Beginning in 2005 and 2008, hexavalent chromium and semi-volatiles, respectively are measured in Underhill. Hexavalent chromium sampling was terminated at Underhill on 6/30/13. Beginning in 2017 and 2018, trace metal analysis is performed on Rutland and Burlington PM₁₀ filters, respectively. Underhill is operated as a rural (background) site as part of the National Air Toxics Trends Station (NATTS) monitoring program. The two (2) other network sites are in Burlington and Rutland. The IMPROVE (Interagency Monitoring of Protected Visual Environments) Network sampling in Underhill fulfills the NATTS requirement for PM_{2.5} speciation. Table 10.1 describes the monitoring sites in further detail.

Table 10.1 Monitoring Site Description

Site	Pollutant	Monitoring Objective	Representativeness	Sampling Frequency	Site Description
Underhill (NATTS)	VOCs, Carbonyls, Trace Metals, Semi-volatiles,	Transport / background and population	Regional scale	1-in-6 day	Located at the Proctor Maple Research Facility. This site will be operated as a rural (background) site in the NATTS network.
Burlington	VOCs, Carbonyls, Trace Metals	Population	Neighborhood scale	1-in-12 day	Located at the 150 S. Winooski Ave. in a commercial/residential downtown area.
Rutland	VOCs, Carbonyls, Trace Metals	Population	Neighborhood scale	1-in-12 day	Located in a parking lot at 96 State Street in a commercial/residential area.

10.2 Pollutant Selection

The targeted pollutants were identified by representatives of Vermont AQCD and were selected based on historic monitoring data, use in air quality/ source apportionment modeling, existing state standards and the capabilities of available analytical equipment. See Tables 5.1, 5.2, and 5.3 for a list of the target pollutants.

10.3 Sampling Equipment

Four types of 24-hour samples will be collected at each site:

- ▶ VOC samples will be collected following guidelines in TO-15. Samples are collected in 6-liter RESTEK SilcoSteel canisters (with SilcoSteel-coated valve and gauge) using an ATEC Model 2200 combination canister/cartridge sampler. Prior to January 2012, an ATEC Model 301 Canister sampler was used to collect VOC samples. The Model 2200 is a computer-controlled sampler, which uses a mass flow controller (MFC) and the

canister vacuum to draw ambient air from a common borosilicate glass manifold into the canister.

- ▶ Carbonyl samples will be collected following guidelines in TO-11A. Carbonyl samples are collected in Waters DNPH cartridges using an ATEC Model 2200 combination canister/cartridge sampler. Prior to January 2012, an ATEC Model 300 Cartridge sampler was used to collect Carbonyl samples. The Model 2200 is computer-controlled sampler, which is designed with a sample pump, mass flow controller (MFC) and heated copper-coil ozone denuder (controlled at $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$). The sample pump draws a controlled flow of ambient air from a common manifold through a heated ozone denuder then through the DNPH cartridge.
- ▶ Trace metal samples are collected following guidelines in IO-3.5 and following the EPA PM10 FRM. Collocated trace metals samples will be collected on a tare-weighed 47 mm Teflon filters using an TEI 2000i and 2025i sequential sampler. The TEI 2000i and the 2025i are automated samplers which draw a controlled ambient air sample at a nominal flow rate of 16.7 lpm through a size selective inlet to separate suspended particles ≤ 10 micrometers in aerodynamic diameter in a slip stream which is directed through the filter where the particles are collected.
- ▶ Semi-volatile samples are collected following the ERG SOP *ERG-MOR-049* and guidelines in TO-13A and ASTM D6209. This method is designed to collect particle and gas phase semi-volatile compounds through a special sampling module containing a polyurethane foam (PUF) plug insert combined with a special adsorbent (XAD-2: styrene-divinylbenzene resin) and a 104-mm quartz-fiber filter. The sampling module is loaded into a Tisch PUF+ sampler. The sampler is microprocessor controlled automated sampler designed to draw a controlled flow of ambient air thru the sampler/filter module.

Sampling methods are discussed in more detail in Section 11.0 of this document. Precision for VOC and Carbonyl methods will be assessed using collocated samplers at the Burlington Main Street site in the Vermont AQCD Network. Separate collocated canister and cartridge samples will be collected on the EPA one-in-twelve day (1/12) sampling schedule. The 1/12 schedule will provide 30 collocated sample comparisons for VOC and Carbonyl methods or 20% of the network samples. Precision for the Trace Metal method will be assessed using collocated samplers at the Underhill site on a once every month frequency (exceeds EPA policy=10% of samples).

10.4 Analysis

- ▶ VOCs listed in Table 5.1 will be analyzed by the Vermont VAEL following TO-15 Guidelines. The VAEL analytical equipment consists of an ENTECH 7100 pre-concentrator, a Hewlett-Packard 6890 gas chromatograph connected to a 5973 mass spectrometer (GC/MS) with a mass selective detector operated in the SIM mode.
- ▶ Carbonyls listed in Table 5.2 will be analyzed by the Vermont VAEL following TO-11A Guidelines. The analytical equipment consists of a WATERS Corporation High Performance Liquid Chromatograph (HPLC) with a multi-wavelength UV detector configured for wavelength of 360 nanometers.

- ▶ Trace metals listed in Table 5.3 will be analyzed by the Vermont VAEL following EPA 6020A and Compendium Method IO-3.5 Guidelines. The analytical equipment consists of a TEI iCAP RQ Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) with standard mode and kinetic energy displacement (KED).
- ▶ Semi-volatiles listed in Table 5.3 will be analyzed by the ERG laboratory following TO-13A and the ERG SOP, *Standard Operating Procedure for analysis by EPA Compendium Method TO-13A (ERG-MOR-049)* and ASTM D6209. The analytical equipment consists of a GC/MS.

Analytical procedures are described in more detail in Section 13.0 of this document. Analytical precision for all four methods will be assessed using replicate sample analysis. Analytical accuracy will be assessed by analysis of performance evaluation audit samples prepared by an independent lab (EPA or VT AQCD Contract Lab).

10.5 Sampling Frequency

At the Underhill site (NATTS), samples for VOC, carbonyl, semi-volatile compounds, and trace metals will be collected on the EPA one-in-six-day (1/6) schedule. VOC, carbonyl and trace metals sample collection at the Rutland and Burlington sites is on the EPA one-in-twelve-day (1/12) schedule.

11.0 Sampling Methods Requirements

Prior to sample collection, some sample preparation activities are necessary for all 3 methods used in the Air Toxics Monitoring Network. They are listed in Tables 11.1-3 below:

Table 11.1 VOC Pre-sample Activities

VOC Pre-sample Activities	Check/Frequency
Canister Integrity	Leak checks conducted prior to each analysis
Canister Cleaning	After each analysis
Canister Certification	Performed on one canister from every cleaning batch after cleaning
Canister Storage/Transport	Room temperature, indefinite pre-sample hold time as long as vacuum maintained.
Sampler Integrity	Upon receipt, check against manufacturer's specs.
Sampler Certification	Zero and upscale check upon receipt and then every 2 years thereafter (upscale check optional).
Sampler System Equilibration	24-hour ambient air purge prior to each sample day
Sampler Flow Rate	Computer controlled MFC with stored 5 minute flow verification data during sampling
Sample System Integrity	Canister vacuum verified and system leak check performed after canister installed and at the start of sample collection
Canister Stability	Upon receipt, conduct 30-day hold time study with zero air and/or 1 ppbv calibration standard.

Table 11.2 Carbonyl Pre-sample Activities

Carbonyl Pre-sample Activities	Check/Frequency
DNPH Cartridge Background Verification	Upon receipt, 3 cartridges from Lot# extracted/analyzed
DNPH Cartridge Storage/Transport	≤4°C, vendor hold time tracked by staff
Sample Breakthrough	At each site at start of monitoring
Sampler Integrity	Upon receipt, check against manufacturer's specs.
Sampler Certification	Zero check upon receipt and every 2 years thereafter.
Sampler Flow Rate	Flow verified prior to sampling. MFC stored every 5 minutes data during sampling
Sample System Integrity	System leak check performed after cartridge installed

Table 11.3 Trace Metal Pre-sample Activities

Trace Metal Pre-sample Activities	Check/Frequency
Filter Equilibration prior to pre and post weighing	Minimum 24 hours at 20-23°C and 35-40% RH
Filter Storage/Transport	≤4°C after sampling through post weighing, then Room temperature
Filter Integrity	flow controller data recorded every 5 minutes during sampling.

Table 11.4 Semi-volatile Pre-sample Activities

Semi-volatile Pre-sample Activities	Check/Frequency
Clean Tisch metal sample assembly	Conducted monthly by AQCD per ERG SOP
Glass sleeve/thimble (PUF/XAD) and quartz filter loaded into TISCH metal sampling assembly	Conducted by AQCD per ERG SOP before and after every sample
Filter and PUF/XAD storage and transport	Freezer storage, transported in cooler w/ice blocks
Sampler Flow Rate	Computer controlled Flow controller with stored flow verification data during sampling

11.1 VOC Sampling

VOC samples will be collected following the schedule in Section 10.5 and the procedures identified in the SOP in Appendix A. Cleaned, certified and evacuated RESTEK Silco-steel 6-Liter canisters are obtained from the Vermont VAEL and picked up by the field staff at the Barre, VT AQCD field operations facility and transported to each site and installed a few days prior to the scheduled sample date (no more than 5 days prior for 1/6 schedule). The canister is attached to the ATEC 2200 samplers using a 1/8" GC-grade stainless steel line with an ENTECH silonite-coated Micro-QT valve. The canister connection is leak-checked during the 2200 computer's automated setup procedure. The sampler's imbedded computer is programmed to perform a 24-hour purge prior (using a bypass from the carbonyl sample pump inside combination sampler) to the start of the sampling period and then begin sample collection at the proper date and time (midnight to midnight). The sampler's computer setup procedure provides sample setup verification on the screen before finishing the setup.

At each sampling location the ATEC 2200 is located inside a permanent temperature controlled shelter and connected to a common borosilicate glass sampling manifold (the Underhill and Rutland shelters use a glass manifold and a 3/8" Teflon down tube from the shelter roof) using a 1/4" GC-grade stainless steel line. The sampler performs an automatic leak check during the first minute of the sample period and will suspend sampling if a leak is detected. During each 24-hour sample collection, the ATEC 2200 MFC is set to operate and maintain a constant nominal flow rate of 3.6 ccpm, which provides a final sub-atmospheric canister pressure of 12.7 psia (set in computer parameters). Canister samples are recovered within 5 days after collection. The ATEC 2200 computer stores information about the sample collection period including, the purge and sample date and time, the elapsed time, average, min and max flow rate for sample period, sample volume, any error codes (such as power failure or flow error) and the canister pressure recorded each 5 minutes during the sampling period. This information is downloaded from the sampler's computer to a thumb drive via USB and emailed from the shelter to the Supervisor using the station's networked computer. The general sample information above (everything except 5 minute data) is printed on a self-adhesive label which is attached to the field data sheet. The field staff returns the canister samples to the Barre, VT AQCD facility, where the canisters are verified against the field sheets. The canisters are transported to VAEL and logged into the LIMS. It is important to note that AQCD policy forbids the storage of any product or solvent containing any VOC's inside the permanent shelters at monitoring sites.

11.2 Carbonyl Sampling

Carbonyl samples will be collected following the schedule in Section 10.5 and the procedures identified in the SOP in Appendix A. DNPH cartridges from the same certified lot # are picked up at the Barre, VT AQCD facility and transported to each site (at $\leq 4^{\circ}\text{C}$ - cooler with 2 blue ice packs) and installed a few days prior to the scheduled sample date (no more than 5 days prior for 1/6 schedule). The field staff wear polyethylene gloves when handling cartridges. The cartridge is attached to the ATEC 2200 samplers using an 1/8" Teflon tube with Luer®-Lock connectors. The cartridge connection is leak-checked during the 2200 computer's automated setup procedure. The sampler's imbedded computer is programmed for the proper purge and sample date and time. The sampler is programmed to purge the sample line for 15 minutes prior to the

start of the 24-hour sampling period (midnight-midnight). A second cartridge, serving as a Field Blank, is handled identically to the sample cartridge and setup (on a dedicated connection on the ATEC 2200) with each sample at every site, providing field blanks for 100% of the network samples.

At each sampling location, the ATEC 2200 is located inside a permanent shelter and connected to a common borosilicate glass sampling manifold using a ¼" Teflon line. The sampler performs an automatic leak check during the first 20 seconds of the sample period and will suspend sampling if a leak is detected. The ATEC 2200 maintains the internal ozone denuder temperature at $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to reduce condensation and catalyze the ozone reduction reaction. The ATEC 2200 uses a vacuum pump and MFC to pull ambient air through the heated ozone denuder, then through the DNPH cartridge at a nominal flow rate of 0.9 slpm. This provides for a nominal total 24-hour sample volume of 1300 liters (1.300 m^3 at EPA Standard Conditions of 25°C ; 760 mm Hg).

Cartridge samples and field blanks are recovered within 5 days after collection. While wearing polyethylene gloves, the field staff places the DNPH cartridge in its original zip-lock foil pouch, sealed and transported at $<4^{\circ}\text{C}$ (cooler with 2 blue ice packs). The ATEC 2200 computer stores information about the sample collection period including, the purge and sample date and time, the elapsed time, sample volume and average, min and max flow rate, any error codes (such as power outage or flow error) and average flow rate and denuder temperature recorded every 5 minutes during the sample period. This information is downloaded from the sampler's computer to a thumb drive via USB and emailed to the Supervisor using the station's networked computer. The general sample information above (everything except 5 minute data) is printed on an adhesive label which is attached to the field data sheet. Upon return to the Barre, VT AQCD facility, the cartridges are stored at $\leq 4^{\circ}\text{C}$ in a dedicated refrigerator. The cartridges are transported as soon as possible at $\leq 4^{\circ}\text{C}$ (cooler with 2 blue ice packs) to the VAEL, logged into the VAEL LIMS and then delivered to the dedicated TO-11A refrigerator in the HPLC room at the VAEL.

11.3 Trace Metal Sampling

The trace metals will be collected using a low-volume PM10 sampler on 47 mm Teflon filters. PM10 samples are collected using TEI 2000i and 2025i sequential sampler using a size selective inlet to separate suspended particles ≤ 10 micrometers in aerodynamic diameter for collection on the Teflon filters. The 2000i and the 2025i are automated computer controlled samplers that uses a vacuum pump and dynamic volumetric flow controller (uses MFC and temperature and pressure sensors) to provide a nominal sample flow rate of 16.7 liters per minute (local conditions), for a nominal sample volume of 24 m^3 for the normal 24-hour sample period.

Sample filters are pre and post weighed by the Connecticut DEEP after equilibration for at least 24 hours in humidity and temperature controlled room ($20\text{-}23^{\circ}\text{C}$ and 35-40% RH). Post weighing is performed "as soon as practical" (per the reference method) but within 30 days of sampling.

The 2000i/2025i sampler uses filter magazines which contain 1-3 filter cassettes (depending on sampler, sample and field blank schedule). Each filter cassette contains one tare weighed Teflon filter. The cassette and magazine protect the Teflon filters and provides for minimal handling, safe transport and setting up multiple samples at one time.

The field staff pick up pre-loaded filter magazines at the Barre, VT AQCD field operations facility for transport to the site. At the site the field staff will first recover the filter magazine that contains previously collected samples and all pertinent sample information from the sampler's computer (downloaded to a palm pilot for returning information for retrieval back at the AQCD facility). The new filter magazine is loaded into the 2025i sampler and the appropriate sample information and programming is performed for next sample collection period(s). The filter magazine exchange is performed approximately 1-2 times/week depending on sample and field blank schedule.

At the AQCD facility, sampled filters are removed from the magazine and cassette and placed in a protective slide container for return shipment to CT DEEP for equilibration (see above) and weighing for gravimetric determination of PM10 concentration. After weighing, filter samples are shipped by CT DEEP to the Barre AQCD where they are stored in the protective slide at $\leq 4^{\circ}\text{C}$ until they are placed in hot block polypropylene digestion tubes for transport to the Vermont VAEL for extraction and trace metals analysis. Refer to SOPs in Appendix 3 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18* for all standard operating procedures associated with low-volume PM10 sampling on Teflon filters.

11.4 Semi-volatile Sampling

Semi-volatile samples are collected following the schedule in Section 10.5 and the *PUF+ Field Sampling Operations* SOP in Appendix A. A dedicated cleaned metal sampling assembly provided by Tisch is used to house specially prepared glass thimbles containing poly urethane foam (PUF) plugs sandwiched around special adsorbent XAD (XAD-2: styrene-divinylbenzene resin) combined with a 104 mm quartz-fiber filter, both of which ERG provides. The sample/filter assembly is stored in a dedicated freezer at the Barre, VT AQCD facility prior to and after sampling. The field staff transport the metal PUF filter/thimble sampling assembly to the monitoring site $\leq 4^{\circ}\text{C}$ in a cooler with blue ice packs. At the monitoring site the filter assembly is connected to the inlet of the Tisch PUF+ sampler and secured by 2 quick release connectors. The inlet is connected to a flow venturi which is connected to a brushless vacuum motor similar to particulate samplers. The venturi pressure drop is used to control flow by regulating motor speed a user-defined set point. The sampler's timer/controller is programmed to start on the scheduled sample date. During sample collection, ambient air is drawn through the filter assembly at nominal flow rate set point of 160 sccpm. This provides for a nominal sample volume of 200m^3 for 24-hrs. The samples are collected for a 24-hr period (midnight-midnight) which is controlled and verified by the sampler's microprocessor. After sampling, the metal PUF/filter assembly is removed from the sample inlet line, sealed, and returned to the VAEL in coolers with blue ice packs and stored in a dedicated freezer prior to disassembly by the AQCD technician and shipment to the ERG laboratory. Semi-volatile samples are shipped in the coolers in which they were received. Additional details of the semi-volatile sampling and analysis procedures are presented in ERG's SOP (*ERG-MOR-049*) presented in Appendix C of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support)*, Contract No. EP-D-14-030, 2018

11.5 Failure Response

11.5.1 VOC and Carbonyl

When a failure (any non-conformance with standard operating procedure) is observed in a sample collection system, the Supervisor must be consulted immediately. The Supervisor is ultimately responsible for sampler maintenance, troubleshooting and repair and may involve the Field Staff at his discretion.

If the Supervisor determines troubleshooting and repair cannot be performed immediately upon discovery, corrective action and/or sampler replacement will be scheduled using the outlook field schedule calendar and notification emails to staff. The VOC and Carbonyl sample collection schedule typically allows sample setup non-conformances to be corrected prior to the scheduled collection day. Non-conformances observed during sample recovery will be resolved prior to the next scheduled collection date. If the non-conformance resulted in a missed sample, a makeup sample will be scheduled as soon as is practical.

Record of the corrective action (which includes troubleshooting) will be documented on the appropriate Field Datasheet and in the Operations Database. At a minimum, documentation will include a unit history note and a related work record. The Supervisor will ensure all corrective actions are satisfactory.

11.5.2 Trace Metals

See Section 20 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18* for failure response procedures for PM10 low-volume sampling.

11.5.3 Semi-volatile Compounds

When a failure (any non-conformance with standard operating procedure) is observed in a sample collection system, the Supervisor must be consulted immediately. The Supervisor is ultimately responsible for sampler maintenance, troubleshooting and repair and may involve the field staff at his discretion. The Supervisor will notify ERG of any significant problems immediately.

If the Supervisor determines troubleshooting and repair cannot be performed immediately upon discovery, corrective action and/or sampler replacement will be scheduled using the field calendar scheduler and notification emails to staff. If the non-conformance resulted in a missed sample, a makeup sample will be scheduled as soon as is practical.

Record of the corrective action (which includes troubleshooting) will be documented on the appropriate Field Datasheet and in the Operations Database. At a minimum, documentation will include a history note and a related work record. The Supervisor will ensure all corrective actions are satisfactory.

12.0 Sample Handling and Custody

12.1 VOCs

Cleaned, certified and evacuated VOC sample canisters are obtained from the VAEL and stored at room temperature in a designated area in the Barre VT AQCD field operations facility. The canisters are transported to and from the field in state vehicles. A VOC canister field data sheet is transported with each canister to the field sites. Each canister has a unique, permanently attached ID#. Two canisters and two separate data sheets will be sent to the designated collocated site. When a sample is setup and recovered, the field staff completes the field data sheet according to the SOP (see Appendix A). Information recorded includes canister #, sample date, start and stop times verified, elapsed time, average flow, beginning and ending canister pressure, operator ID and leak check status. The field staff returns the field data sheet with the canister to the AQCD facility. At that point the AQCD field operations center analyst verifies the field data sheet is complete and accurate and the canister has not leaked since recovery (canister #, final pressure etc....) and then notes the unique LIMS sample ID on the field sheet. The pertinent sample information is entered into the VOC ACCESS database on the Y-network drive. Approximately every two weeks, the canisters are transported by field staff to the VAEL @ UVM for analysis. At the VAEL, field staff delivers samples to VAEL sample custodians, who log the samples into the LIMS system using the information provided prior in the sample notification form submittal. Once the VAEL login is complete, the VAEL Environmental Scientist is notified that logged samples are officially onsite and ready for analysis. The LIMS also provides a hardcopy chain of custody record after the samples are logged in (identifies the sample information and the specific Lab ID#s) and physically transferred to the Lab. The canister is then delivered to the designated TO-15 room. The field sheet and LIMS login chain of custody sheets are submitted to the Supervisor for review and storage in dedicated logbook and/or electronically on Y drive.

The Laboratory Environmental Scientist documents all the canister samples, method blanks and quality control samples for each analytical batch in a dedicated Laboratory Notebook/Log.

12.2 Carbonyls

DNPH cartridges (from certified lot #'s) are obtained from the VAEL Environmental Scientist. DNPH cartridges for samples and field blanks are transported to and from the field in coolers with multiple ice packs ($\leq 4^{\circ}\text{C}$). A carbonyl field data sheet is transported with each cartridge to the field sites. Two cartridges and two separate data sheets will be sent to the designated collocated site. The field staff wears polyethylene gloves (or equivalent) when handling the DNPH cartridges during setup and recovery. During sample setup and recovery, the field staff completes the field data sheet according to the SOP (see Appendix A). Information recorded includes cartridge lot #, sample date, start and stop times verified, elapsed time, beginning flow rate, flow average, sample volume, denuder temperature, operator ID and leak check status. During sample recovery, each DNPH cartridge is capped on both ends and is placed in the original foil pouch package which is sealed (Ziplok) and labeled with sample location, sample date, "sample" or "field blank" and field staff initials. The field staff returns the sample ($\leq 4^{\circ}\text{C}$) and field data sheet to the AQCD field operations facility. At that point the AQCD Analyst verifies the field data sheet is complete and

accurate and then notes the unique LIMS sample ID on the field sheet. The pertinent sample information is entered into an ACCESS database.

Approximately every two weeks, the cartridge samples are transported by field staff ($\leq 4^{\circ}\text{C}$) to the VAEL @ UVM for analysis. At the VAEL, field staff delivers the cartridge samples to the VAEL sample custodians, who log the samples into the LIMS system using the information provided prior in the sample notification form submittal. Once the VAEL login is complete, the VAEL Environmental Scientist is notified that logged samples are officially onsite and ready for analysis. The LIMS also provides a hardcopy chain of custody record after the samples are logged in (identifies the sample information and the specific Lab ID#s) and physically transferred to the Lab. The cartridge samples are then delivered to the designated refrigerator in the designated VAEL TO-11A room. The field sheets and the LIMS chain of custody hardcopy printout are submitted to the Supervisor for review and are stored in a dedicated logbook and/or electronically on the Y drive.

The Laboratory Environmental Scientist documents all the cartridge samples, blanks, matrix spikes, and quality control samples which are extracted in an Extraction Notebook. Information on each analytical batch run is also documented in the Laboratory Notebook.

12.3 Trace Metals

See Section 12.0 of the *Vermont AQCD Quality Assurance Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18* for sample handling and custody requirements for PM10 sampling. Once the PM10 Teflon filter samples have been weighed by CT DEEP and returned to the Barre AQCD field operations facility and validated, the Analyst places each sample or field blank into 50 ml hot block digestion tubes (provided by the VAEL) using Teflon tweezers (while wearing gloves). A permanent marker is used to note the filter ID and sample date, location and type. The tubes are placed in a test tube rack and the rack is placed in a large plastic Ziplok bag for transport by field staff to the VAEL for extraction and trace metal analysis by ICP-MS.

Approximately, once a month, the field staff deliver the Teflon filter samples to the VAEL sample custodians, who log the samples into the LIMS system using the information provided prior in the sample notification form submittal. Once the VAEL login is complete, the VAEL Environmental Scientist is notified that logged samples are officially onsite and ready for analysis. The LIMS also provides a hardcopy chain of custody record after the samples are logged in (identifies the sample information and the specific Lab ID#s) and physically transferred to the Lab. The PM10 metals samples are then delivered to the designated ICP-MS room at the VAEL. The field sheets and the LIMS chain of custody hardcopy printout are submitted to the Supervisor for review and are stored in a dedicated logbook and/or electronically on the Y drive.

12.4 Semi-volatile

See Section 9.0 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, 2018* for sample handling and custody requirements for semi-volatile sampling. Specially prepared glass thimbles and 104-mm quartz filters received from ERG are obtained from a designated freezer in the Barre, VT AQCD facility. Following ERG guidelines, the AQCD

Analyst carefully loads the glass thimble and quartz filter into the dedicated, hexane-cleaned metal sample housing provided with the Tisch PUF+ sampler (performed at AQCD field operations facility). Loaded sampling assemblies are stored in the dedicated AQCD freezer until the field staff transports it to and from the field at $\leq 4^{\circ}\text{C}$ (cooler with ice blocks). An ERG-supplied field data sheet is transported with each filter assembly to the field sites. Each filter has a unique ID# identified on the sheet. When a sample is setup and recovered, the field staff completes the field data sheet according to the SOP (see Appendix A). Information recorded includes site location, and AQS code, operator, setup and collection date, programmed start and stop times, elapsed time, beginning and ending flow rates and total sample volume from PUF+ microprocessor. The field staff returns the field data sheet and the sample filter assembly to the AQCD field operations facility at $\leq 4^{\circ}\text{C}$. Upon return the sample filters are stored in the same dedicated freezer until they are disassembled by the AQCD Analyst (reverse of setup SOP). After disassembly, the PUF/XAD glass thimble and quartz filter are placed in the original containers, packed in a small cooler with blue ice packs and shipped by next-day air to ERG for analysis.

13.0 Analytical Methods Requirements

13.1 VOC Analysis

VOCs listed in Table 5.1 will be analyzed by the Vermont Vael following TO15 Guidelines. Details of the analytical method equipment and procedures can be found in the *Standard Operating Procedure (SOP) for Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO15) (Revision 6, 12-7-15)* in Appendix A. In summary, the analytical equipment consists of an ENTECH 7100A pre-concentrator, a Hewlett-Packard 6890 gas chromatograph connected to a 5973 mass spectrometer (GC/MS) with a mass selective detector operated in the SIM mode. The software used by the HP GC/MS is HPCHEM Enviroquant (Windows NT). The pre-concentrator is connected to a 16-port ENTECH auto-sampler, which the canisters are connected to. A known volume of sample (400cc) is withdrawn from the canister and concentrated in the ENTECH 7100A cold trap dehydration system. Water and CO₂ are removed while the VOCs in the sample are concentrated on a series of two sequential focusing modules. The concentrated VOC compounds are then finally refocused on a third module at -160°C. The sample is then released by thermal desorption and carried into the GC column where the compounds are separated. The column terminates in a mass spectrometer, which is used to identify and quantitate the compounds in selective ion monitoring (SIM) mode. The program goal is to perform analysis within 14 days of the sample day, but canister samples must be analyzed no later than 30 days after the sample day.

The canister cleaning system used to prepare sample canisters for use and reuse after analysis consists of an AADCO 737-series pure air generator combined with an ENTECH 3100A canister cleaning system. The cleaning system includes a heated oven for canister vacuum/pressure baking cycles, a roughing pump for initial canister evacuation, and a molecular drag pump for final evacuation. Canisters are cleaned following the procedure identified in the *Standard Operating Procedure (SOP) for Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO15)* in Appendix A. The system is computer controlled using ENTECH software.

13.2 Carbonyls Analysis

Carbonyls listed in Table 5.2 will be analyzed by the Vermont Vael following TO11A Guidelines. Details of the analytical equipment and procedures can be found in the *Standard Operating Procedure (SOP) for Determination of Toxic Organic Compounds in Ambient Air (Carbonyls)(Revision 9 10-1-2015)* in Appendix A. In summary, the analytical equipment consists of a WATERS Corporation High Performance Liquid Chromatograph (HPLC) with a multi-wavelength UV detector configured for wavelength of 360 nanometers. The HPLC has an auto-sampler and data acquisition interface using WATERS Millennium 32 software.

DNPH sample cartridges are stored at ≤4°C prior to analysis. The program goal is to extract DNPH cartridges as soon as possible, ideally within 7 days of sampling, opposite the direction of the sample flow, using 5 ml of carbonyl-free Acetonitrile but the cartridges must be extracted within 14 days of sampling. The extract can be stored at ≤ 4°C for up to 30 days. Ideally the extract sample is analyzed within 14 days of the extraction procedure.

13.3 Trace Metal Analysis

PM₁₀ low-volume filter preparation/handling work is performed by the CT DEEP in the temperature and humidity controlled weighing room at the Windsor, CT Laboratory. See CT DEEP QAPP/SOP *Section 1.8.5 Analysis, PM_{2.5}, PM₁₀, PM_{10-2.5} via TS/R&P Models 2025 and 2025i with PM_{10-Pb} Revision 7 10/13/16* for more information on the filter weighing requirements and procedures.

Metals listed in Table 5.3 will be extracted and analyzed using Inductively Coupled Plasma/Mass Spectrometer (ICP-MS) by the Vermont VAEL following *EPA IO-3.5 and 6020A Guidelines*. Details of the analytical equipment and procedures can be found in the *Standard Operating Procedure (SOP) for Extraction of 47 mm Teflon Air Filters for Metals Analysis (Revision 2, December 12, 2017)* and *Standard Operating Procedure (SOP) for Metals Analysis by ICP-MS (Revision 9, 3-13-2017)* in Appendix A. In summary, the Teflon filter samples are digested in trace metal grade 4% nitric acid on a hot block apparatus and the analytical equipment consists of a TEI iCAP RQ ICP-MS with standard and kinetic energy displacement modes. The ICP-MS is computer controlled and has an auto-sampler.

PM₁₀ Teflon sample filters are stored at room temperature prior to analysis. The program goal is to analyze the filters as soon as possible but not later than 180 days after sampling.

13.4 Semi-volatile compounds

See Section 10.6.2 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, 2018* and SOP (*ERG-MOR-049*) for analytical method requirements for semi-volatile analysis.

14.0 Quality Control Objectives

The following tables (14.1-14.3) contain the Quality Control objectives for the sample collection portions of the Vermont Air Toxics Monitoring Network. Quality Control objectives for the analytical portions of the network are provided in the following Tables:

- ▶ VOC Analysis; Table 4 in *Standard Operating Procedure (SOP) for Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO15), Revision 6, 12-7-15*
- ▶ Carbonyl Analysis; Table in Appendix A of *Standard Operating Procedure (SOP) for Determination of Toxic Organic Compounds in Ambient Air (Carbonyls) Revision 9, 10/1/15* in Appendix A
- ▶ Metals Analysis; Table 23.3 in *Standard Operating Procedure (SOP) for Metals Analysis by ICP-MS (Revision 9, 3-13-2017)*

14.1 VOCs

Table 14.1 VOC Sampling QC Procedures

Assessment	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Canister Background (method blank)	Humid Zero Air Blank	One canister from each canister cleaning batch	≤0.1 ppbv of target VOCs	Additional cleaning and retest.
Sampling System Certification (upscale)	Challenge with select target compounds at expected field levels (<1ppbv)	New and optional thereafter, or after a major repair or PM or if the sample results suggest sampler is contaminated.	80-120% recovery for specific target compounds; overall avg. compound recovery 85-115%	Additional system purge with humidified zero air; repeat challenge
Sampling System Certification (zero air)	Challenge with zero air	New and every 2 years thereafter or after a major repair or PM or if the sample results suggest sampler is contaminated.	≤0.1 ppbv of target VOCs	Additional system purge with humidified zero air; repeat challenge
Time of Day Accuracy for commencement of sample collection	Sampler computer clock check.	Every sample setup	Time within ± 10 minutes of actual EST.	Adjust as needed.
Accuracy of total collection period	Sampler computer Elapsed Time check.	Every sample recovery	Collection period < ± 60 minutes of 24 hours.	Flag sample and analyze at Manager's discretion.
Canister Sample integration period	MFC verification	Biannual	Measured transfer standard flow within 5% of Flow set point.	Recalibrate or replace flow control device
Sampling System Pressure and Temperature Measuring Device Verification	Pressure verification	Biannual	< 10% difference between field and lab measured canister pressure	Recalibrate or replace pressure sensor
Sampler integrity	Verification of Proper final canister pressure	each sample	final canister pressure consistent w/ setpoint (12-13 psia)	verify sampler computer setup parameters
Canister Sample integrity	system leak check	each sample	system leak check passes following sampler SOP setup routine	Investigate cause. Check system for leaks and repeat test. Install backup canister
Sample Volume	Ensure adequate sample for analysis	each sample	final pressure 12-13 Psia < 1 Atm. (0- 4 "Hg Vac)	flag sample for review but analyze
Method Precision	Comparison of collocated canister sample results	All samples at Burlington monitoring location on 1-in-12 th day sampling. Frequency = 20% of field samples	Collocated results agreement within 30% RPD for compounds > 5X MDL (or 15% CV: NATTS Calculations) Assessed Quarterly	Perform sampler PM; repeat duplicate sampling; check analytical precision; check canisters or sampler for leaks

14.2 Carbonyls

Table 14.2 Carbonyl Sampling QC Procedures

Assessment	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Accuracy of Sample Volume	Flow control check	Biannually	Measured transfer standard flow within 5% of indicated flow	Recalibrate or replace flow control device
Sampling System Certification	Collect sample cartridge sampling carbonyl-free zero air.	New and every 2 years thereafter or after a major repair or PM or if the sample results suggest sampler is contaminated.	Target compounds detected \leq TO11A Method Blank levels or \leq MDL, as appropriate.	Additional system purge with humidified zero air; repeat challenge
Sample integrity	Flow documentation, cartridge leak check and Ozone denuder temperature	each sample	pre and post flow < 5% different; system leak free, denuder temperature > 45°C	Mark sample as suspect if flow or denuder criteria exceeded. Investigate cause. Check system for leaks and repeat test. Adjust Denuder temp. as needed.
Accuracy of collection period	Sampler computer clock check.	Each sample setup	< 10 minutes off actual EST .	Adjust time.
Accuracy of total collection period	Sampler computer Elapsed Time check.	Every sample recovery	Collection period < \pm 60 minutes of 24 hours.	Flag sample and analyze at Supervisor's discretion.
Method Precision	Comparison of collocated cartridge sample results	Every 12 th day sample at Burlington Monitoring Location. Frequency= 20% of field samples	Collocated results agree within 20% RPD for target compounds > 5X MDL (or 15% CV following NATTS Calculations) Assessed Quarterly.	Perform sampling system PM; repeat duplicate sampling; check analytical precision; check sampling system for leaks
Method Background levels.	Field Blanks	100% of field samples	See Carbonyl Field Blank Correction SOP in Appendix A	Blank Correct data
Sample volume	Ensure adequate sample for analysis and verify proper sample collected.	each sample	Minimum sample volume > 1000 liters. Nominal target sample volume = 1300 liters (based on 0.9 LPM and 1440 minutes). Minimum flow of 0.75 Lpm and Elapsed time between 1380-1500 minutes	If minimum criteria not met, flag sample and analyze at Supervisor's discretion

14.3 Trace Metals

See Section 14.0 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18* for PM10 low-volume sampling and weighing quality control requirements.

14.4 Semi-volatile

Sampling related QC procedures are identified in Table 14.3. See Section 11 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, 2018* for quality control requirements for semi-volatile sample analyses.

Table 14.3 Semi-volatile Sampling QC Procedures

Assessment	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Accuracy of Sample Flow rate	Flow check/audit	Biannually	Measured transfer standard flow within 10% of indicated flow	Recalibrate or replace flow control device
Sampling period	24 hours; midnight to midnight EST	Verified for Each sample; clock time and ET	+/- 1 hour	Reset timer/controller
Shipping	In coolers with blue ice	All samples and FB	N/A	N/A
Storage	In Freezer	Prior to and after sampling	N/A	N/A
Field Blank		monthly	Method/ ERG criteria	Collect additional FB and investigate source of background

15.0 Instrument/Equipment Testing, Inspection and Maintenance Requirements

15.1 VOCs

The ATEC 2200 canister sampler design is based on EPA Method TO15 and NATTS TAD and is assumed to be of sufficient quality for the data collection portion of this program. Prior to field installation, each VOC sampler is tested to verify performance. Testing included internal and external leak checks, pressure and flow checks, test sample collections, computer software and sample program verification, data collection and printing. Regular checks of these parameters (to ensure they are appropriate) are inherent to the SOP for sample handling (See Appendix A). Bi-annually, a manifold sample line leak check is performed (from end-of-line).

Every 2 years (or after a major repair or preventative maintenance or if the sample results suggest sampler is contaminated) each sampler is tested at the AQCD Barre field operations facility or the VAEL (or sent to a contract lab) for certification following EPA Method TO15 and NATTS TAD Guidelines. Due to the passive design of the ATEC 2200 (no pump) the sintered stainless steel 2 μm particulate filter is changed only every 5 years (or as needed) due to the low system flow rate (3.5 ccpm). The certification testing includes a zero and optional upscale challenge to verify the lack of sampler bias. Refer to Table 14.1 for criteria. The 1/4" stainless steel manifold line is rinsed with DI water annually for 1/6 day sampling sites and every 2 years for 1/12 day sampling sites.

Details of the VOC analytical inspection, testing and maintenance procedures can be found the *Standard Operating Procedure (SOP) for Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO15), Revision 6, 12-7-15* in Appendix A.

15.2 Carbonyls

The ATEC 2200 cartridge sampler design is consistent with EPA's Method TO11A and the NATTS TAD Guidelines and is assumed to be of sufficient quality for the data collection portion of this program. Prior to field installation, each carbonyl sampler was tested to verify performance. Testing includes denuder temperature and flow checks, test sample collections, computer software and sample program verification and data collection and printing. Regular checks of these parameters (to ensure they are appropriate) are inherent to the SOP for carbonyl sample handling (See Appendix A). Bi-annually, the MFC is audited with a NIST-traceable Laminar Flow Element transfer standard, the Teflon particulate filter is changed, and a manifold-line leak check is performed.

For samplers collecting 1/12 day samples, the copper ozone denuder is changed every 12 months. For 1/6 day sample collection it is changed every 6 months. Also, every 2 years (or after a major repair or preventative maintenance or if the sample results suggest sampler is contaminated) each carbonyl sampler undergoes separate testing to confirm the absence of any bias (this test involves collecting a DNPH cartridge while sampling carbonyl-free zero air). The 1/4" Teflon sample inlet line (from the manifold) is replaced annually for 1/6 day sampling sites and every 2 years for 1/12 day sampling sites. Refer to Table 14.2 for criteria.

Details of the Carbonyl analytical inspection, testing and maintenance procedures can be found the *Standard Operating Procedure (SOP) for Determination of Toxic Organic Compounds in Ambient Air (Carbonyls)*, Revision 9, 10-1-15 in Appendix A.

15.3 Trace Metals

See Section 15.0 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1*, 11/1/18 for PM10 sampler maintenance requirements.

Details of the Metals analytical inspection, testing and maintenance procedures can be found the *Standard Operating Procedure (SOP) for Metals Analysis by ICP-MS (Revision 9, 3-13-2017)* in Appendix A.

15.4 Semi-volatiles

See Section 12.4 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support)*, Contract No. EP-D-14-030, 2018 for instrument and equipment testing, inspection and maintenance requirements related to semi-volatiles.

16.0 Instrument Calibration and Frequency

16.1 VOCs

The components of the ATEC 2200 Canister Sampler that require calibration are the MFC and pressure transducer. These are calibrated by the manufacturer and as needed after that. The calibration of these components is verified as needed using a CME Transfer Laminar Flow Element flow standard (TLFE). The CME TLFE has a NIST-traceable Manufacturer's Calibration which is routinely verified by the AQCD using its Primary Standard NIST-traceable Laminar Flow Element.

The calibration procedure for the GC/MS instrumentation is detailed in *the Standard Operating Procedure (SOP) for Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO15), Revision 6, 12-7-15* in Appendix A. In summary, the calibration of the GC/MS is accomplished as needed or at least every 3 months, using humidified standards at input levels of 0.06, 0.10, 0.2, 0.5, 1, 2, 3 ppbv. The standards are prepared in dedicated individual 6-liter or 15-liter RESTEK *Silco-Steel* canisters using an ENTECH 4700 static diluter. Cleaned, certified and evacuated canisters are humidified to ~40% using a clean, dedicated syringe to add an appropriate amount of DI water to the canister valve. An ENTECH silonite-coated micro-QT valve is added onto the canister valve and the canister is connected to the 4700 static diluter. Based on the desired concentration of the standard in each canister, the concentration of the primary or second source calibration cylinders (containing all target compounds from Linde-Spectra and/or Air Liquide-Scott) and the desired final pressure in the canister is used by the static diluter to calculate and deliver the appropriate pressure of primary standard gas to the canister. Finally, the diluter brings the canister to precise final pressure with high purity zero air from the AADCO 737 pure air generator.

The NIST traceable primary standard has a +/- 5% analytical tolerance and is verified every 2 years either by independent lab analysis or by the gas vendor. The primary standard cylinder was originally purchased in 1998 and has had at least 6 re-certifications during its many years of use which have indicated insignificant change in certified concentrations (<5%) for all compounds. This indicates concentrations are stable and annual re-certification is unwarranted. Acceptable results from participation in PE and round robin audit programs also indirectly verify the integrity of the primary standard. The GC/MS also uses an internal/tuning standard containing Pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5 and Bromofluorobenzene (obtained from Linde-Spectra Gas), which is injected through the ENTECH 7100A canister interface device into every sample, standard and QC sample analyzed.

16.2 Carbonyls

The only component of the ATEC 2200 Canister Sampler that requires calibration is the MFC. This is calibrated by the manufacturer and as needed after that. The MFC calibration is verified through biannual audits using a CME Transfer Laminar Flow Element flow standard (TLFE). The CME TLFE has a NIST-traceable Manufacturer's Calibration which is routinely verified by the AQCD using its Primary Standard NIST-traceable Laminar Flow Element.

The calibration procedure for the HPLC instrumentation is detailed in the *Standard Operating Procedure (SOP) for Determination of Toxic Organic Compounds in Ambient Air (Carbonyls), Revision 9, 10-1-15* in Appendix A. In summary, the calibration of the HPLC is accomplished at least biannually, using certified liquid standards (obtained from Supelco) containing derivatized target list carbonyl compounds. The calibration input levels are 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 µg/ml. The calibration standards are stored at ≤ 4°C and used no longer than six months.

16.3 Trace Metals

See Section 16.0 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18* for PM10 low-volume sampler related calibration and their frequency.

The calibration procedure for the ICP-MS instrumentation is detailed in the *Standard Operating Procedure (SOP) for Metals Analysis by ICP-MS (Revision 9, 3-13-17)* in Appendix A. In summary, the calibration of the ICP-MS is performed before each analysis batch utilizing standard concentrations of 0.5, 1 and 10 ug/L (ppb) from a multi-element liquid standard (diluted in nitric acid) containing the compounds listed in Table 5.3. The calibration is verified by low level checks including an ICV at 2.5 ppb and low-level checks at concentrations of 0.1 and 0.05 ppb. The calibration standard hold time is 1 week.

16.4 Semi-volatile

The Tisch PUF+ microprocessor/controller includes a flow control system that requires periodic calibration. The procedure is based on the manufacturer's guidelines and is included in the *PUF+ Field Sampling Operations (SOP 3535)* in Appendix A. The flow calibration is verified through biannual audits using a GMW "top-hat" orifice calibrator which is verified by sending the orifice to IML Air Science (Division of Inter-Mountain Laboratories) in Sheridan, WY (or equivalent vendor) for recertification.

The calibration procedure for the analytical equipment used for semi-volatile analysis is identified in Section 13.5 of the *ERG QAPP Category 1 Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, 2018.*

17.0 Inspection/Acceptance for Supplies and Consumables

17.1 VOCs

Prior to field installation, each VOC sampler was tested to verify performance. Testing included internal and external leak checks, temperature, pressure and flow verification, software and program test sample collections, program verification and data collection and printing.

Only GC-grade SS tubing (with or without Silco coating) is used for the manifold and canister inlet lines. The GC-grade designation from the vendor is adequate for acceptance of this product. Only new 2 µm sintered SS filters and ¼" stainless steel *Swagelok* fittings are installed in the sampler as indicated in this manual.

RESTEK SilcoSteel 6-liter canisters when new and annually thereafter are tested for target list stability for the 30-day hold time following criteria in EPA Method TO15 (zero air and/or upscale standard). Canisters that do not meet a <0.1ppbv for zero test and 70-130% recovery for upscale test after 30 days storage at room temperature are recleaned and retested. If a second failure occurs, they are rejected and not used in this program. Canisters are leaked checked with each sample period as well as during the analysis (auto-sampler) and canister cleaning oven.

Inspection and acceptance testing procedures for supplies and consumables for the VOC analysis such as liquid cryogen, helium carrier gas, internal/tuning standards, pure air generator filters etc... can be found in the *Standard Operating Procedure (SOP) for Determination of Volatile Organic Compounds in Ambient Air By GC/MS (TO15), Revision 6, 12-7-15* in Appendix A. .

17.2 Carbonyls

Prior to field installation, each carbonyl sampler was tested to verify performance. Testing included external and internal leak checks, denuder temperature and flow verification, test sample collections, program verification and data collection and printing. Every 2 years (1 year for 1/6 sampling frequency), new Telfon tubing is installed from the common sample manifold to the carbonyl sampler. Copper ozone denuders are recharged by the Supervisor or other section staff following Appendix 2 of the *SOP ATEC 2200 Sampler Certification, Maintenance & Performance Verification #3554* (see Appendix A of this document) and guidelines in EPA's Method TO11A and the NATTS TAD.

Prior to use, each lot# of DNPH cartridges and "carbonyl-free" acetonitrile solvent are tested for acceptable contaminant levels following guidelines in EPA Method TO11A. Details of these procedures and acceptance limits are provided in the *Standard Operating Procedure (SOP) for Determination of Toxic Organic Compounds in Ambient Air (Carbonyls), Revision 9, 10-1-15* in Appendix A. Any lot# not meeting the criteria will be rejected and not used in this program. Inspection and acceptance testing procedures for other supplies and consumables for the Carbonyl analysis can be found in the same SOP above.

17.3 Trace Metals

Refer to Section 17.0 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18* for inspection and acceptance criteria for PM10 low-volume sampler related supplies and consumables. Calendar year PM10 filters will be inspected and pin-holed by the CT DEEP lab technician relative to the calendar year filter criteria provided by EPA with the filters.

Refer to the *Standard Operating Procedure (SOP) for Metals Analysis by ICP-MS (Revision 9, 3-13-2017)* in Appendix A for inspection and acceptance for ICP-MS related supplies and consumables.

17.4 Semi-volatiles

See Section 14 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, 2018* for inspection and acceptance for supplies and consumables related to semi-volatile sample analyses.

18.0 Data Acquisition Requirements (non-direct measurements)

Chemical and physical properties and conversion constant data that is not determined from the monitoring regulations or EPA TO and IO methods and TAD guidance documents will be obtained from the following source: *CRC Press Handbook of Chemistry and Physics*.

Geographic locations and elevations will be determined by GPS measurements.

19.0 Data Management

19.1 VOCs, Carbonyls and Trace Metals

VOC sample collection information from the field data sheet is entered into a dedicated ACCESS database by the field operations center Analyst where it is permanently stored and used to process analytical results. The Analyst and the Supervisor review the sample collection information from the field data sheets and the database to ensure completeness and to make the initial determination of whether a valid and proper sample collection event took place to allow for subsequent analysis. Paper records, field data sheets for samples and performance audits, are kept in binders maintained by the Supervisor. Sampler performance verification, maintenance and troubleshooting information is also input into the Operations Database.

Details of data management procedures for the VOC, Carbonyl and Metals analytical results are provided in their respective analytical SOP's contained in Appendix A. The VAEL uses the LIMS to store valid VOC, Carbonyl and Trace Metal analytical results (by lab ID#) and store QA/QC results by batch ID#. PDF files of results and QA/QC are provided to the Supervisor for visual review and verification (and printout if necessary). The Analysts or Supervisor receives the analytical results in excel spreadsheets from the VAEL's LIMS system and imports this data into separate, dedicated VOC, Carbonyl and Metals ACCESS databases. All databases are maintained on the Agency network (Y:\AP_Monitoring\Databases see 9.1.2) and are backed up every night. The Analyst or Supervisor creates the data files for EPA AQS upload using the Access database. EPA AQS is the final repository for all 24-hour average results associated with this QAPP. ACCESS database and associated metadata will be retained 6 years. After 6 years, records will be backed up and retained on a transferable media or network.

The VOC results are provided by the VAEL in a ppbv concentration format and undergo minimal processing once imported into ACCESS. The ACCESS VOC database links the results with the sample collection information for subsequent processing, review, final validation, conversion to $\mu\text{g}/\text{m}^3$ (at EPA standard conditions), summarization and reporting.

The carbonyl results are provided by the VAEL in a $\mu\text{g}/\text{cartridge}$ format and undergo processing (using ACCESS) that corrects for background contaminant levels using average field blank levels for specific DNPH cartridge lots and then uses sample collection information (sample volume) from a linked ACCESS table to calculate a final concentration in $\mu\text{g}/\text{m}^3$ (at EPA standard conditions). Details on the Field Blank correction procedures are provided in the *Carbonyl Field Blank Correction SOP* in Appendix A. The final carbonyl concentration results are stored in ACCESS for subsequent processing, review, final validation, summarization and reporting.

The trace metals results are provided by the VAEL in a ng/filter format and undergo processing (using ACCESS) that uses sample volume from a linked ACCESS table to calculate a final concentration in ng/m^3 (at local conditions). The final trace metals concentration results are stored in a dedicated ACCESS database for subsequent processing, review, final validation, summarization and reporting.

Paper records, including sampler data sheets, are kept in binders maintained by the Supervisor. Pertinent sampler information is also input into the Operations Database.

19.2 Semi-volatiles

See Section 15 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support), Contract No. EP-D-14-030, 2018* for data management requirements related to semi-volatile sample analyses.

Results are reported to VT AQCD via excel and .pdf files in ng/m³. The Supervisor reviews the data and notifies ERG regarding any suspect values. The data is stored in the semi-volatiles database in ACCESS and is maintained by the Supervisor.

Data files for AQS are created and uploaded by the ERG after data is reviewed by AQCD Supervisor.

Paper records, including sampler data sheets, are kept in binders maintained by the Supervisor. Pertinent sampler information is also input into the Operations Database.

20.0 Assessment and Response Actions

20.1 VOCs and Carbonyls

Internal and external assessment activities, which will be performed to ensure VOC and Carbonyl data quality, are listed in Table 6.1. The Analyst or Supervisor will compile and review assessment data as it is generated. This includes field performance audit results, analytical performance evaluation audit samples, Technical Systems Audits (TSA), co-located precision results, NATTS audits etc.... All assessment results are reviewed by the Analyst or Supervisor and QA Coordinator to determine questionable, problematic or nonconformance observations and to verify that MQOs are being met. The Analyst, Supervisor and QA Coordinator will come to a collective decision as to how to respond to assessment results and resolve situations as necessary to improve data quality. This may involve working with VAEL to perform additional review and provide additional QA/QC results if necessary and then work to come to a consensus on data quality and proper flagging/reporting to AQS. If there were changes to be made to the monitoring program, they would be made in consultation with the EPA-New England contact.

20.2 Trace Metals

Trace metals data will be assessed on a continual basis as samples are analyzed and reports are generated. For the detailed assessment and response actions relative to the PM10 sampling portion of this program, refer to Section 20 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18*. Table 6.2 of this document lists the various project assessment activities related to trace metals. These activities include Technical Systems Audits (TSA), performance evaluations, performance audits and method precision (collocated samples). All assessment activities and results are reviewed by the Supervisor and QA Coordinator to determine questionable or problematic or nonconformance observations and to verify MQOs are being met. The Supervisor and QA Coordinator will come to a collective decision as to how to respond. This may involve working with VAEL to perform additional review and provide additional QA/QC results if necessary and then work to come to a consensus on data quality and proper flagging/reporting to AQS. If there were changes to be made to the monitoring program, they would be made in consultation with the EPA-New England contact.

20.3 Semi-volatiles

Semi-volatile data will be assessed on a continual basis as samples are analyzed and reported by ERG. Table 6.3 lists the various project assessment activities related to semi-volatile results. These activities include performance evaluations, field performance audits and method precision. All assessment activities and reports are reviewed by the Supervisor and QA Coordinator to determine questionable or problematic observations. The Supervisor, the QA Coordinator and ERG will come to a collective decision as to how to respond. If there were changes to be made to the monitoring program, they would be made in consultation with the EPA-New England contact.

21.0 Reports to Management

Reports to management for VOCs, carbonyls, semi-volatiles and trace metals are listed in Table 21.1 and are available upon request.

Table 21.1 Reports to Management

Report	Frequency	Preparer	Recipient(s)	Expected Management Use
AQS Quick Look Reports	Updated quarterly	Analysts	AQCD staff	Information
Quarterly Data Report	Quarterly	Analyst or Supervisor	Monitoring Supervisor and QA Coordinator	Review; approval required for data upload to AQS
Annual Network Review	Annual	Monitoring Supervisor	AQCD staff after review, signature and submittal to EPA by AQCD Director	Information; review, signature and submittal to EPA by AQCD Director
Annual SLAMS Data Certification	Annual	Monitoring Supervisor	AQCD Director	Review, signature and submittal to EPA
Annual Data Summary	Annual	Monitoring Supervisor and Staff	AQCD Staff	Information
Accuracy audit datasheets	As generated	Supervisor	QA Coordinator, Monitoring Supervisor and AQCD Director	Information and review
Technical System Audits	Annual	QA Coordinator	Supervisor, Monitoring Supervisor and AQCD Director	Information and review; AQS data upload contingent on QA Coordinator approval
National Performance Audit Program Audit Reports	As received	Supervisor	Monitoring Supervisor and AQCD Director	Information, review and as appropriate decisions on quality improvement

22.0 Data Review, Verification, and Validation

22.1 VOCs and Carbonyls

The AQCD Analyst and the Supervisor review the sample collection information from the field data sheets and the ACCESS database to ensure completeness. The Analyst or Supervisor then makes an initial determination of whether a valid and proper sample collection event occurred to allow for subsequent analysis.

Details of data review procedures for the VOC and Carbonyl analytical results are provided in the applicable VAEL SOPs in Appendix A. In summary, the VAEL Environmental Scientists conducting the VOC and Carbonyl analyses review all of the data generated for each batch to verify proper compound identification and quantification and batch MQOs are met. The analysis and batch reports for each program are then peer-reviewed for verification by another VAEL Environmental Scientist not conducting the analysis. Any abnormal observations are documented as qualifier flags and/or in an “irregularity report” which is provided to the Laboratory QA Coordinator and the Lab Director and the Supervisor (upon request). The Lab Director and the Lab QA Coordinator review the QA/QC and sample results before authorizing them as valid and authorizing them in the LIMS to be reported to the Supervisor.

Excel files of both the sample and QA/QC results are obtained by the Analyst or Supervisor from the VAEL LIMS for review and verification. This verification involves a visual review of the sample and QA/QC results for each analytical batch. The overall analytical results for each sample are visually reviewed noting any data flags, analyst comments, and determining the presence of any unusual values for the particular site (based on historic information/results) or data entry errors. The Analyst or Supervisor will create scatter, fingerprint, and time-series plots in an effort to identify data-reduction problems, potential outliers, or other inconsistencies within the dataset based on historical trend information. The Analyst and/or Supervisor will investigate the validity of any unreasonable value. The QA/QC results are reviewed to verify MQOs were met.

22.2 Trace Metals

The PM10 filter data is reviewed and validated in accordance with the procedures in Section 22 of the *Vermont AQCD Quality Assurance Project Plan for Criteria Gas & Particulate Matter Pollutant Monitoring Revision 2.1, 11/1/18*. Refer to the *Standard Operating Procedure (SOP) for Metals Analysis by ICP-MS (Revision 9, 3-13-2017)* in Appendix A for information on analytical data review, verification and validation for trace metal analysis. In summary, the VAEL reviews all the trace metals analytical data generated for each batch to verify proper compound identification and quantification and batch MQOs are met.

The Supervisor will consult with the AQCD QA Coordinator regarding the quality assurance and validation status of the filter sample’s gravimetric-based concentration results as these databases are directly linked. Excel files of both the sample and QA/QC analytical metal results are obtained by the Supervisor from the VAEL Lab LIMS for review and verification. This verification involves reviewing the sample and QA/QC results for each analytical batch. The overall analytical results are visually reviewed noting any negative values, data flags, analyst

comments, and determining the presence of any unusual values for the particular site (based on historic information/results) or data entry errors. The Supervisor will create scatter, fingerprint, and time-series plots in an effort to identify data-reduction problems, potential outliers, or other inconsistencies within the dataset based on historical trend information. The Supervisor will investigate the validity of any unreasonable value. The QA/QC results are reviewed to verify MQOs were met. Samples may be flagged or invalidated for due cause.

22.3 Semi-volatiles

The semi-volatile data is reviewed and validated in accordance with the procedures in Section 18.5 of the ERG QAPP Category 1 *Support for the EPA National Monitoring Programs (UATMP, NATTS, CSATAM, PAMS, and NMOC Support)*, Contract No. EP-D-14-030, 2018 and then sent to the AQCD Supervisor for review.

Once the semi-volatile data review is complete, the Supervisor will import all data into the semi-volatile database. The Supervisor will then review the concentration data by crosschecking log sheets with the database and creating scatter and time-series plots in an effort to identify data-reduction problems, potential outliers, or other inconsistencies within the dataset based on historical information. The Supervisor will investigate all questionable values. The QA/QC results are reviewed to verify MQOs were met.

23.0 Verification and Validation Methods

Previous sections of this QAPP identify methods to verify various sampling and analysis components of this project for each pollutant method to ultimately provide results of known and acceptable quality consistent with the DQOs. Methods for sample collection verification include sampling equipment inspection/acceptance testing, certification (where applicable) and performance assessment/audits, sample handling procedures and field blank collection (where applicable), sample media certification/background assessment. Verification methods for analysis include analytical equipment/method verification (NATTS/internal PE audit, Second Source standards, lab blanks, round robin/split sample audits). Verification methods for the overall project include internal and EPA Technical System audits. The sections below provide specific verification/validation methods for the analytical results for each pollutant method prior to reporting to AQS.

23.1 VOCs

The VOC results in ppbv are provided by the VAEL and undergo minimal processing once imported into ACCESS VOC database and are linked directly to the sample collection information. The Analyst or Supervisor reviews the QA/QC batch report, the final concentration data, field information, field and analytical comments for each sample, and any applicable scatter, fingerprint, time-series plots, internal marker compound concentrations (Freons, chloromethane, carbon tetrachloride etc), compound ratios (such as benzene and toluene) in an effort to identify analytical or data-reduction problems, potential outliers, or other inconsistencies within the dataset based on historical trends. This information is used to perform the final validation in the ACCESS database using a validation flag field. AQS null data codes, QA qualifier codes and sample specific comments are used in the validation process and reporting to AQS. NATTS work plan requires at a minimum that the following QA qualifier codes be reported to AQS: Non detects = ND; results below the MDL=MD; results below the lowest calibrant=7.

23.2 Carbonyls

The Carbonyl results are provided by the VAEL in a $\mu\text{g}/\text{cartridge}$ format and undergo processing (using ACCESS) that corrects for background contaminant levels using average field blank levels for specific DNPH cartridge lots (following the *Carbonyl Field Blank Correction SOP* in Appendix A) and then uses sample collection information (sample volume) from a linked ACCESS table to calculate a final concentration in $\mu\text{g}/\text{m}^3$ (at EPA standard conditions). The Analyst or Supervisor reviews the QA/QC batch report, the final concentration data and field information and comments for each sample in the ACCESS Carbonyl database and any applicable scatter, fingerprint, time-series plots in an effort to identify analytical or data-reduction problems, potential outliers, or other inconsistencies within the dataset based on historical trends. This information is used to perform the final validation in the ACCESS Carbonyl database using a validation flag field. AQS null data codes, QA qualifier codes and sample specific comments are used in the validation process and reporting to AQS. NATTS work plan requires at a minimum that the following QA qualifier codes be reported to AQS: Non detects = ND; results below the MDL=MD; results below the lowest calibrant=7. Additional QA codes include CB for values are blank corrected.

23.3 Trace Metals

The trace metal results are provided by the VAEL in a ng/filter format and undergo processing (using ACCESS) that uses sample collection information (sample volume) from a linked ACCESS table to calculate a final concentration in ng/m³ (at local conditions). The Supervisor reviews the QA/QC batch report, the final concentration data and field information and comments for each sample in the ACCESS Metals database and any applicable scatter, fingerprint, time-series plots in an effort to identify analytical or data-reduction problems, filter background, potential outliers, or other inconsistencies within the dataset based on historical trends. This information is used to perform the final validation in the ACCESS database using a validation flag field. AQS null data codes, QA qualifier codes and sample specific comments are used in the validation process and reporting to AQS. NATTS work plan requires at a minimum that the following QA qualifier codes be reported to AQS: Non detects = ND; results below the MDL=MD; results below the lowest calibrant=7

23.4 Semi-volatiles

The semi-volatile data provided by ERG are in nanograms per cubic meter (ng/m³ at EPA standard conditions). Corrections may be applied for background concentrations using average field blank levels or individual field blank values corresponding to the appropriate sample day. The Supervisor reviews the final concentration data, QA/QC results and field information and comments for each sample in the semi-volatile databases and performs the final validation using a validation flag field. QA qualifier flagging suggestions (bias, elevated field or method blank results, negative values) are provided to ERG for inclusion with their EPA submittal.

24.0 Reconciliation with User Requirements

The Analyst or Supervisor will produce a Data Summary Report on an annual basis which will assess and determine whether DQOs were met for a given calendar year. This report will be reviewed by the QA Coordinator and Monitoring Supervisor. The Analyst, Supervisor and QA Coordinator must agree on the contents of the report. The QA Coordinator will include a certifying statement in the report. The report will be distributed to all AQCD personnel and the EPA – New England contact. Any other data analysis would be performed by the AQCD Planning Section and is outside the scope of this QAPP. Regarding the Underhill NATTS site, EPA performs regular QA and Network summaries evaluating and summarizing network performance and achievement of DQOs. The following equations will be used to assess the various DQOs identified in Section 7 of this document.

Precision: [Based upon valid collocated sample or replicate results (see Tables in Section 14 for criteria)]

$$\%RPD = \frac{y - x}{\frac{y + x}{2}} \times 100$$

Where: x = *primary sample result* and y = *collocated result*

Accuracy: [Based upon Audit results such as PE audit sample, Field Flow checks or Second Source Standards]

$$\%Error = \frac{y - x}{x} \times 100$$

Where: x = *known audit input value* y = *response to audit input*

Completeness: [Typically assessed for the calendar quarter, it is based upon the total # of valid samples collected (scheduled and makeup) compared to the total # of scheduled samples for the period in question.

$$\%datacapture = \frac{\#validsamples(scheduled + makeup)}{Total\#schedulesamples}$$

MDL: Results of annual MDL study will be reviewed by the Supervisor and compared with previous year's results for acceptability based on applicable 8/28/17 MUR updated criteria in *40 CFR Part 136, Appendix B* and the EPA TAD for NATTS, Revision 3.

25.0 References

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Appendix A – Standard Operating Procedures

AQCD VOC SOPs.....	Section 1
AQCD Carbonyl SOPs	Section 2
AQCD Trace Metals SOPs	Section 3
DEC Laboratory Analytical SOPs	Section 4
ERG Field SOP.....	Section 5
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