# North Carolina Department of Environment & Natural Resources Division of Air Quality

# Quality Assurance Project Plan for the

# Urban Air Toxics Monitoring Program

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<u>31/19</u> Date

<u>8/11/14</u> Date

7/31

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# List of Revisions since Last Version

- 1. Comments by EPA Region 4 reviewing the last revision were addressed.
- 2. Aldehyde sampling and analysis was resumed effective June 2013 at two sites.
- 3. Blackstone site added November 2013, monitoring for VOCs and aldehydes.
- 4. Changed organizational chart, titles, and Distribution List according to Division of Air Quality reorganization 3/17/14 and personnel changes.
- 5. Increased completeness Measurement Quality Objective (MQO) to 85% and specified collocated precision MQO to be 20%.

# **Quality Assurance Project Plan**

# Preface

The NC Division of Air Quality (DAQ) established and operates an urban air toxics (UAT) monitoring network in conjunction with the national program originally proposed and designed by the EPA in 1999 to meet the requirements in section 112(k), Urban Air Toxics on the 1990 Clean Air Act Amendments. DAQ recognizes the importance of this network and supports the continuation of the program. Currently, the North Carolina program includes 6 "urban" and 1 "rural" monitoring sites. Air monitoring capabilities included volatile organic compounds (VOC) begun January 2002, aldehydes begun May 2003, ended January 2010, resumed June 2013, and semi-volatile organic compounds (SVOC) begun January 2007 and ended July 2008. Monitoring for VOCs occurs at 6 sites and aldehyde sampling at 2 sites effective June 2013. The Blackstone site monitoring VOCs and aldehydes began November 2013.

This document presents the Quality Assurance Project Plan (QAPP) for the North Carolina UAT Monitoring Program. This QAPP describes the quality assurance practices for field sampling, network operations, meteorological data collection, chemical analysis of field-collected samples, auditing, oversight, and data management, reporting and analysis. Those involved in the project work must read, understand, and follow all the protocols and procedures.

This QAPP was generated following the EPA Quality Assurance (QA) guidance and relevant provisions from federal air monitoring regulations described in the following:

- EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans.<sup>1</sup>
- EPA QA/G-5, Guidance for Quality Assurance Project Plans.<sup>2</sup>
- Title 40 Code of Federal Regulations, Part 58 Appendix A, Part 136 Appendix B

This QAPP may be revised as necessary. The Project Manager, the Quality Assurance Manager (QAM), and the Project Administrator will initial, date, and incorporate any changes in the monitoring program into all official copies of the document. All suggestions and changes should be forwarded to the QAM for consideration and incorporation into the QAPP.

#### Any mention of equipment manufacturers is not an endorsement.

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# **Acronyms and Abbreviations**

AIRS	Aerometric Information Retrieval System
AMS	North Carolina Division of Air Quality, Ambient Monitoring Section
AQS	Air Quality System (EPA AIRS database)
CAS	Chemical Abstract Service
CFR	Code of Federal Regulations
COC	chain of custody
DAQ	North Carolina Division of Air Quality
DENR	North Carolina Department of Environment and Natural Resources
DNPH	2,4-dinitrophenylhydrazine
DQO	data quality objectives
EPA	Environmental Protection Agency
HAP	hazardous air pollutant
LAB	DAQ, AMS, Laboratory Analysis Branch
LUESA	The Mecklenburg County, Land Use and Environmental Services Agency
MSA	metropolitan statistical area
NATTS	National Air Toxics Trends Stations
NATTS NIST	National Air Toxics Trends Stations National Institute of Standards and Technology
NIST	National Institute of Standards and Technology
NIST PAMS	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations
NIST PAMS PPB	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch
NIST PAMS PPB QA/QC	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch quality assurance/quality control
NIST PAMS PPB QA/QC QAM	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch quality assurance/quality control Quality Assurance Manager
NIST PAMS PPB QA/QC QAM QAPP	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch quality assurance/quality control Quality Assurance Manager Quality Assurance Project Plan
NIST PAMS PPB QA/QC QAM QAPP SVOC	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch quality assurance/quality control Quality Assurance Manager Quality Assurance Project Plan semi- volatile organic compounds
NIST PAMS PPB QA/QC QAM QAPP SVOC SOP	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch quality assurance/quality control Quality Assurance Manager Quality Assurance Project Plan semi- volatile organic compounds standard operating procedures
NIST PAMS PPB QA/QC QAM QAPP SVOC SOP TAP	National Institute of Standards and Technology Photochemical Assessment Monitoring Stations DAQ, AMS, Projects and Procedures Branch quality assurance/quality control Quality Assurance Manager Quality Assurance Project Plan semi- volatile organic compounds standard operating procedures toxic air pollutant
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# A. Project Overview

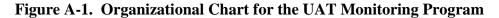
North Carolina Division of Air Quality (DAQ) has established an Urban Air Toxics (UAT) monitoring network in conjunction with a national network of other State and Local Programs originally proposed and designed by the Environmental Protection Agency (EPA) in 1999<sup>4</sup> to meet the requirements in section 112(k), Urban Air Toxics on the 1990 Clean Air Act Amendments. The origination of the monitoring network was due in part to the EPA's effort to address toxic air pollutant emissions in urban areas. This effort provided grant funding to the DAQ, as well as local environmental programs within the state, to assist in the establishment and operation of the UAT monitoring network. The UAT monitoring network or program is a collaborative effort of the following state and local agencies:

- The NC Division of Air Quality, Laboratory Analysis Branch (LAB)
- The NC Division of Air Quality, Ambient Monitoring Section (AMS)
- The NC Department of Environment and Natural Resources, Wilmington Regional Office (WiRO)
- The NC Department of Environment and Natural Resources, Fayetteville Regional Office (FRO)
- The NC Department of Environment and Natural Resources, Raleigh Regional Office (RRO)
- The Western NC Regional Air Quality Agency
- The Forsyth County Environmental Assistance and Protection Department
- The Mecklenburg County Air Quality a part of Land Use and Environmental Services Agency

The intent of the QAPP is to codify policies and procedures to ensure that data of appropriate quality are obtained. This QAPP describes the quality assurance practices for field sampling operations, meteorological data collection, chemical analyses of field-collected samples, auditing, oversight and project data collection, management, auditing and reporting.

#### A.1 Project and Task Organization

The LAB has responsibility for the overall operation of the UAT network including design and implementation of a QAPP and sample and data analysis. Operation of the network is accomplished with the assistance of various agencies listed above. An organization chart of the personnel participating in this monitoring effort is presented in **Figure A-1**, and descriptions of their roles are presented in **Table A-1**.



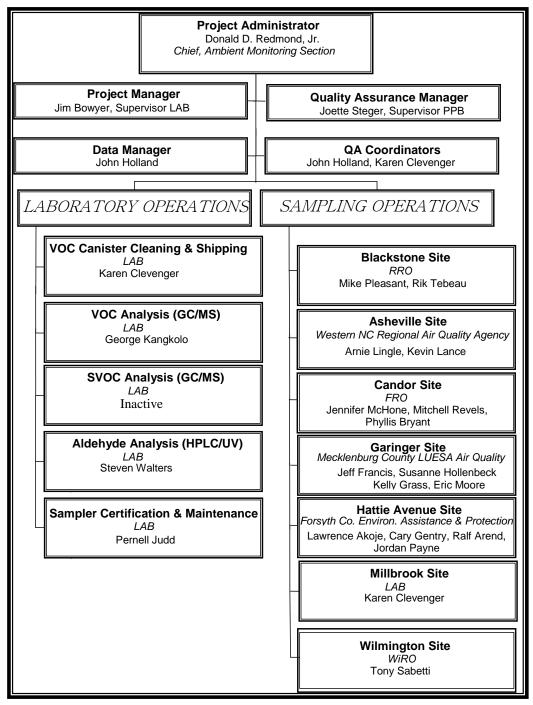


Table A-1. Roles of Key Project Personnel				
Position	Role			
Project Administrator	The Project Administrator has overall supervision of this project. The Project Manager and Quality Assurance Manager (QAM) report to the Administrator.			
Project Manager	The Project Manager is responsible for the establishment of the network sites as well as training all staff in site operation and sample handling. The Project Manager is also responsible for ensuring successful outcomes and managing all aspects of the study. Personnel from the NC Local Agencies receive direction and make all inquiries through the Project Manager. All staff except the QAM report to the Project Manager.			
Quality Assurance Manager	The QAM is responsible for coordinating, and assessing the effectiveness of the quality system for the project.			
Quality Assurance Coordinator	The QA Coordinator performs system and performance audits, data validation and data quality assessment.			
Field Site Operations	Field site operators are responsible for collecting and deploying samples and retrieving meteorological data, when necessary, at the various monitoring sites. The staff from designated local agencies operate the monitoring sites within the jurisdiction of their local programs.			
Laboratory Operations	Laboratory personnel are responsible for accomplishing all analytical work including sample analysis, QA checks, equipment maintenance and certification and sampling media preparations. Laboratory personnel are also responsible for providing supplies to the Field Operations staff.			
Data Manager	The Data Manager assists in the development of SOPs for data management and is responsible for data management of both the analytical and meteorological data. The Data Manager assists in the preparation of periodic reports including preparing data for submission to EPA's Air Quality System (AQS).			

# A.2 Project Description

In 1999, the EPA Office of Air Quality Planning and Standards (OAQPS) drafted an Air Toxics Monitoring Concept Paper<sup>4</sup> that was developed in concert with Regional monitoring staff and reflected comments from the State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution Control Officials. The paper described the air toxics program and the role of ambient monitoring and presented a strategic monitoring approach for establishing an air toxics monitoring network. The objectives of this network were stated as follows:

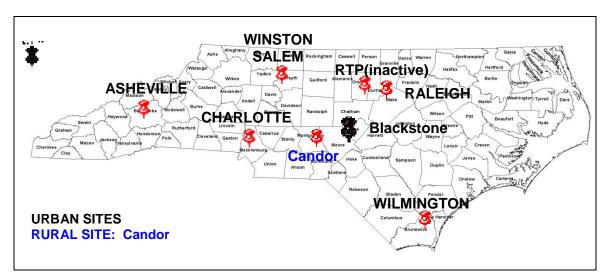
- 1. Measure pollutants of concern to the air toxics program.
- 2. Use scientifically sound monitoring protocols to ensure nationally consistent data of high quality.
- 3. Collect a sufficient amount of data to estimate annual average concentrations.
- 4. Complement existing national and State/local monitoring programs.
- 5. Reflect "community-oriented" urban population exposure.
- 6. Represent geographic variability in annual average ambient concentrations.

In July 2004, the EPA OAQPS drafted a document, "National Monitoring Strategy – Air Toxics Component,"<sup>5</sup> to provide a current status of the air toxics monitoring program and to provide direction for agencies participating in the national air toxics monitoring program. The document set forth a clear distinction between State and Local scale programs and the national trends-scale program. The State and Local scale monitoring programs provide a "flexible" approach to address a wide range of toxic air pollutant (TAP) issues:

"They are intended to probe potential problem areas throughout the nation that may require subsequent attention with respect to more dedicated monitoring and aggressive emission mitigation strategies. In some instances, these studies will be used to better characterize impacts of diesel emissions, or to define spatial concentration patterns throughout an area that simply is not achievable with a single [National Air Toxics Trends Site] NATTS site."<sup>4</sup>

The North Carolina UAT network (**Figure A-2**) was developed with these objectives in mind to focus on urban areas within the State and to work collaboratively with the three local government agencies that regulate air quality programs in their respective jurisdictions. The network complements the TAP programs of each agency and provides a "flexible approach" to address TAP issues in the local areas. The UAT network provides a framework to conduct more dedicated monitoring to characterize the spatial concentration patterns of specific TAPs within urban areas and to concentrate on problem areas.





The UAT network consists of seven currently operating monitoring sites. One of the original sites established in 1999, "RTP," was removed in November 2008 because the location was acquired for road expansion. These sites are located in six urban areas across the state and one rural site for comparison (**Figure A-2**).

Each monitoring site within the network contains equipment designed to collect 24-hour ambient air samples in SUMMA® canisters for VOC analysis via EPA Compendium Method TO-15<sup>8</sup>. Three of the sampling sites contain equipment designed to collect 24-hour ambient air samples on 2,4-dinitrophenylhydrazine (DNPH) cartridges for aldehyde analysis via EPA Compendium Method TO-11A<sup>9</sup>. The cleaning and certification of the SUMMA® sampling canisters, the analysis of samples for VOC and the analysis of cartridges for aldehydes are conducted at the LAB in Raleigh, NC.

#### A.3 Network Site Descriptions

Six sites selected for the North Carolina UAT network, were established in urban areas. The seventh site was established in a rural area. An "urban" area is defined by EPA<sup>6</sup> as a county with either a metropolitan statistical area (MSA) population of at least 250,000 or a county with at least 50% urbanization as defined by the US Census Bureau. A "rural" area is defined as a county that has less than 50% urbanization as designated by the US Census Bureau. **Table A-2** shows the population statistics for all of the MSAs in North Carolina based on the 2010 Census. **Table A-2** also provides population statistics for their respective urban counties and the population statistics of the "rural" site used to provide comparison monitoring data.

Metropolitan Statistical Area (MSA)	MSA Population <sup>a</sup>	County (monitoring site)	County <sup>a</sup> Population	County Area <sup>a</sup> (mi <sup>2</sup> )	County <sup>b</sup> Density (Pop/mi <sup>2</sup> )	% Urban <sup>a</sup>
Charlotte- Gastonia- Rock Hill, NC-SC	1,758,038	Mecklenburg (Charlotte-Garinger)	919,628	523.84	1756	99%
Raleigh-Cary	1,130,490	Wake (Raleigh-Millbrook)	900,993	835.22	1079	94%
Greensboro- High Point	723,801	Guilford	433,406	645.70	671	87%
Durham- Chapel Hill	504,357	Durham (RTP)	267,587	285.975	936	94%
Winston- Salem	477,717	Forsyth (Winston Salem-Hattie Ave.)	350,670	408.148	859	93%
Asheville	424,858	Buncombe (Asheville-AB Tech.)	238,318	656.67	363	76%
Hickory- Lenoir- Morganton	365,497	Catawba	154,358	398.72	387	70%
Fayetteville	366,383	Cumberland	319,431	652.315	490	87%
Wilmington	362,315	New Hanover (Wilmington- Battleship)	202,667	191.53	1058	98%
Sanford	57,866	Lee (Blackstone)	57,866	259.33	223	54%
Rural Comparison Site		Montgomery (Candor)	27,798	491.76	57	23%

Table A-2. Metropolitan Areas of North	Carolina
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<sup>a</sup> Source: US Census Bureau, 2010 Census

<sup>b</sup> County Population divided by County Area

**Table A-3** provides the location and EPA Air Quality System (AQS) identification for each site. The sites selected for Asheville, Winston-Salem and Charlotte are located in populated residential areas relatively close to their downtown business districts. The Raleigh Millbrook site is located in a North Raleigh suburb, a mixture of commercial and residential land uses 7 miles from downtown Raleigh. These four sites are on the premises of or near schools.

The Wilmington site is located near the USS North Carolina Battleship Memorial on the west side of the Cape Fear River on Eagle Island, directly across from the downtown area. Eagle Island is mostly wetland marshes located between the city and populated areas of eastern Brunswick County. There are industrial complexes to the north and west of the site and commercial loading docks located on the river to the north and south of the site.

The now-closed Research Triangle Park (RTP) site was a commercial area located in Durham County near the Wake County line about 5 miles west of the Raleigh-Durham International airport. This site was located at the center of the Raleigh-Durham-Chapel Hill combined statistical areas. The Raleigh-Millbrook site is approximately 18 miles east.

The Candor site is located on private property rented by U.S. EPA from the Perry family. It borders on the Uwharrie National Forest approximately 2 miles SW of Candor, NC. The Uwharrie Federal Game Lands are located to the SE and NW of the site.

The Blackstone site is located in an open field about 8 miles SW of Sanford, NC, in Lee County.

Site	County	Address	Latitude Longitude (in degrees)	Sampling* Conducted as of 1/1/14	AQS Site #
Asheville	Buncombe	AB Technical College Asheville, NC	35.572381 -82.558726	VOCs	37-021-0035
Hattie Avenue	Forsyth	1300 block of Hattie Ave. Winston-Salem, NC	36.110902 -80.224421	VOCs	37-067-0022
Garinger	Mecklenburg	Garinger High School 1130 Eastway Dr. Charlotte, NC	35.240106 -80.785654	VOCs	37-119-0041
Candor	Montgomery	112 Perry Drive Candor, NC	35.263125 -79.836653	VOCs, aldehydes	37-123-0001
Wilmington	New Hanover	USS North Carolina 1 Battleship Drive Wilmington, NC	34.235517 -77.955857	VOCs	37-129-0010
Millbrook	Wake	Millbrook Middle School 3801 Spring Forest Rd. Raleigh, NC	35.856226 -78.574095	VOCs, aldehydes	37-183-0014
RTP (inactive)	Durham	EPA Campus RTP, NC	35.892622 -78.876940	no sampling	37-063-0014
Blackstone	Lee	4110 Blackstone Dr. Sanford, NC	35.4325 -79.2887	VOCs, aldehydes	37-105-0002

#### Table A-3. Network Site Information

\*Sampling capabilities for each site may be expanded

# A.4 Background

#### A.4.1. Introduction

DAQ regulates 97 TAPs via North Carolina Administrative Code, and 187 hazardous air pollutants (HAPs) via federal Section 112(b) of the 1990 Clean Air Act Amendments (CAAA). Seventy-six TAPs are also HAPs. These pollutants have been associated with a wide variety of adverse health and ecosystem effects. These toxic/hazardous air pollutants are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these toxic air pollutants. While in some cases the public may be exposed to an individual pollutant, more typically people experience exposures to multiple pollutants and from many sources. Potential adverse exposures can result from breathing these pollutants, but exposure can also occur through other routes such as ingestion or skin absorption.

#### A.4.2 The Urban Air Toxics Strategy (UATS)

EPA published the final Integrated Urban Air Toxics Strategy (UATS) in the Federal Register on July 19, 1999<sup>7</sup>. The UATS states that emissions data are needed to quantify the sources of toxic air pollutants and aid in the development of control strategies, while ambient monitoring data are then needed to understand the behavior of pollutants in the atmosphere after they are emitted. Since ambient measurements cannot practically be made everywhere, estimates based on air dispersion modeling are needed to extrapolate and add to the understanding of the impacts to locations without monitors. Exposure assessments and health effects information are integrated to characterize risk--their potential impacts on people's health.

#### A.4.3 List of Pollutants

There are 33 HAPs identified in the UATS<sup>7</sup> as Urban HAPs. These are a subset of the 187 HAPs listed in Section 112(b) of the CAAA and were "judged to present the greatest threats to public health in the largest number of urban areas." A pilot study from 2001-02 'focused on 18 "core" HAPs, which were chosen for their representativeness, risk, and methods availability relative to ease and accuracy of measurement.'

Currently, the North Carolina UAT monitoring program provides sampling and analysis of toxic pollutants using the EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS)"<sup>8</sup> and EPA Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)."<sup>9</sup>

These methods provide for the identification and quantification of 12 of the 18 "core" HAP compounds, 32 other HAPs, and 31 TAPs. **Tables A-4** and **A-5** list the respective VOC and aldehyde compounds currently determined using these analytical methods. Verified data are reported to EPA using the AQS.

Compound Name	CAS	UATS Core	EPA HAP	NC TAP
Acetonitrile	75-05-8		X	
Acrolein	107-02-8	X	X	X
Benzene	71-43-2	X	X	X
Benzyl chloride	100-44-7		X	X
Bromodichloromethane	75-27-4			
Bromoform	75-25-2		X	
Bromomethane (methyl bromide)	74-83-9		X	
1,3-Butadiene	106-99-0	X	X	X
Carbon Disulfide	75-15-0		X	X
Carbon Tetrachloride	56-23-5	X	X	X
Chlorobenzene	108-90-7		X	X
Chlorodifluoromethane (CFC-22)	75-45-6			
Chloroethane (ethyl chloride)	75-00-3		X	
Chloroform	67-66-3	X	X	X
Chloromethane (methyl chloride)	74-87-3		X	
Cyclohexane	110-82-7			
Cyclopentane	287-92-3			
1,2-Dibromoethane (ethylene dibromide)	106-93-4		X	X
<i>m</i> -Dichlorobenzene	541-73-1			
<i>o</i> -Dichlorobenzene	95-50-1			
<i>p</i> -Dichlorobenzene	106-46-7		X	X
1,1-Dichloroethane (ethylidene chloride)	75-34-3		X	
1,2-Dichloroethane (ethylene dichloride)	107-06-2		X	X
1,1-Dichloroethene (vinylidene chloride)	75-35-4		X	X
1,2-Dichloroethene	540-59-0			
1,2-Dichloropropane (propylene dichloride)	78-87-5	X	X	
cis-1,3-Dichloropropene	10061-01-5 542-75-6		X	
trans-1,3-Dichloropropene	10061-02-6 542-75-6		X	
Dichlorodifluoromethane (CFC-12)	75-71-8			X
Dichlorotetrafluoroethane (CFC-114)	76-14-2			

# Table A-4. VOCs Determined using EPA Method TO-15

Compound Name	CAS	UATS Core	EPA HAP	NC TAP
1,4-Dioxane	123-91-1		X	X
Ethylbenzene	100-41-4		X	
Ethyl Propyl Ketone (3-hexanone)	589-38-8			
Hexane	110-54-3		X	X
Isobutene	115-11-7			
Isoprene	78-79-5			
Methacrolein	78-85-3			
Methylene Chloride	75-09-2	X	X	X
Methyl Butyl Ketone (2-hexanone)	591-78-6			
Methyl Ethyl Ketone (MEK)	78-93-3			X
Methyl Iodide	74-88-4		X	
Methyl Isobutyl Ketone	108-10-1		X	X
Methyl tert-Butyl Ether (MTBE)	1634-04-4		X	
Methyl Vinyl Ketone	78-94-4			
Pentane	109-66-0			
2-Pentanone (methyl propyl ketone)	107-87-9			
3-Pentanone (diethyl ketone)	96-22-0			
Propene	115-07-1			
Styrene	100-42-5		X	X
Toluene	108-88-3		X	X
1,1,2,2-Tetrachloroethane	79-34-5		X	X
Tetrachloroethylene (PCE)	127-18-4	X	X	X
1,2,4-Trichlorobenzene	120-82-1		X	
1,1,1-Trichloroethane (methyl chloroform)	71-55-6		X	X
1,1,2-Trichloroethane (vinyl trichloride)	79-00-5		X	
Trichloroethylene (TCE)	79-01-6	X	X	X
Trichlorofluoromethane (CFC-11)	75-69-4			X
Trichlorotrifluoroethane (CFC-113)	76-13-1			X
1,2,3-Trimethylbenzene	526-73-8			
1,2,4-Trimethylbenzene (pseudocumene)	95-63-6			
1,3,5-Trimethylbenzene (mesitylene)	108-67-8			
Vinyl Acetate	108-05-4		X	
Vinyl Chloride	75-01-4	X	X	X

Compound Name	CAS	UATS Core	EPA HAP	NC TAP
<i>m</i> -, <i>p</i> -Xylene	1330-20-7		X	X
m-Xylene	108-38-3			
p-Xylene	106-47-6			
o-Xylene	1330-20-7		X	X
	95-47-6			

# Table A-5. Aldehyde Compounds Determined using EPA Method TO-11A

Compound Name	CAS	UATS Core	EPA HAPs	NC TAPs
Acetaldehyde	75-07-0	X	X	X
Acrolein	107-02-8	X	X	X
Benzaldehyde	100-52-7			
Butyraldehyde/Isobutyraldehyde	123-72-8/78-84-2			
Crotonaldehyde	123-73-9			
2,5-Dimethylbenzaldehyde	5779-94-2			
Formaldehyde	50-00-0	X	X	X
Glutaraldehyde	111-30-8			
Hexaldehyde	66-25-1			
Isovaleraldehyde	590-86-3			
Methacrolein	78-85-3			
Methyl Ethyl Ketone	78-93-3			
Propionaldehyde	123-38-6		X	
Tolualdehydes (o-, m-, p)	977041-69-2			
Valeraldehyde	110-62-3			

#### A.5 Project Task/Description A.5.1 Description of Work

A goal of the UAT network is to measure and report verified toxic air pollutant monitoring data to AQS, which is a national database. This body of information can be accessed and used for a variety of purposes such as estimating annual pollutant concentrations, supplementing other state/local/national monitoring initiatives, reflect urban population exposures and evaluate geographic variability of pollutants.

The following sections summarize the field and laboratory activities for the network.

#### A.5.2 Procurement Activities

- All supplies, materials, and instrumentation shall meet or exceed the requirements as specified in the respective EPA method.
- Primary standards shall be traceable to the National Institute of Standards and Technology (NIST).
- Supplies and materials shall be maintained in sufficient quantities to allow sampling and analyses for at least one calendar quarter.
- Supplies and materials shall be stored as specified in the respective EPA method.
- Supplies and materials shall be "acceptance tested" on receipt from provider. Details shall be written in standard operating procedures (SOPs) for specific methods.
- Supplies and materials that do not meet these specifications will be returned to the vendor.

# A.5.3 Field Activities

Field activities for the UAT program include setting up the equipment to collect 24-hour samples, shipping and receiving materials, and field observations which typically includes three phases:

# **Pre-Sampling**

- Preparing samplers, data loggers and associated media.
- Transporting the samplers, data loggers and media to the monitoring sites.
- Installing and testing samplers and data loggers at the site.
- Receiving the prepared media from the laboratory.
- Performing equipment maintenance.
- Storing media prior to field use.

#### Sampling

- Making in-field pressure measurements prior to sample collection.
- Verifying flow rates and leak checks.
- Performing equipment maintenance.
- Observing and documenting any conditions that could affect the sample.
- Performing quality assurance/quality control (QA/QC) activities as specified in the SOP.

# **Post-Sampling**

- Verifying sampling completion (pressure, volume and/or elapsed time).
- Packaging and shipping the sampled media to the laboratory.
- Downloading data from field instruments and data loggers.
- Performing QA/QC activities as specified in the SOP.

# A.5.4 Laboratory Activities

Laboratory activities for the UAT program include the analysis of samples and preparing the media and equipment for field sampling, which includes three general phases:

#### **Pre-Sampling**

- Receiving, preparing, and storing all sampling media and instruments at the laboratory.
- Maintaining analytical equipment at specified environmental conditions.
- Performing equipment maintenance and calibrations.
- Performing QA/QC activities as specified in the SOP.

#### Shipping/Receiving

- Shipping and receiving media to and from the field and documenting this information.
- Shipping and receiving sensors, parts and data loggers to/from manufacturers for calibration and repairs.
- Storing media for analysis.
- Performing QA/QC activities as specified in the SOP.

#### **Post-Sampling**

- Receiving and checking media integrity.
- Storing sampling media prior to analysis.
- Preparing sampling media as appropriate for the particular media for analysis.
- Analyzing samples by the respective methodology.
- Performing QA/QC activities as specified in the SOP.

#### A.5.5 Project Assessment Techniques

An assessment is an evaluation process used to measure the performance or effectiveness of a system and its elements. As used here, assessment is an all-inclusive term used to denote any of the following.

- Performance evaluation (PE) or proficiency test (PT). See Section C.1.3.
- Field and laboratory systems audits (EPA conducts every three years; internal conducted every other year at each site).
- Management system audits conducted by DENR Quality Assurance Manager (QAM)
- Quarterly QA review of data and procedures.
- Peer review, inspection, or surveillance.

#### A.5.6 Schedule of Activities

The following table (**Table A-6**) reflects the status of the program effective July 2013. Feedback from the local programs and other stakeholders will initiate improvements to the program.

Activity	Target Completion Date
Network Development	Complete
Site Setup	Complete
Sampler Order	Complete
Personnel Requirements	Ongoing
QAPP	Reviewed at least Annually
Final Network Design	Complete
Samplers Arrival	Complete
Sampler Siting	Complete
Routine Sampling	Ongoing
Sample Analysis	Ongoing
Data Validation	Ongoing
Data Assessment	Ongoing
Interim Reporting of Data to Local Programs	Within 90 days after each Quarter
AQS Submittals	Within 90 days after each Quarter
Final Report	Annually

### Table A-6 Schedule of Activities

#### A.5.7 Project Records

The Laboratory Analysis Branch's Quality Assurance Manual establishes procedures for the timely preparation, review, approval, issuance, use, control, revision and maintenance of documents and records.

#### A.6 Data Quality Objectives

The data quality objective (DQO) process described in EPA's QA/G-4<sup>10</sup> and QA/G-9<sup>11</sup> guidance documents provide a general framework for ensuring that the data collected meets the needs of the intended decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality and quantity needed to meet a program's goals. The goals of the UAT monitoring program are as follows:

- > To determine and characterize ambient concentrations of specific air pollutants in representative monitoring areas.
- To analyze data (including trend analysis) and evaluate the effectiveness of pollution programs.

The UAT program has the following data quality objectives:

- **Data Comparability:** The methods and procedures used in this program should be consistent with existing national, State, and local monitoring programs. This is accomplished by following standard methods asdetailed in Sections B.3 through B.8.
- **Method Sensitivity:** Methods used to characterize air pollutants should have the sensitivity to monitor at concentrations likely to be of health and/or regulatory concern if

at all possible. Sensitivity is tracked by determining method detection limits; these are discussed in Section A.7 below.

- **Representativeness:** Except for the rural site, the monitoring site locations should be reflective of urban population exposure to estimate long-term population risk. The details documenting site locations as "urban" are listed in Section A.3 above.
- **Sampling Frequency:** The appropriate sample collection frequency and length of sampling time should be sufficient to characterize long-term exposure and trends. The current 24-hour sample every six days is sufficient to estimate annual average concentrations if the data completeness MQO, see below, is met.

# A.7 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) have been developed by EPA for the national Air Toxics Monitoring Program. MQOs are designed to evaluate and control various phases (sampling and analysis) of the measurement process to ensure that the total measurement uncertainty is within the range prescribed by the DQOs. MQOs can be defined in terms of the following data quality indicators: <sup>12</sup>

• **Precision** – a measure of mutual agreement among individual measurements of the same property using prescribed similar conditions. The coefficient of variation (CV) is used as an estimator of precision. The CV values will be computed according to the equation below. It is the same form as the CV equation found in the NATTS Network Assessment draft report.

$$CV = \sqrt{\frac{\sum_{i=1}^{n} \left[\frac{(p-r)}{0.5 * (p+r)}\right]^{2}}{2n}} LCL = CV * \sqrt{\frac{n}{X^{-1}(0.05,n)}} UCL = CV * \sqrt{\frac{n}{X^{-1}(0.95,n)}}$$

Where:

p = primary data r = replicate, repeated or collocated data n = # of pairs  $X^{-1} = inverse of the one-tailed probability of the chi-squared distribution$ LCL = lower control limitUCL = upper control limit

Also computed are the arithmetic mean and median difference and % differences. These tend to be lower than the CV values. They are presented because they are easier to compute and to visualize in terms of the actual measurements. The difference data are in ppb, the units of the lab's measurement.

mean difference = 
$$\left[\sum(p-r)\right] / n$$
 mean % difference =  $100 * \sum_{i=1}^{n} \left[\frac{(p-r)}{0.5 * (p+r)}\right] / n$ 

• **Bias** – the distortion of a measurement process which causes error in one direction. Bias is determined by estimating the positive or negative deviation from the true value and can be expressed as a percentage of the true value.

- Accuracy a term frequently used to represent closeness to "truth".
- **Completeness** a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained.
- **Method Detection Limit (MDL)** the lowest concentration level that can be determined to be statistically different from a blank with 99% confidence

While the UAT quality assurance program strives to optimize data quality, acceptance criteria for measurement quality are:

- Precision not to exceed 20% CV as measured by collocated samples and 15% as measured by repeated analyses of samples on different days or different instruments
- Accuracy 70% of compounds tested from Tables A-4 and A-5 should be within 20% on internal and external performance tests such as the NATTS performance tests twice per year. See also Section C.1.3.
- Completeness greater than 85% valid data submitted to AQS
- MDLs as low as practical, but measured at least annually according to EPA NATTS TAD<sup>13</sup> and at least 70% of compounds in Table A-4 have a MDL at or below 0.05 ppbv and 70% of compounds in Table A-5 have a MDL at or below 0.02 μg/mL

#### A.8 Training Requirements

#### A.8.1 Field and Laboratory Operations

All field personnel and laboratory personnel will have completed all required training. The following are required before working on data generating projects:

Reading this document and the LAB QA Manual Reading all SOPs specific to their assigned duties Receiving on-the-job training from experienced personnel

#### A.8.2 Air Monitoring Training

No specific ambient air monitoring or quality assurance coursework or degree is required. However, only personnel who have completed appropriate instructional coursework or have equivalent, relevant experience are hired. Appropriate courses include chemistry, physics, laboratory safety, mathematics, statistics and electronics. Personnel are encouraged to attend relevant training classes. Organizations offering specialized courses on air monitoring and quality assurance topics include:

- EPA's Air Pollution Training Institute (APTI) http://www.epa.gov/apti
- Air & Waste Management Association (AWMA) http://awma.org/education
- American Society for Quality (ASQ) http://asq.org/learninginstitute/index.html

#### A.9 Documentation and Records

Any record that describes, defines, specifies, reports, certifies, or provides data or results pertaining to the study must be retained in accordance with NC DAQ records retention schedules. The Project Manager is responsible for securing all project records until project completion. Examples include:

- QA Project Plans
- Network description and site characterization files
- Standard Operating Procedures
- Field and laboratory notebooks
- Sample handling/custody records
- Inspection/maintenance records
- Original data (sample and QA data)
- Electronic data files including email
- System and performance audit reports
- Periodic and Final reports

# **B.** Sampling System, Analytical Measurement and Data Acquisition

#### **B.1** Sampling System Design

The sampling system design includes the experimental design of the study, information on the type of samples collected, sampling frequency, sampling period, and sample site locations. The two components of the field operations are the ambient air sampling and the meteorological data collection (Table B-1). The sampling design for both components is discussed in this section.

Parameter	Equipment	Sampling Frequency		
Wind speed (WS)	Anemometer	Meteorological data is averaged and recorded at 15 minute and 1 hour intervals by an on-site data logger.		
Wind direction (WD)	Wind vane			
Temperature (T)	RH/Temperature probe			
Relative Humidity	RH/Temperature probe			

Table B-1.	<b>Meteorological Data</b>	Collected
	nieveoi ologicui zuvu	concerea

All sampling, monitoring and analytical instruments used for this program are vendor supplied and were designed specifically for their prescribed use. The equipment meets the design and the specifications described in the EPA compendium methods<sup>8,9</sup> and EPA's Technical Assistance Document.<sup>13</sup>

#### **B.1.1 Ambient Air Monitoring Sampling Systems**

Each monitoring site is equipped with a XonTech 911A air sampler for VOCs. The VOC sampler is designed to collect a 24-hour sample collected midnight to midnight local time in a 6-Liter polished stainless steel SUMMA<sup>®</sup> canister. The sampling schedule will follow the 6-day schedule established for the criteria pollutant monitoring program. That schedule yields approximately 60 samples per year for each site.

Three monitoring sites are equipped with ATEC 2200 cartridge air samplers for aldehydes. The ATEC sampler is designed to pump air through an adsorbent cartridge coated with DNPH to collect a 24-hour time-integrated sample. The sampler is programmed to collect a sample midnight to midnight local time. The sampling schedule will follow the 6-day schedule established for the criteria pollutant monitoring program. That schedule yields approximately 60 samples per year for each site. For each sampling site, 1 field blank sample will be collected at least every three months. A collocated sample will be collected on a rotating basis.

#### **B.1.2 Meteorological Sampling System**

A 10-meter meteorological tower is installed at each air monitoring location, and wind measuring equipment placed at 10 meters on the tower. A temperature and humidity sensor is mounted approximately 2-5 meters from the ground at each site. Outputs from these sensors are fed to a data logger for storage and averaging.

#### **B.2 UAT Measurement System Siting**

The siting criteria for the network monitoring sites are based on the guidance given in the "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume 4" <sup>14</sup> and 40 CFR Part 58, Appendices D and E<sup>15</sup> and incorporate the following specifications for the ambient monitoring sites.

- The distance between a possible obstruction and the monitor will be at least twice the height of the obstruction.
- The monitors will be placed at least 10 meters from the tree drip-line.
- The monitors will be placed such that there is an arc of at least 270° of unrestricted airflow around the site.
- The distance between roadways and the sampler probe inlet will be at least 10 to 30 meters, depending on the number lanes and the volume of traffic.
- The inlet to the gas sampling system will be between 2 and 7 meters above ground level and at least 1 meter vertically or horizontally away from the supporting structure.
- Probe and sample line material will be stainless steel or borosilicate glass and kept as short as possible.
- Wind speed and wind direction sensors will be located 10 meters above ground level, at least 10 times the height of the nearest obstruction distant from that obstruction, and over grass or gravel.
- Temperature and humidity sensors will be located 2 to 5 meters above ground and 1.5 times the diameter of the tower away from the tower.

Where possible the sampling sites were established in accordance with the above criteria. The following figures (**Figures B-1 through B-8**) provide an aerial photo and four ground photos of the sites facing North, South, East, and West. The aerial photos are provided for greater understanding of the overall clearance around each site.

**Figure B-1**. The Asheville site is located on the campus of the Asheville-Buncombe Technical Community College on Victoria Road about 2 miles south of downtown Asheville, NC. The site is about 300 meters NE of the railroad tracks that are visible in the lower left corner of the aerial photo. The railroad tracks run along the east side of the French Broad River. The site is located on a hill approximately 37 meters higher than the railroad and has approximately 290° of unrestricted airflow. The height of the trees to the NE of the site is less than 2 times the distance to the trees from the site.

**Figure B-2**. The Hattie Avenue site is approximately 1 mile NE of downtown Winston-Salem. The site is in an open field to the north of a preschool/daycare which closed in October 2009. The area around the site is flat and open. There is a line of trees to the west of the site, however the distance between these potential obstructions and the site meet the siting criteria. The site has approximately 290° of unrestricted.

**Figure B-3**. The Garinger site is located to the side of a baseball field west of Garinger High School. The school is located about 2 miles NE of downtown Charlotte. There are no trees within 50 meters, and the site has approximately 360° of unrestricted airflow.

**Figure B-4**. The Candor site is located on private property rented by U.S. EPA from the Perry family. It borders on the Uwharrie National Forest approximately 2 miles SW of Candor, NC. The Uwharrie Federal Game Lands are located to the SE and NW of the site. The site is in a field about 100 meters from the nearest tree line. An EPA CASTNET site CND125 is located approximately 25 meters to the SW of the site building. The site has approximately 360° of unrestricted airflow.

**Figure B-5**. The Millbrook site is located to the east of Millbrook Middle School in Raleigh, NC. It is situated between the parking lot and the parking lot of a daycare center and is directly across Spring Forest Road from a number of large apartment complexes. The area is approximately 6 miles north of the downtown Raleigh. The site is approximately 1 mile south of the intersection of I-540 and US 1. There are no trees around the site with the exception of a small tree approximately 30 meters away. The distance from the sampling port to the edge of Spring Forest Road is approximately 43 meters. The distance from the sampling port to driveway into the school parking lot west of the site is approximately 25 meters. Traffic into the school parking lot is heavy for approximately 20 minutes in the morning and afternoon during school days. The site has approximately 360° of unrestricted airflow.

**Figure B-6**. The Wilmington site is at the USS North Carolina Memorial on the west side of the Cape Fear River from downtown Wilmington, NC, on Eagle Island. There are tall grasses approximately 100 meters to the west of the site. The site is in an area used for the storage of materials approximately 50 meters SW of a small maintenance building. The site building is approximately 20 meters from a storage container and there is an anti-aircraft gun that is located about 11 meters from the SW corner of the site building (visible in the photos). The gun is approximately 2 meters tall and is below the 3 meter level of the sampling port located approximately 12 meters away. The site has approximately 290° of unrestricted airflow.

**Figure B-7(inactive site)**. The RTP site was located on the north end of the EPA RTP campus near the intersection NC 54 and T.W. Alexander Drive. It was approximately 800 meters south of the intersection of I-40 and the Durham Freeway and approximately 300 meters southeast of the intersection of T.W. Alexander Dr. and the Durham Freeway. There were trees to the east of the site, however the distance between these potential obstructions and the site met the siting criteria. The site had at least 270° clearance around the site.

**Figure B-8**. The Blackstone site is located in an open field about 8 miles SW of Sanford, NC, in Lee County.

# Figure B-1: Photos of Asheville Site

Aerial View of AB Tech Community College taken on 10/20/2010 © Google 2011



The site is approx. 10 meters lower than the <sup>1</sup>/<sub>4</sub> pie-shaped parking lot and approx. 15 meters higher than the maintenance building to the NW.



Asheville Site facing West



Asheville Site facing East



Asheville Site facing South



# Figure B-2 Photos of Winston-Salem Hattie Avenue Site



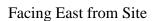
Aerial View of Hattie Avenue taken on 7/6/2010 © Google 2011

The height of the tallest trees to the west of the site is less than 2 times the distance to the trees.

Facing North from Site



Facing South from Site





Facing West from Site





# Figure B-3 Photos of Charlotte Garinger Site



Aerial View of Garinger High School Site © Google 2013

Site facing North

Site facing East



Site facing West

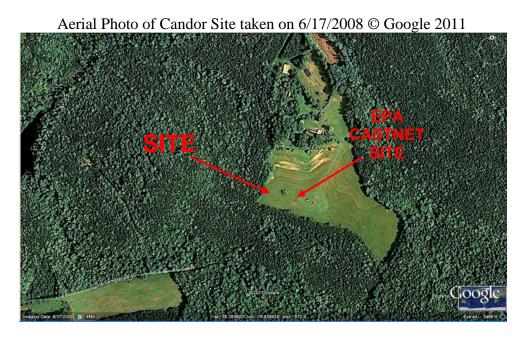




Site facing South



# Figure B-4 Photos of Candor Site



Candor Site facing North

Candor Site facing East





Candor Site facing West



Candor Site facing South



# Figure B-5 Photos of Raleigh Millbrook Site



Aerial Photo of Millbrook Middle School taken on 7/5/2010 © Google 2013

Distance from the sampling port to the edge of Spring Forest Road is approximately 43 meters.

Millbrook Site facing North



Millbrook Site facing West



Millbrook Site facing East



Millbrook Site facing South



# Figure B-6 Photos of Wilmington Site



Aerial View of Wilmington taken on 10/22/2010 © Google 2011

Site facing North

Site facing East











# Figure B-7 Photos of RTP Site (inactive)



USGS Aerial Photo of RTP Site taken on 3/28/2002

The height of the tallest trees to the east of the site is less than 2 times the distance to the trees. Site facing North Site facing East



Site facing West

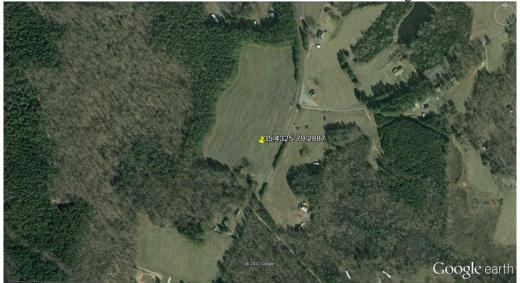


Site facing South





# Figure B-8 Photos of Blackstone Site



Aerial View of Blackstone taken on 1/31/2006 © Google 2013

The height of the tallest trees to the southwest of the site is less than 2 times the distance to the trees. Site facing North Site facing East



Site facing West







#### **B.3** Sampling Methods Requirements

Sampling is accomplished in agreement with the following EPA compendium method:

- EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometry"<sup>8</sup>
- EPA Compendium Method TO-11a, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography"<sup>9</sup>

#### **B.4 Sample Handling and Custody Requirements**

#### **B.4.1** Chain of Custody

Chain of custody (COC) refers to tracking the sampling media from the time the media are sent to the field until collected samples are analyzed and validated. Strict chain of custody documentation is required for each transfer to insure the integrity of the sample. A sample with a broken or missing COC seal could have been tampered with and will be appropriately documented as such and not analyzed; an exception may be made if a sample is brought immediately from the site to the lab by the site operator.

The COC also documents the amount of time between sample collection and analysis (holding time). Canister samples are to be analyzed within a 30-day holding time. Samples with a holding time of 31 to 35 days are analyzed but flagged as past holding time. Samples with holding times longer than 35 days are not analyzed. DNPH-cartridge samples are to be extracted within 14 days and analyzed within 30 days after extraction.

#### **B.4.2 VOC Sample Handling Requirements**

VOC samples are labeled to indicate the site location, the sampling date, and starting and ending canister pressures. The VOC Chain of custody form (Appendix) also serves as a sample information sheet that documents:

- Canister serial number
- Certification Batch of the canister
- The Sample Shipment Information
- Vacuum check prior to shipment
- ♦ Set-up Information
- Sample Date and Information
- Starting and final canister pressures
- COC Information

Upon receipt in the laboratory, the sample is logged in and assigned a unique laboratory identification number traceable to the field site, sample date, canister certification batch, and the resulting analytical raw data files.

#### **B.4.3** Aldehyde Sample Handling Requirements

Sampled DNPH cartridges will be placed in the sample envelope provided by the vendor for the samples. The envelopes will be labeled to indicate the site location, the sampling date, and sample volume. The DNPH cartridges are stored refrigerated and are transferred or shipped to the lab on cold packs. Sampled cartridges are stored refrigerated until extracted. Extracts are stored refrigerated until analyzed. The Aldehyde Sample Information Sheet form (Appendix) includes:

- Cartridge Lot Number
- Set-up Information
- Sample Date and Information
- The Sample Shipment Information
- Average flow rate during sampling
- Final sample volume
- COC Information

Upon receipt in the laboratory, the sample will be logged in and assigned a unique laboratory identification number traceable to the field site, sample date, DNPH cartridge lot, and the resulting analytical raw data files.

#### **B.5** Analytical Methods Requirements

Analysis is accomplished in agreement with the same EPA compendium methods specified in B.3 above.

#### **B.6 Quality Control Requirements**

#### **B.6.1** Air Sampling Systems

#### Collocated Sampling

Collocated samples are collected to estimate precision. Collocated sampling is conducted at least at one selected site at a time, and that site will be rotated so that each site has collocated sampling once every 18 months or less.

#### Blanks

Because the VOC sample is collected into an evacuated canister, the collection of a blank is not possible. One VOC canister is filled with zero air and analyzed following each cleaning batch to certify the batch as clean, and one canister is filled with zero air through a sampler following its cleaning to certify the sampler as clean. In addition when any canister fails to collect a sample in the field for any reason, that canister is returned to the lab, filled with zero air and analyzed as a field blank. Field blanks will be collected with the aldehyde samples. A schedule for collecting blanks has been prepared consistent with the national program. For each sampling site, 1 field blank sample will be collected at least every three months.

#### **B.6.2** Meteorological System

Recommended system accuracy for the meteorological sensors is shown in **Table B-2**. Also shown in the table are measurement resolutions, which are defined as the smallest parameter measurement that can be distinguished. All recommendations in the table are from the *On-Site Meteorological Program Guidance for Regulatory Modeling Applications*.<sup>16</sup> Assurance of parameter accuracy will be determined approximately 6 months after installation of recently calibrated equipment through Collocated Transfer System<sup>14</sup> (CTS) performance audits of the meteorological equipment or independent audits. Annually the equipment will be returned to the manufacture for calibration. Data loggers will be returned to the manufacturer for calibration every two years. This calibration method and schedule meets the requirements for Photochemical Assessment Monitoring Stations (PAMS) sites given in EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements, Version 2.0 (Final)<sup>14</sup>.

 Table B-2. System Accuracies and Resolutions for Meteorological Parameters

Meteorological Variable	System Accuracy	Measurement Resolution
Wind Speed	$\pm$ (0.2 m/s + 5% of observed)	0.1 m/s or 0.2 mph
	$\pm$ (0.45 mph + 5% of observed)	
Wind Direction	$\pm 5$ degrees	1 degree
Ambient Temperature	$\pm 1^{\circ}$ C or $1.8^{\circ}$ F	0.1 °C or 0.2 °F
Vertical Temperature Difference,	± 0.1 °C or 0.2 °F	0.02 °C or 0.04 °F
if deployed		
Relative Humidity / Dew Point	± 10 % / ±3°C	0.5 % / 0.1 °C
Barometric Pressure	±3 hPa*	0.5 hPa*

\*1 hPa = 1 hectopascal = 1 millibar = 0.75 mm Hg

#### **B.6.3** Analytical Data

**Table B-3** lists the quality assurance parameters for the GC/MS data that are to be used in the project. The criteria in the table are derived from Compendium Method TO-15. "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometry"<sup>8</sup>

LAB Flag	Parameter	Criteria	Corrective Action	AQS Code
1	Daily BFB tune*	See Table B-5	Samples should not be run until passes (Sample runs voided if not passing)	n/a
2	Daily Zero Air	All target compounds	Flag failing compounds. If >8 compounds, then	AT
	(Blank)	<0.2ppb	samples should not be run	or 7
3a	Calibration	>0.99	Samples should not be run until passes (Failing	AT
	Curve r <sup>2</sup>		compounds marked as "estimate")	or 7
3b	Calibration	within window	If outside window, calibration will show compound	AT
	Curve RT		missing and will not calibrate for this compound	
3c	Calibration	≥35%	Flag each sample run under this calibration curve in	AT
	Curve %RSD		the database. (Only the failing compounds)	
3c1	Calibration	31-34%	Flag each sample run under this calibration curve in	LJ
	Curve %RSD		the database. (Only the failing compounds)	
3d	Calibration	Compound not found	Flag compound if found in later chromatograms	AT
	Curve			
4	Daily Calibration	<30% difference from	All values for the samples run on this day is marked	AT
	Check	initial calibration	as "estimate" if $\geq 30\%$ .	or 7
5	Replicate	Differs by >20%	Flag all values for each failing compound	n/a
	analysis	-		
	Values <lql< td=""><td></td><td>Flag all values below LQL.</td><td>7</td></lql<>		Flag all values below LQL.	7
6a	Sample hold time	31-35 days	All values marked as "estimate"	LJ
бb	Sample hold time	>35 days	No values reported	TS

## Table B-3 GC/MS QC Parameters and Corrective Action Limits

\*GC/MS performance acceptance test when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

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**Table B-4** lists the quality assurance parameters for the HPLC data that are to be used in the project. The criteria in the table are derived from Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography"<sup>9</sup>

LAB Flag	Parameter	Criteria	Corrective Action	AQS Code
2a	Blank Cartridge analysis	Formaldehyde <0.15µg/cartridge Acetaldehyde <0.10µg/cartridge < 0.30 µg/cartridge Acetone < 0.10 µg/cartridge all others	There should be $\leq 3$ compounds flagged 2a or the batch fails.	MB
2b	Field Blank	All target compounds must be $\leq$ 0.06 µg/mL to pass	There should be $\leq 3$ compounds flagged 2b or the batch fails.	MB
3a	Calibration Curve QA	Correlation Coefficient r <sup>2</sup> >0.999 in order to pass	If $r^2 < 0.999$ , the compound fails and is flagged	AT
3b	Calibration Curve QA	Offset $\leq 0.01 \text{AU*min}$	There should be $\leq 3$ compounds flagged 3b or the batch fails.	AT
3c	Calibration Curve QA	%RSD on Calibration <20%	If %RSD>20%, compound fails and is flagged.	AT
3d	Calibration Curve QA	Compound not found in calibration mixture	If compound is not identified in the calibration curve it is flagged.	AT
4	Daily Calibration Check	Check standard is <20% of the calibrations curve expected value.	Compare to calibration "expected" value. If difference >20%, compound fails and is flagged.	AT
5	Replicate analysis	Absolute Relative % difference of two analyses	If difference >20%, compound fails & is flagged	AS
ба	Cartridge past hold time limit	>14 days after sampling date	If cartridges are >14 days without being extracted, they are flagged 6a.	TS
6b	Extract past hold time limit	>30 days after extraction date (or 44 days from sampling date)	If the extract has gone over 30 days (or 44 days after sampling date) it is flagged 6b and not analyzed.	TS

Table B-4 HPLC QC Parameters and Corrective Action Limits

#### **B.7** Instrument and Equipment Testing, Inspection, & Maintenance Requirements

#### **B.7.1** Ambient Air Monitoring Sampling Systems

The field operator will perform preventive maintenance on the air sampling system. SOPs describe the preventive maintenance that will be followed throughout the study. They include the following:

- Leak checking prior to every sampling event
- Flow checking checked quarterly or as needed

- Inspecting the sample train inspected weekly and inlet cleaned as needed
- Conducting grounds maintenance and housekeeping activities at monitoring sites
- Checking shelter temperature/humidity.

#### **B.7.2** Meteorological Equipment

Each week the field operator will conduct a visual inspection of the meteorological equipment and note any problems in the field logbook. In addition the time and date, the general condition of the meteorological equipment, any QA/QC and maintenance activities taken, and other pertinent information will be included.

#### **B.7.3** Analytical Instruments

The performance of the laboratory equipment used in the analysis will be monitored and documented in the appropriate equipment logbooks. SOPs describe the preventive maintenance procedures to be followed.

Prior to sample analysis, an air/water check and BFB tune check will be conducted to verify the performance of the mass spectrometer. The acceptance criteria for the BFB tune check are listed in Table B-5. These are recommended by the instrument manufacturer and are more stringent than those established in the EPA Compendium Method TO-15.<sup>8</sup>

m/z	Abundance
50	15 – 40% of 95 intensity
75	30 – 80% of 95 intensity
95	Base peak, assigned 100%
96	5-9% of 95 intensity
173	<2% of 174 intensity
174	>50% of 95 intensity
175	5-9% of 174 intensity
176	>95 and < 101% of 174 intensity
177	5 – 9% of 176 intensity

 Table B-5. Tune Acceptable Limits

#### **B.8 Instrument Calibration and Frequency**

#### **B.8.1 Field Equipment**

Since an incorrect flow rate can compromise data quality, the field operator will leak-check the sampling system and will check the flow rate quarterly (see B.7.1). An initial leak-check will be performed prior to each sampling event. They will follow steps outlined in standard operating procedures and instrument manuals.

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#### **B.8.2** Meteorological Equipment

Meteorological equipment is calibrated by the manufacturer prior to installation. If an audit of the equipment reveals that the equipment is outside of calibration limits (see Table B.2), then the equipment will be removed from the field and returned to the manufacturer for recalibration. It will be replaced with equipment that is calibrated.

#### **B.8.3** Analytical Instruments

Analytical procedures are standardized in that the detector responses of unknown samples are compared to those of known standards. The instrument does not perform a direct measurement and, in this sense, does not require calibration. However, standardization procedures included in Method TO-15 and Method TO-11A will be followed, and the analyst will ensure that the QC performance criteria for the GC/MS system as specified in **Table B-3** are met. Any calibration steps outlined in standard operating procedures and instrument manuals will be performed.

#### **B.9** Inspection and Acceptance Requirements for Consumables

A zero air sample (laboratory blank) will be analyzed with each sample run to insure that zero air meets method specifications. The control limits for the zero air samples are included in **Table B-3**.

Cylinders of NIST-traceable gas standards will be used to prepare canisters of working standards. New standard cylinders will be verified by analyzing a working standard prepared from the new cylinder with a previous standard calibration.

Each new lot of DNPH cartridges will have three randomly selected cartridges tested before the lot is used for sampling. Criteria are listed in **Table B-4**. Similarly, each new lot of solvents will be analyzed before the lot is used for extraction or analysis of samples.

#### **B.10 Data Management**

The data management program involves collecting, entering, transferring, verifying, validating, summarizing, and reporting the data generated in this program. These data include descriptive and historical information about each site (e.g. log books, worksheets, etc.), all analytical and meteorological data, and summaries and reports about the study. Each quarter, the Data Manager will present validated, quality-coded analytical data to the local programs. All data will be submitted to AQS and electronically archived on the DAQ server.

## C. Assessment and Oversight

#### C.1 Assessments and Response Action

#### C.1.1 Field Equipment

Audits of the field equipment are imperative to insure proper sampler operation. At least once each year LAB personnel will visit all sampling sites in order to verify that sampling equipment is operating properly. Pressure readings from the VOC sampler are checked before and after each sample. A leak check and flow check are recorded for each aldehyde sample. If the VOC final pressure is not consistent with past performance the flow is adjusted or the LAB is informed. All VOC flow checks will be documented in the site logbook and all regular leak, flow and pressure checks are recorded on the COC forms (See Appendix). If any field equipment fails, it will be replaced with recently certified/calibrated equipment.

#### **C.1.2 Meteorological Equipment**

Prior to installation at a monitoring site, any previously used meteorological equipment will be returned to the manufacturer for recalibration and any necessary repair and will be installed within 6 months of recalibration. New meteorological equipment purchased for this project will be received calibrated by the manufacturer and will be installed within 6 months of calibration.

#### **C.1.3 Laboratory Operations**

All data are reviewed by the analyst (or analytical team) at the time of acquisition. Any data not meeting the QC criteria set forth in the established SOPs will require that the analysis be repeated if possible. All data reports will be reviewed for completeness and accuracy, including any electronic data collected. Preliminary results will be reported to the Project Manager.

The completed data package for an analysis batch will undergo an audit conducted by the Quality Assurance Manager and/or the Quality Assurance Coordinator. The data will be reviewed along with any pertinent methods and SOPs. This audit will include an assessment of the overall conduct of the laboratory portion of the study. The Quality Assurance Manager or designee will conduct internal performance tests at least once each year and schedule an external performance test twice per year if available and resources are not constrained. Any findings or concerns from the tests will be addressed to the Project Manager and included in the audit reports.

#### C.1.4 Data Management

The Quality Assurance Manager or designee audits the data management system at least quarterly. Auditing involves comparing the processed meteorological and analytical data with the raw data obtained from the field and laboratory to ensure that the data are being processed correctly according to established SOPs.

#### C.2 Reports to Management

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The Quality Assurance Manager summarizes the results of all audits into audit reports. The reports are distributed to the Local Programs, NC DAQ personnel, and other appropriate persons. The Quality Assurance Manager prepares an annual report.

# **D.** Data Validation and Usability

### D.1 Data Review, Validation, and Verification Requirements

All analytical and meteorological data are reviewed by the Project Manager, the Quality Assurance Manager, and the Project Administrator to determine if these data meet the QAPP objectives. Decisions to reject or qualify data are made by the Project Manager and the Quality Assurance Manager. Quarterly, the Data Manager electronically posts the validated, quality-coded meteorological and analytical data for DAQ personnel and other appropriate persons and distributes it to the Local Programs and others as appropriate. All personnel involved in the study have the opportunity to review these data before they are incorporated into the final report. Due to the nature of the network program, a final study report date is not known.

#### **D.2 Validation and Verification Methods**

#### Verification

The Laboratory Analyst and Shipping and Receiving personnel electronically back up all data that are obtained from the field and the laboratory. These backup copies will be maintained until the data are transferred to the network and verified. Verification entails a review to ensure that all the data for the collection period are accounted for. The verified, raw data will be maintained on the dedicated computer throughout the study period, as long as deemed necessary by the Program Administrator.

#### Validation

The purpose of data validation is to detect any data value that may not represent actual air quality conditions at the sampling locations. Both the meteorological data and the analytical data will be validated to ensure that the quality goals of the study are met.

#### **D.3** Reconciliation with User Requirements

As needed or at least annually, determinations of precision, completeness, and accuracy will be performed to verify data quality objectives are met. If data quality indicators do not meet the project specifications, then a corrective action plan will be developed and implemented.

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# APPENDIX

#### VOCs Chain of Custody Form 2013-2014

#### Air Toxics Analytical Support Team Summa Canister Chain of Custody

ale	3 Reedy Cre eigh, NC 27		a				ATAST Investigation #:				
	) 733-9777		19) 715-0	890			Investigation/Study Site	:			
							Pre-Sample				
U NO.	Sa	mple IC			Vacuum, es Hg		DC Sealed By/Date &	coc	COC Bro		
Can	Canister #	Batch #	ATAST ID #	Lab Reading	Field Verif.		Time (Lab)	No.	Tin	ne (Field)	
1											
2											
3											
				Ormlater	Deserves		Post-Sample				
Can No.	Samplin	g Infor		A second s	Pressure si		DC Sealed By/Date &	coc		oken By/[	Date &
č	Date	Start Time	End Time	Field Reading	Lab Verif.	-	Time (Field)	No.	Ti	me (Lab)	
1											
2											
3											
	nments:						Sar	npler "l	eak check		
GR	AB SAMPLE C		Wind Direct Wind Spece	ed: Calr	n Light		Gentle Modera		Gusting		ng
GR	AB SAMPLE C		Wind Spee Sky Condi	ed: Calr	n Light ar Scatte	red			Rain		ng
GR			Wind Spee Sky Condi	ed: Calr tions: Clea emperature (°	n Light ar Scatte	red 	Gentle Moder Broken Overca		Rain		ng
iR.	Print Nam		Wind Spee Sky Condi Average T	ed: Calr tions: Clea emperature (° sh By:	n Light ar Scatte	Time	Gentle Moder Broken Overca	Relinqu	Rain	Date	Time
SR.			Wind Spee Sky Condi Average T Relinqui	ed: Calr tions: Clea emperature (° sh By:	n Light ar Scatte F)		Gentie Moder Broken Overca	Relinqu	Rain ish To:	Date	
GR.			Wind Spee Sky Condi Average T Relinqui	ed: Calr tions: Clea emperature (° sh By:	n Light ar Scatte F)		Gentie Moder Broken Overca	Relinqu	Rain ish To:	Date	
GR			Wind Spee Sky Condi Average T Relinqui	ed: Calr tions: Clea emperature (° sh By:	n Light ar Scatte F)		Gentie Moder Broken Overca	Relinqu	Rain ish To:	Date	

Misc. Notes: COC Sealed By/Date & Time: COC Broken By/Date & Time: COC No.: Relinquish By & To: Canister Vacuum Reading: Canister Pressure Reading:

Signature of personnel initiating sealed sample chain of custody and date & time Signature of personnel that 'breaks' the COC tag for that particular canister with date & time COC tag number Printed name & signature of personnel relinquishing/receiving the sample canister(s), **not breaking the COC**. Canister pressure checked at Toxics Laboratory prior to transport to field and in field before sampling period. Canister pressure checked in field after sampling period and at Toxics laboratory after arrival.

## Aldehyde Chain of Custody Form 2013-2014

Air To:	ics Analytical Support Team	
Aldehyde Comp	ounds Chain Of Custody	Form Indicate (x) Type of Samp Sample Duplicate
ATAST Investigation #		Field Blank
Field Setup Information		
Study Site:	Sample ID #:	
Setup Date/Time:	Sampling Start Date/Time:	
Sampler Display Date/Time:	Sample Set Up Duration:	ł
DNPH Cartridge Lot #:	Leak Check (circle one):	PASS FAIL
Sample Setup by:	Leak Rate (L/min):	
Field Recovery Information		
Recovery Date/Time:	Actual Start Date/Time:	
Sample Recovered by:	Actual Stop Date/Time:	
FLOW (L/min):	Sample Time:	ł
Avg	n Max	
Sample Volume Using Gloves, Cap the Cartridges and F Laboratory Login Information	e (L): lace in Sample Envelope. Keep and Tra	nsport Samples Cold.*
Sample Received by:	Date Received:	
Sample Status (valid/void):	If void, why:	
*Temperatures as Received (≤ 4°C, 3		

#### Additional Transfers of Sample Custody between the Field and The Lab

Re	elinquished By:			Received By:	
Print Name	Signature	Date/Time	Print Name	Signature	Date/Time

If the person collecting the sample in the field transfers the samples to anyone else to take to the lab, then this transfer of custody must be documented in the spaces above.

Samples Must be Kept Cold or Refrigerated at All Times!!

# VOCs Chain of Custody Form 2014-

NC Divisio 4403 Reed						Sampling S	ite/Location:			
Raleigh, N (919) 733-	C 27607		715-0890						Crah	
		. (919) /	13-0890			Sample Type		HC	Grab	
Sam	ple #	Can	ister Vacu	um inchos		Pre-Sam	ple			
		Gan	Hg	in, inches	cocs	Sealed By	COC No.		Broken By	
Canister #	Batch	T	Lab eading	Field Verified	Date &	Time (Lab)	COC NO.	@ Date &	Time (Fie	ld)
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					5.10					eckeu
			Canister	Pressure,	Post-S	ampie				
Samplin	ng Inform		1	osi		Sealed By	COC No.		Broken By	
Date	Start Time	End Time	Field Reading	Lab Verified	Date &	Time (Field)		@ Date &	& Time (La	b)
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Sampling	Day (circle	e): Mor		Ved Thurs	Fri Sat	Sun				
Sampling Ozone An	Day (circle alyzer Op	e): Mor erating?		] NO	Fri Sat	Sun				
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Sampling Dzone An NOx Analy Date Lab Field &/or	Day (circle alyzer Op /zer Oper: Receive	e): Mor erating? ating? d: nments Wind Wind Sky	YES C	NO NO Received	l by: N t Gentle	NEE	SE S Isting Strong	SW W		
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