1999 SOS NASHVILLE FIELD CAMPAIGN QUALITY ASSURANCE PLAN

Prepared by


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# 1999 SOS NASHVILLE FIELD CAMPAIGN
## QUALITY ASSURANCE PLAN

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PROJECT OVERVIEW

The Southern Oxidants Study will conduct a major field campaign in the Southeast during the summer of 1999. The scientists involved in the study will operate out of Nashville Tennessee with the intensive scheduled for a one month period from June 15 through July 15. During the field intensive, measurements will be made using four instrumented aircraft and a wide array of ground-based instrumentation located at three monitoring sites.

This intensive field campaign is part of an on-going effort to improve our understanding of the atmospheric processes responsible for the formation and distribution of ozone and fine particles in the atmosphere. The new insights that will result from the measurement program are intended to inform the policy-making community and will result in more efficient management strategies for these two pollutants.

Participants

The Nashville Field Campaign is a cooperative effort involving scientists from a number of Federal and private sector research institutions (universities, industry, state and local regulators) throughout the U.S. and Europe. A list of the participating institutions is provided below:

*Federal Agencies:*
- NOAA (lead) - AL, ARL, CMDL, ETL
- DOE – PNNL, BNL, ANL,
- EPA – ORD, OAQPS
- TVA
- NSF - NCAR

*Universities:*
- Georgia Institute of Technology
- Ohio University
- Purdue University
- North Carolina State University
- Penn State University
- University of Alabama at Huntsville
- University of Colorado CIRES
- University of Heidelberg
- University of Innsbruck
- University of Innsbruck
- University of Western Michigan

*Industry:*
- Aerosol Dynamics Inc.
- Battelle Memorial Institute

*State and Local:*
- State of Tennessee
- Davidson County Health Dept.
Data Quality Assessment

Much of the instrumentation used during the field campaign is state-of-the-art technology developed by the investigators themselves. The accuracy and precision of these instruments have been assessed by the investigators and the information is available. Where possible, NIST traceable standards will be used for instrument calibration and to document performance. The investigators will exchange these standards during the campaign providing an independent verification of the calibration standards. However, no traceable standards exist for many of the species being measured. In these instances the investigators have developed their own calibration procedures that have been documented. Where possible, duplicate measurements of species using different approaches will be used to evaluate measurement accuracy and instrument performance.

A more comprehensive QA/QC program is planned for the Level II measurement sites. A detailed description of the QA/QC protocols for those measurements are described below.

Two measurement intercomparisons are planned as part of the 1999 field campaign. The first is an intercomparison of the measurement systems installed on the instrumented aircraft that will be used during the study. The second is an intercomparison involving the various groups that will be performing VOC analyses during the study. These intercomparisons are described in more detail below.

Data Management and Archival

Data collection and management during the field campaign will be the responsibility of the individual investigators. In all cases, the data will be collected and stored on site using electronic data loggers. The final repository of the data will be the NARSTO data archive in Oak Ridge Tennessee.

Documentation and Records:

Final results from this project will be published in peer reviewed journals. Documentation on QA/QC checks can be made available upon request as records will be kept of these.
PROJECT ORGANIZATION AND RESPONSIBILITIES

The 1999 Southern Oxidants Study (SOS) Nashville field intensive is truly a collaborative effort involving scientists from the U.S., Canada and Europe representing the government (federal, state, and local) and private sector (universities, industry) research communities. The study is part of a larger SOS effort and falls under the overall direction of the SOS Office of the Director and the SOS Executive Committee.

The SOS Executive Committee has selected Jim Meagher of National Oceanic and Atmospheric Administration’s (NOAA) as Mission Scientist for the Intensive. Jim is responsible for the overall technical direction and management of the Intensive. He will be aided in this role by Peter Daum of Brookhaven National laboratory. Bill Parkhurst of the Tennessee Valley Authority (TVA) is the Logistics Coordinator for study. He will work with the Mission Scientist and the Science Team to locate and obtain use agreements for ground sites, arrange for utilities at the ground sites, provide meeting and office space for participating scientists, and act as a liaison with local industry, state and local regulators, and public interest groups. A site coordinator has been selected for each of the three major monitoring sites. Eric Williams, NOAA will serve as the Site Coordinator for Cornelia Fort while Ken Olszyna will coordinate activities at the Polk Building and Dickson sites. The Site Coordinators will work with the scientists to insure the measurements at each site are properly integrated and that the necessary infrastructure is in place to support the measurements. They will also serve as a liaison with the land/building owners.

The details of the study design and execution have been developed by a Science Team comprised of the principal investigators from the participating organizations. The Science Team is organized into a series of subteams that deal with specific topics:

Aircraft Coordination Team

This team is made up of representatives from each of the four groups with instrumented aircraft that will participate in the Nashville Intensive.

NOAA WP-3D – Fred Fehsenfeld, Michel Trainer, and Gerd Hübler
DOE G-1 – Carl Berkowitz and Rich Barchet
TVA Bell 205 – Roger Tanner, Robert Imhoff, and Ray Valente
NOAA CASA 212 – Michael Hardesty, Bob Banta, and Raoul Alvarez

The team is responsible for developing coordinated flight plans for the following airborne experiments:
- Measurement Intercomparisons
- Diurnal Studies
- Plume Studies – Urban and Power Plant
- Regional Studies
**VOC Measurement Team**

This group is composed of researchers responsible for the quantification of speciated VOCs during the Nashville Intensive and interested bystanders. The measurement of VOCs has been a particularly difficult and contentious part of previous SOS field studies. Therefore, it was felt that this activity was deserving of special attention if we were to insure that the compatibility of the VOC data reported by the participating groups. Jack Calvert and Eric Apel of NCAR have agreed to organize and oversee the VOC measurement intercomparison.

VOC measurements will be performed by the following groups:
- Elliot Atlas, NCAR – canisters, NOAA WP-3
- Eric Apel, NCAR – *in situ*, Dickson
- Paul Doskey, Argonne N L – canisters, Polk Building
- Paul Goldan, NOAA – *in situ*, NOAA WP-3
- Bill Lonneman, EPA – canisters, TVA Bell 205, DOE G-1, source characterization
- William McClenny, EPA – *in situ*, Cornelia Fort
- Valerie Young, Ohio Univ. – *in situ*, Cornelia Fort
- Chuck Lewis, EPA – canisters, Dickson and Cornelia Fort

**PBL Dynamics Team**

This team is responsible for the detailed planning for the PBL dynamics experiments to be conducted as part of the Nashville Intensive. This group is also responsible for siting the wind profiler and surface flux networks.

The Team is made up of representatives from the groups involved in meteorological measurements and meteorological forecasting.
- DOE PNNL – Carl Berkowitz, Will Shaw
- NOAA ETL – Bill Neff, Alan White, and Bob Banta
- NOAA AL – Michael Trainer, Wayne Angeline
- NOAA ARL – Tylden Meyers
- UAH – Dick McNider
- TVA – Steve Mueller

**Surface Chemistry Network Team**

This group is responsible for integrating the measurements being performed at the various ground sites into a coherent data set that can be used to address the science questions that have been posed. The surface chemistry network includes the three sites that have been added specifically to support the study (Dickson, Polk Building, and Cornelia Fort), the other research monitoring sites in the area (specifically the SEARCH sites, Cove Mountain, Look Rock, and Mammoth Cave), and the regulatory networks.

Team members include those involved in the measurements at any of the sites listed above.
SOS Modeling Team

This is a SOS-wide team that has responsibilities and objectives that transcend the Nashville Intensive. This team has two major tasks related to the Nashville Intensive. First, the team will review the measurement plans for the Nashville Intensive and will make recommendations for changes that would benefit the application of the data collected for model evaluation and improvement. Second, the team will provide a mechanism for collaboration among those groups that are utilizing the Nashville 95 data set or are planning to use the 99 data set in modeling studies. This group will also work with SOS-funded emissions inventory efforts to maximize the benefits of those activities.

Dick McNider of UAH leads this team and is planning a workshop for April of 1999 to review ongoing modeling research and develop plans for future collaborations.
NONMETHANE HYDROCARBON MEASUREMENT INTERCOMPARISON

Project/Task Organization
The following are persons participating in the project and their specific roles and responsibilities:

Eric Apel: Ultimately responsible for the completion of project and all aspects of quality assurance and quality control. Actively participates in the science of the project and supervises other individuals in the completion of tasks.

Daniel Riemer: Will assist Eric Apel in conducting the intercomparison experiements and will be co-responsible for measurements at the Dickson site.

Jack Calvert: Oversees overall quality of products produced. David Parrish will serve as a referee during intercomparison study.

Nonmethane Hydrocarbon Measurements

Ambient NMHC concentrations will be determined by several research groups during the study. 1) Daily canister samples will be collected and analyzed for NMHCs at the upwind, background site (Dickson) the downwind urban site (Cornelia Fort) and the downtown site (Polk Building). 2) The TVA helicopter, the DOE G-1 and the NOAA WP-3 aircraft will each collect canister samples for NMHC analysis. 3) The DOE G-1 and the NOAA WP-3 will be equipped with systems (atmospheric pressure mass spectrometry and gas chromatography respectively) for real-time or continuous analyses. The NMHC data from the sources described above will be used to evaluate the contribution of the various NMHCs measured to ozone formation.

As compounds of importance in understanding the atmospheric chemistry of the Nashville region, the following NMHC species have been targeted for analysis:

Alkanes:
- ethane
- propane
- n-butane
- i-butane
- n-pentane
- i-pentane
Alkenes:
- ethene
- propene
- 1-butene
- 2-butene (cis and trans)
- 2-pentene (cis and trans)
- 1,3 butadiene
- isoprene
- alpha pinene

Alkynes:
- Acetylene

Aromatics:
- benzene
- toluene
- o-, m-, p-xylene
- ethylbenzene
- tri-methyl-benzene (3 isomers)

Oxygenates:
- acetaldehyde
- propanal
- MTBE
- methanol
- ethanol

Others:
- tetrachloroethylene

Several research groups will be making NMHC measurements at the various sites. In order to assure the quality and comparability of the individual data sets, we will conduct three important experiments. All experiments will be conducted prior to the start of the 1999 intensive field study.

1) Circulation and comparison of results from a prepared NMHC standard mixture.

This mixture will contain approximately 70 compounds and will include the compounds on the target list. Participants will be asked to identify and quantify the target compounds in the mixture. Reference values will be determined by the NCAR SOS-MTS group. In determining the reference values, the NCAR-MTS method utilizes a manually operated
preconcentration system that was designed to operate in a simple and trouble-free manner (Apel et al., 1994, 1998). The trap consists of a 1/8” x 8” stainless steel (ss) loop filled with 60-80 mesh glass beads. The system operates as follows: The sample is drawn into a 6-position Valco (VICI, Houston, TX) valve and through the trap which was immersed in liquid argon or nitrogen. The compounds of interest are trapped and the permanent gases (N$_2$, O$_2$) are passed through the trap and into a 3.1 L ballast volume. The initial and final pressures is monitored with an MKS Baratron gauge (Type 127, 0-1000 Torr) and recorded. The 6 position valve is then switched through control of the HP Chemstation software, the trap rapidly heated (water, 90°C), and the analytes transferred onto the head of a DB-1, 100m x 0.25 ID fused silica column with a 0.50 μ film thickness (J&W Scientific, Folsom, CA) maintained at an initial temperature of -50 °C and subsequently ramped at 4 °C/min to a final temperature of 150 °C. Baseline separation is observed for most of the compounds. The FID is calibrated with NIST SRM (National Institute of Standards and Technology Standard Reference Material) propane, NIST butane/benzene (Apel et al, 1995), a NIST C$_2$-C$_{16}$ n-alkane mixture and a NIST 16 component hydrocarbon blend. All compounds were identified by retention times. The NCAR-NOMHICE analytical system was designed to handle various sample sizes so that the more concentrated standard mixtures can be run without dilution and without detector overload.

2) Circulation and comparison of results from a Nashville whole air sample.

The NCAR-SOS-MTS group will travel to Nashville and collect whole air samples in 32 L SS containers. We will analyze samples both by GC-MS and GC-FID, prepare aliquots, and ship the samples to participating laboratories. Participants will be asked to identify and quantify the target compounds contained in the sample. Again, reference values will be determined by the NCAR SOS-MTS group using the methodology described above.

3) Field intercomparison of participant NMHC measurement techniques.

The NCAR-SOS-MTS group will serve as organizers and serve as or help designate referees for a field intercomparison of NMHC measurement techniques beginning two weeks prior to the start of the intensive. Groups that will be making NMHC measurements during the field study will make side-by-side measurements of ambient air at the Cornelia Fort site. Groups making in-situ measurements will bring their instruments to the site. Groups making canister measurements will collect canister samples at the same time as the in-situ measurements are being made. The referees will provide a report on the comparison of measurements. Data quality objectives include the proper identification of all present target compounds and agreement to within 25% for these compounds.
Documentation and Records

Final results from this project will be published in peer reviewed journals. Documentation on QA/QC checks can be made available upon request as records will be kept of these.

Sampling Process Design

The SOS science team will determine the sampling process design in accordance with recognized state-of-the-art research techniques.

Sampling methods and handling

Insofar as they exist, established EPA methods will be used for sample collection and handling.

Instrument equipment testing, inspection and maintenance requirements

Normal procedures for maintenance of the systems will be performed and systems will perform in an optimal manner. All gas supplies to systems are checked daily.

Data Management

Data collected during the intercomparison experiment will be turned in and assessed by Dr. Calvert to ensure self-consistency amongst measurements. NCAR-SOS-MTS will provide a template for experimentalists to report their data upon.

The data collected at the Dickson site will be available for preliminary peer review during weekly science team meetings. All final data processing will be done at the NCAR laboratory in Boulder, CO.

Data validation and usability

As this is a research project all data will initially be accepted pending system and calibration checks. If the system appeared to be operating normally and the calibration was stable and reproducible during the measurements, then cross checks with the different methods involved along with the stated uncertainties in the measurements will eventually lead to rejection of some data as not within specified measurement criteria precision and accuracy.
References


INTERCOMPARISON OF AIRCRAFT INSTRUMENTATION

The four heavily instrumented aircraft participating in the study will be used to characterize the three-dimensional distribution of pollutants and track the transformation and removal of these pollutants over time. The four aircraft have widely varying capabilities. Three of the aircraft (NOAA WP-3D, DOE G-1, and TVA Bell 205) will make in situ measurements mainly in the atmospheric boundary layer; the fourth (NOAA CASA 212) will make remote-sensing measurements from above the boundary layer. The NOAA WP-3D and the DOE G-1 have sufficient range and endurance to survey large areas. This provides the opportunity to contrast the pollutant mix and meteorology in vicinity of Nashville to that of the Midwestern U.S. The TVA Bell 205 helicopter will be used to obtain detailed chemistry measurements over the urban area and in power plant plumes. The NOAA CASA 212 is equipped with instrumentation to remotely sense ozone, aerosols and surface temperature. The aircraft participating in the study are listed below along with the affiliations of the groups providing the aircraft and a description of the installed instrumentation.

Instrumented Aircraft

CASA 212-200: Private vendor /NOAA Environmental Technology Laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time Resolution</th>
<th>Vertical Resolution</th>
<th>Method</th>
<th>Det. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>3-8 s</td>
<td>90 m</td>
<td>DIAL Lidar</td>
<td>4-10 ppb</td>
</tr>
<tr>
<td>Aerosol Backscatter</td>
<td>3-8 s</td>
<td>15 m</td>
<td>DIAL Lidar</td>
<td>5 x 10^-6 m^-1 sr^-1</td>
</tr>
<tr>
<td>Surface Temp.</td>
<td>1 s</td>
<td>NA</td>
<td>IR Radiometer</td>
<td>0.2 °C</td>
</tr>
</tbody>
</table>

Table 1. Aircraft Instrument Package for the NOAA CASA 212-200
**Lockheed WP-3D Orion:** NOAA Aircraft Operations Center / NOAA Aeronomy Laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time Resolution</th>
<th>Method</th>
<th>Det. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone (O₃)</td>
<td>10 s</td>
<td>UV Absorption</td>
<td>1 ppb</td>
</tr>
<tr>
<td>Fast O₃ (FO₃)</td>
<td>1 s</td>
<td>NO/O₃ Chemiluminescence</td>
<td>0.2 ppb</td>
</tr>
<tr>
<td>Fast CO (FCO)</td>
<td>1 s</td>
<td>VUV Resonance Fluorescence</td>
<td>25 ppb</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>≤ 1 s</td>
<td>NDIR</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>2 s</td>
<td>UV Pulsed Fluorescence</td>
<td>1 ppb</td>
</tr>
<tr>
<td>Nitric Oxide (NO)</td>
<td>1 s</td>
<td>NO/O₃ Chemiluminescence</td>
<td>30 ppt</td>
</tr>
<tr>
<td>Nitrogen Dioxide (NO₂)</td>
<td>3 s</td>
<td>Photolysis, NO/O₃ Chem.</td>
<td>100 ppt</td>
</tr>
<tr>
<td>Total Nitrogen Oxides (NOₓ)</td>
<td>1 s</td>
<td>Au Converter, NO/O₃ Chem.</td>
<td>50 ppt</td>
</tr>
<tr>
<td>PAN</td>
<td>1 s / every 6 min</td>
<td>Dir. Injection, GC/ECD</td>
<td>&lt; 5 ppt</td>
</tr>
<tr>
<td>PPN</td>
<td>1 s / every 6 min</td>
<td>Dir. Injection, GC/ECD</td>
<td>&lt; 5 ppt</td>
</tr>
<tr>
<td>MPAN</td>
<td>1 s /every 6 min</td>
<td>Dir. Injection, GC/ECD</td>
<td>&lt; 5 ppt</td>
</tr>
<tr>
<td>Nitric Acid (HNO₃)</td>
<td>1 s</td>
<td>C I Mass Spectrometry</td>
<td>10 ppt</td>
</tr>
<tr>
<td>NH₃</td>
<td>5 s</td>
<td>C I Mass Spectrometry</td>
<td>50 ppt</td>
</tr>
<tr>
<td>In-situ VOCs</td>
<td>1 min./every 15 min</td>
<td>Cryo Collection, GC/FID</td>
<td>&lt; 10 ppt</td>
</tr>
<tr>
<td>Canister VOCs</td>
<td>&lt;1 min.</td>
<td>Canister Sampling, GC/MS</td>
<td>&lt; 10 ppt</td>
</tr>
<tr>
<td>CH₂O</td>
<td>20 s every min</td>
<td>Tunable Diode Laser</td>
<td>30 ppt</td>
</tr>
<tr>
<td>Peroxides (incl. H₂O₂)</td>
<td>1 min</td>
<td>Dual Enzymatic / Fluorimeter</td>
<td>30 ppt</td>
</tr>
<tr>
<td>Aerosol size distribution</td>
<td>1 s</td>
<td>NMASS</td>
<td>5 - 90 nm</td>
</tr>
<tr>
<td>Aerosol size distribution</td>
<td>1 s</td>
<td>ERAST</td>
<td>70 - 1000 nm</td>
</tr>
<tr>
<td>Total Radiation</td>
<td>1 s</td>
<td>Eppley Pyranometers - Zenith &amp; Nadir</td>
<td>0.28 – 2.8 μ</td>
</tr>
<tr>
<td>UV Radiation</td>
<td>~10 s</td>
<td>Spectral Radiometer - Zenith &amp; Nadir</td>
<td>295- 480 nm</td>
</tr>
<tr>
<td>Visible Radiation</td>
<td></td>
<td>Visible Absorption Spectrometer</td>
<td>420 – 700 nm</td>
</tr>
<tr>
<td>Water Vapor (H₂O)</td>
<td>1 s</td>
<td>Lyman Alpha Absorption</td>
<td></td>
</tr>
<tr>
<td>Air Temperature</td>
<td>1 s</td>
<td>Platinum Thermistor</td>
<td></td>
</tr>
<tr>
<td>Dewpoint/Frostpoint</td>
<td>≤ 3 s</td>
<td>Chilled Mirror</td>
<td></td>
</tr>
<tr>
<td>Wind Speed</td>
<td>1 s</td>
<td>Derived from INE</td>
<td></td>
</tr>
<tr>
<td>Wind Direction</td>
<td>1 s</td>
<td>Derived from INE</td>
<td></td>
</tr>
<tr>
<td>Altitude</td>
<td>1 s</td>
<td>Barometric</td>
<td></td>
</tr>
<tr>
<td>Position</td>
<td>1 s</td>
<td>GPS, INE</td>
<td></td>
</tr>
<tr>
<td>Air Speed</td>
<td>1 s</td>
<td>Barometric</td>
<td></td>
</tr>
<tr>
<td>Biometer</td>
<td></td>
<td>3-wavelength IR Absorption</td>
<td></td>
</tr>
<tr>
<td>Atmospheric Reflectivity</td>
<td></td>
<td>C &amp; X Band Radars</td>
<td></td>
</tr>
</tbody>
</table>
**Grumman G1:** DOE Pacific Northwest National Laboratory

- **Endurance:** 6 hrs
- **Ceiling:** 3.5 km
- **Payload:** 1300 kg
- **Research Speed:** 100 m/s

Table 3. Aircraft Instrument Package for the DOE Grumman G-1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time Resolution</th>
<th>Method</th>
<th>Det. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone (O₃)</td>
<td>10 s</td>
<td>UV Absorption</td>
<td>25 ppb</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>20 s</td>
<td>NDIR</td>
<td>20-25 ppb</td>
</tr>
<tr>
<td>Fast CO (FCO)</td>
<td>5 s</td>
<td>UUV Resonance Fluorescence</td>
<td>5 ppb</td>
</tr>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>2 s</td>
<td>UV Pulsed Fluorescence</td>
<td>200-300 ppt</td>
</tr>
<tr>
<td>Nitric Oxide (NO)</td>
<td>&lt;10 s</td>
<td>NO/O₃ Chemiluminescence</td>
<td>20 ppt</td>
</tr>
<tr>
<td>Nitrogen Dioxide (NO₂)</td>
<td>&lt;10 s</td>
<td>Photolysis NO/O₃ Chem.</td>
<td>50 ppt</td>
</tr>
<tr>
<td>Nitrogen Dioxide (optional)</td>
<td>&lt;10 s</td>
<td>Luminol Chemiluminescence</td>
<td>0.015 ppbv</td>
</tr>
<tr>
<td>Total Nitrogen Oxides (NOₓ)</td>
<td>&lt;10 s</td>
<td>Mo Converter. NO/O₃ Chem.</td>
<td>300-400 ppt</td>
</tr>
<tr>
<td>PAN</td>
<td>1 sample/7 min</td>
<td>Cyrogenic GC</td>
<td>15 ppt</td>
</tr>
<tr>
<td>CH₂O (optional)</td>
<td>Continuous (1min delay)</td>
<td>Fluorescence</td>
<td>100 ppt</td>
</tr>
<tr>
<td>PAN</td>
<td>4 s</td>
<td>Tandem Mass Spectrometry</td>
<td>400 ppt</td>
</tr>
<tr>
<td>HNO₂</td>
<td>4 s</td>
<td>Tandem Mass Spectrometry</td>
<td>400 ppt</td>
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<td>HNO₃</td>
<td>4 s</td>
<td>Tandem Mass Spectrometry</td>
<td>400 ppt</td>
</tr>
<tr>
<td>NH₃ (optional)</td>
<td>4 s</td>
<td>Tandem Mass Spectrometry</td>
<td>~2 ppb</td>
</tr>
<tr>
<td>Formic/Acid acids (optional)</td>
<td>4 s</td>
<td>Tandem Mass Spectrometry</td>
<td>100 ppt</td>
</tr>
<tr>
<td>Canister VOCs</td>
<td></td>
<td>Canister Sampling, GC/FID</td>
<td>0.1 ppbv</td>
</tr>
<tr>
<td>bcat</td>
<td>1 s</td>
<td>Nephelometer</td>
<td>0-103/Mm</td>
</tr>
<tr>
<td>Aerosol size distribution</td>
<td>1 s</td>
<td>PCASP</td>
<td>(0.17 - 3μm)</td>
</tr>
<tr>
<td>Aerosol size distribution</td>
<td>1 s</td>
<td>FSSP</td>
<td>(2 – 47 μm)</td>
</tr>
<tr>
<td>Particle Number</td>
<td>1 s</td>
<td>CNC (two)</td>
<td>(&gt;7 nm, &gt;3 nm)</td>
</tr>
<tr>
<td>UV Radiation</td>
<td>1 s</td>
<td>Eppley Pyranometer</td>
<td>(295-385 nm)</td>
</tr>
<tr>
<td>Short-wave Irradiance</td>
<td>1 s</td>
<td>Eppley PSP</td>
<td>(285-2800 nm)</td>
</tr>
<tr>
<td>Long-wave Irradiance</td>
<td>1 s</td>
<td>Eppley PIR</td>
<td>(4-50 microns)</td>
</tr>
<tr>
<td>Water Vapor (H₂O)</td>
<td>1 s</td>
<td>Lyman Alpha Absorption</td>
<td>±0.1 g m⁻³(esp.)</td>
</tr>
<tr>
<td>Air Temperature</td>
<td>1 s</td>
<td>Platinum Resistance</td>
<td>±0.5 °C</td>
</tr>
<tr>
<td>Dewpoint/Frostpoint</td>
<td>1 s</td>
<td>Chilled Mirror</td>
<td>D.P. ±0.2 °C, F.P. ±0.4 °C</td>
</tr>
<tr>
<td>Wind Components (u,v,w-)</td>
<td>1 s</td>
<td>Gust Probe</td>
<td>&lt;0.5 m s⁻¹</td>
</tr>
<tr>
<td>Altitude</td>
<td>1 s</td>
<td>Barometric</td>
<td>&lt;1mb</td>
</tr>
<tr>
<td>Position</td>
<td>1 s</td>
<td>GPS</td>
<td>&lt;3m</td>
</tr>
<tr>
<td>Air Speed</td>
<td>0.1 s</td>
<td>Barometric</td>
<td>&lt;20 cm s⁻¹</td>
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</table>
**Bell 205 Helicopter:** TVA Environmental Research Center

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time Resolution</th>
<th>Method</th>
<th>Det. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone (O₃)</td>
<td>1 s</td>
<td>NO Chemiluminescence</td>
<td>2 ppb</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td></td>
<td>NDIR or HgO reduction</td>
<td></td>
</tr>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>5 s</td>
<td>UV Pulsed Fluorescence</td>
<td>0.5 ppb</td>
</tr>
<tr>
<td>Nitric Oxide (NO)</td>
<td>1 s</td>
<td>NO/O₃ Chemiluminescence</td>
<td>1 ppb</td>
</tr>
<tr>
<td>Nitrogen Dioxide (NO₂)</td>
<td>5 s</td>
<td>Photolysis, NO/O₃ Chem.</td>
<td>1 ppb</td>
</tr>
<tr>
<td>Total Nitrogen Oxides (NOₓ)</td>
<td>1 s</td>
<td>Au Converter, NO/O₃ Chem.</td>
<td>1 ppb</td>
</tr>
<tr>
<td>NOₓ *</td>
<td>1 s</td>
<td>NOₓ detection + Nylasorb Filter</td>
<td>1 ppb</td>
</tr>
<tr>
<td>Canister VOCs</td>
<td>1 min</td>
<td>Canister Sampling, GC/FID</td>
<td></td>
</tr>
<tr>
<td>b_{cat}</td>
<td>5 s</td>
<td>Nephelometer</td>
<td>&lt;10⁶ m⁻¹</td>
</tr>
<tr>
<td>Aerosol Size Distribution</td>
<td>1 s</td>
<td>PCASP</td>
<td>(0.17 - 3μm)</td>
</tr>
<tr>
<td>Particle Composition</td>
<td>variable</td>
<td>Filter Pack, IC analysis</td>
<td></td>
</tr>
<tr>
<td>Particle Composition by Size</td>
<td>variable</td>
<td>Anderson Cascade Impactor</td>
<td></td>
</tr>
<tr>
<td>Air Temperature</td>
<td>5 s</td>
<td>Platinum Thermistor</td>
<td></td>
</tr>
<tr>
<td>Dewpoint</td>
<td>5 s</td>
<td>Capacitance Sensor</td>
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</tr>
<tr>
<td>Altitude</td>
<td>5 s</td>
<td>Barometric</td>
<td></td>
</tr>
<tr>
<td>Position</td>
<td>5 s</td>
<td>GPS</td>
<td></td>
</tr>
<tr>
<td>Air Speed</td>
<td>5 s</td>
<td>Pitot- Static Pressure</td>
<td>2 m/s</td>
</tr>
<tr>
<td>Heading</td>
<td>5 s</td>
<td>Flux Gate Compass</td>
<td>0.5 deg.</td>
</tr>
</tbody>
</table>

**Measurement Intercomparisons**

The use of four aircraft and the diversity of the instrumentation flown on these platforms make a thorough intercomparison of the various instruments/measurements mandatory. These intercomparisons are especially important since the aircraft resources will be used in a complementary manner. We envision staggered deployment of some platforms (either on the same day and/or by flying alternating platforms on consecutive days) in order to extend the time coverage of the measurements. The planned intercomparisons will enhance the value of the accumulated data sets and assure the compatibility of the data collected on the various platforms.
Three types of intercomparisons are planned 1) circulation of standards, 2) side-by-side intercomparison flights, and 3) over-flights of ground-based monitoring and profiling sites.

Circulation of standards - A standard exchange will help insure that the different measurements are tied to comparable standards. A pre-intensive intercomparison will enable a correction of any detected problems prior to the science flights. NOAA Aeronomy Laboratory will provide NIST traceable gas standards for NO, CO, and SO2 that will be circulated among the groups operating in situ sampling aircraft.

Side-by-side intercomparison flights - The in-flight intercomparisons will give the maximum possible confidence that the data sets are comparable throughout a range of environmental conditions and provide an opportunity to identify and resolve problems as soon as possible. The intercomparison flights are of the highest priority and are scheduled for the very beginning of the intensive.

The three in situ sampling aircraft will be paired for a series of side-by-side flights. It is crucial that the various platforms are operated in their normal measurement mode if the intercomparisons are to be meaningful. For the NOAA WP-3D and the DOE G-1 the intercomparison flights are relatively straightforward. These two aircraft will fly side-by-side at four different altitudes (e.g., three within the mixed layer, one above) on tracks normal to the mean wind over rural Tennessee west of Nashville. The altitudes legs will each be about 90 km long (15 min. duration) and evenly spaced depending on meteorological conditions. The NOAA CASA 212 will over-fly the same track at least twice during this period.

Side-by-side flights involving the TVA Bell 205 helicopter are more challenging due to the differences in aircraft performance. During intercomparison flights between either the DOE G-1 or the NOAA WP-3D and the smaller and slower helicopter, the larger aircraft will fly the pattern described above while the helicopter will fly a shorter pattern centered parallel to the flight track of the larger aircraft with an appropriate horizontal offset.

In-flight intercomparisons will be conducted under conditions suitable to the experiment to be conducted. Well-mixed conditions will produce the most uniform concentration fields and, therefore, are the most desirable. Conditions to be avoided include low clouds, precipitation and low visibility. Good communications between the aircraft are essential.

Data collected during the in-flight intercomparisons will be exchanged and reviewed as soon as possible after the intercomparison flights so any problems/issues can be resolved in a timely manner. The following procedure will be followed in evaluating the results of the intercomparison flights.

Each group will use their standard procedures to reduce their data for the parameters to be intercompared. (temperature, dew point, position, ozone, SO2, CO, NO, NO2, NOy,
The data will be turned around within 24 hours of the intercomparison flights. The data managers (one from each platform) will constitute a QA team that will combine the data in a manner that will facilitate the intercomparison. The data managers will also provide estimates of measurement accuracy, precision, and other relevant information to permit quantitative evaluation of agreement or disagreement. After the data sets have been combined, the data managers will review the combined data sets with their respective measurement specialists. This will provide an opportunity for individual groups to review the data and determine if there are obvious reasons for differences, if any are detected. The QA team will then meet to develop a consensus evaluation of the intercomparison data, discuss whether any changes in measurement procedures need to be made, and to formulate a presentation to the study participants.

A more comprehensive analysis will be presented at a data analysis workshop to be held approximately 6 to 8 months after the measurement program is complete.

**Over-flights of ground-based monitoring and profiling sites** - In addition to the measurements from the airborne platforms ground based measurements will be made over a large region and a combined data set will be used for modeling studies. Therefore, the data sets from the two domains need to be tied together through over-flights of the ground stations.

Over-flights of these ground sites will provide additional intercomparison opportunities, particularly for the TVA Bell 205 helicopter and the NOAA CASA 212 airborne lidar. The helicopter is particularly well suited for low elevation flight near the monitoring stations at Dickson and Cornelia Fort. On several occasions during the intensive the Bell 205 will perform spirals over these two sites to the top of the mixed layer. These flights will allow a comparison of measurements on-board the aircraft with those on the ground and provide information on the vertical distribution of pollution above these sites.

The ozone profiles obtained with the NOAA CASA 212 airborne lidar will be compared with data collected at two ground-based profiling sites. A lidar will be operated at the Cornelia Fort site providing vertical distributions of ozone and aerosol backscatter up to 3-10 km on a semi-continuous basis. In addition, ozone sondes will be released at noon each day from the National Weather Service site in Nashville. It should be possible to intercompare the airborne data with similar data from one, or both, of these ground sites during each flight.
QA/QC FOR LEVEL 2 AIR MONITORING STATIONS

Project Organization

Roger L. Tanner is the Project Manager for all aspects of the project. Kenneth J. Olszyna will be leading all Task 1 activities, both those associated with the deployment and operation of the Level 2 stations at Dickson and downtown Nashville, as well as the deployment and operation of the NO/NO\textsubscript{y} systems at Dickson and Hendersonville for a more extended period. William J. Parkhurst will be directing all logistics support activities associated with providing centralized facilities near aircraft operations, and making modifications to both the Level 2 site at the Polk building in downtown Nashville and the enhanced monitoring site at Cornelia Fort airport. The TVA Quality Assurance manager will be Bonnie S. Ginn.

Problem Definition and Background

The atmospheric production of PM\textsubscript{2.5} is intimately linked to the oxidation processes that produce O\textsubscript{3}. However a better understanding of the mechanisms that couple O\textsubscript{3} and fine particles is needed. Not only are there significant uncertainties in the mechanisms that produce tropospheric O\textsubscript{3} and PM\textsubscript{2.5} but there may also be important chemical, physical, and radiative links between these mechanisms. The effect of control strategies will depend upon the relative strengths of the various coupling mechanisms. The elucidation of these links is broadly recognized as one of the major scientific challenges confronting the atmospheric chemistry community in the coming decade.

Little information is available on the non-linear relationship between O\textsubscript{3} and PM\textsubscript{2.5} production mechanisms. For example, how does the temporal and spatial chemical composition of PM\textsubscript{2.5} correlate with O\textsubscript{3} levels and its precursor compounds? Does the rapid production of PM\textsubscript{2.5} occur during the initial, middle, or final stages of the atmospheric O\textsubscript{3} formation process; i.e., does the maximum production rate for PM\textsubscript{2.5} occur during the NO to NO\textsubscript{2} conversion processes, the NO\textsubscript{x} to NO\textsubscript{z} conversion processes, or the latter stages when the air mass has been chemically aged, i.e., for NO\textsubscript{x}/NO\textsubscript{y} ratios around 70% or greater? Or does the production rate for PM\textsubscript{2.5} occur during the entire O\textsubscript{3} production process? Is there a relationship between the rate and amount of excess O\textsubscript{3} produced and the amount of PM\textsubscript{2.5} produced or its chemical composition in urban plumes, power plant plumes, or ambient rural background?
Project Description and Schedule

Task 1a:

TVA will install and operate two enhanced (Level 2) surface-level monitoring stations during the 1999 Nashville/Middle Tennessee Field Study. These stations will be located near Cumberland Furnace in Dickson County, TN, and on top of the James K. Polk Building in downtown Nashville. High-sensitivity, short time resolved (1 or 5 minute concentrations) gas measurements include sulfur dioxide (SO$_2$), carbon monoxide (CO), ozone (O$_3$), nitrogen oxide (NO), nitrogen dioxide (NO$_2$), and total oxides of nitrogen (NO$_X$). The meteorological measurement package will include wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), and solar radiation (RAD). These stations will be installed during late winter/early spring, will begin routine operation on or before June 1, 1999, and cease operation no earlier than July 31, 1999. All Level 2 data will be validated and available to SOS participants as of December 1, 1999.

Although the PM$_{2.5}$ data will not have this short time resolution, the data from the Level 2 stations will provide precursor concentration details that may explain anomalies in the PM$_{2.5}$ data. These stations will be operated in an automatic mode similar to the Level 2 station operations during the 1995 SOS/Nashville intensive.

Task 1b:

TVA will install and operate two high-sensitivity nitrogen oxide/total nitrogen oxides (NO/NO$_Y$) sampling systems in support of SCISSAP particle sampling for two years (assuming continued funding for the June 1, 2000-May 31, 2001 period) beginning in April, 1999. These stations will be located near Cumberland Furnace in Dickson County, TN, and near Hendersonville in Sumner County, TN. The systems will be installed during late winter/early spring 1999, commence routine operation on or about April 1, 1999, and cease operation on or about March 31, 2001. All data from the first year of operation will be validated and available to SCISSAP and SOS participants by approximately September 30, 2000.

Data compilations are expected from both tasks 1a and 1b and, following validation, will be submitted for inclusion in the AIRS database as described below. Reports based on the results of each year of data collection will be prepared on an annual basis and will include complete calibration results and a report of annual auditing activities.

Measurements And Data Acquisition

This document describes the Quality Assurance / Quality Control procedures to be employed for the ground-based air monitoring network for the 1999 SOS/Nashville field intensive. The network consists of two level 2 stations and two stations to measure NO-NO$_Y$ levels and local met conditions. One of the level 2 stations is located on the top of
the James K. Polk Building in downtown Nashville. The other level 2 station is located about 40 miles west of Nashville near Cumberland Furnace in Dickson County. One of the NO-NO\textsubscript{y} measurements station is also located at the Dickson County site. The other NO-NO\textsubscript{y} measurement site is located at Hendersonville near the Old Hickory dam about 15 miles northeast of Nashville.

The following sections in this document include:
- DATA QUALITY ASSESSMENT
- QA/QC PROCEDURES FOR NETWORK OPERATIONS DURING INTENSIVE
- DESCRIPTION OF SAMPLING PROCEDURES & INSTRUMENTATION
- QA/QC PROCEDURES FOR SPECIFIC CONTINUOUS GAS MEASUREMENTS
- LIST OF NOMINAL CONCENTRATION LEVELS FOR QA/QC ACTIVITIES

Since the level 2 stations employ enhanced measurement procedures, the performance audits must also employ enhanced procedures. These procedures include gas challenges at the sample line inlets to determine the accuracy of the entire measurement system, not only the monitoring instrument. These gas challenges are made at concentration levels that typify the ambient measurement levels as well as the full scale instrument range. The current performance audits conducted by federal and state regulatory agencies do not employ these procedures. These agencies however can either provide the independent gas sources and dilution devices or conduct traceability measurements on the gas sources and dilution devices and also provide “independent witness” to the audit procedure.

Performance audits consist of gas challenges using gas sources and dilution devices that are independent of the gas sources and dilution devices that are used in the station operations. We are proposing the following procedures be used to conduct the performance audits on the ground based air monitoring stations for the 1999 SOS/Nashville intensive.

1) The EPA/NERL laboratory verify the gas cylinder concentrations and an O3 transfer standard that will be used in the performance audits.
2) The EPA/NERL laboratory provide transfer standards for mass flow meters in the range of 1 sccm to 20 slpm.
3) The EPA regional office or state agency provide an “independent witness” (or video camera) to the performance audit procedure, conducted by TVA operators using the EPA/NERL standards.

**Data Quality Assessment**

Comparability of data collected by the different sites is assured, where feasible, by network wide adoption of the same protocols, QA Plan and auditing procedures, and by the network wide use of the same measurement techniques and equipment. The definition of data completeness objectives for this program is the number of measurements made during the study divided by the number of measurements scheduled. The data completeness objective for the intensive is 90%. The project objective for
precision and bias are listed in table 1 as the warning limits (WL) and control limits (CL), respectively, indicated for each measurement for the daily QC span and precision checks.

Internal systems audits of sites will be performed by the Network manager at the start of the study and on an as needed basis. These audits will verify that the established protocols are being followed and will examine all documentation to assess the traceability, accuracy, precision, and completeness of all data.

Accuracy of the measurement systems will be determined from the enhanced performance audits. The enhanced performance audits are challenges of the measurement systems with traceable reference materials to document the deviation of the output of these systems from the true value. The enhanced performance audits are designed to determine the accuracy of the observed ambient measurements, an improvement over previous performance audits that determined only the accuracy of response of the monitoring instrument.

The representativeness of the measured data as ambient data is assured with the QA/QC daily checks that are conducted at the sample line inlets. The Dickson site is located in a rural area that will be representative of the rural, regional air quality. Specifically, the Dickson County site, at an elevation of 225 meters above sea level, is located on Daniel Lane off Route 48 between Charlotte and Cumberland Furnace, Tennessee approximately 35 miles west of Nashville in an open pasture approximately 100 meters from the nearest wooded area. The sample inlet elevation is 10 meters above ground level. Two TVA power plants are in near proximity but the data collected at this site in 1995 show clear evidence of when this site was impacted by the power plant plumes.

The urban Nashville site is located atop the James K. Polk Building on the corner of Fifth and Deadrick Avenues in Nashville, Tennessee at a ground elevation of 160 meters above mean sea level. The station is located within the penthouse level of the building with gas sample lines extending from the station to an elevation of 4 meters above the top of the southeast corner of the building on a fixed tower. The sample inlet elevation is 110 meters above ground level. This site is located in the center of the city and is representative of the urban air quality. Dependent on the meteorological conditions, the air samples are representative of about a 1 to 10 km footprint of the urban ground level air emissions. As shown in the data collected in 1995, this site eliminates the canyon effects and single source emission effects associated with ground level urban sites.

**QA/QC Procedures for Network Operations during the Intensive**

*Field Study Command Center:*
The ground based air monitoring network for the 1999 SOS/Nashville intensive is managed by Kenneth J. Olszyna of TVA. Data files are provided daily by the network manager to the Nashville Intensive Command Center for display and use during briefings and planning meetings. The network manager also has the responsibility to conduct and review remote QA/QC tests, dispatch repair and maintenance teams, and provide replacement parts and instruments.
Standard Operating Procedures:

Data Collection:
Air quality and meteorological data is collected by a Campbell CR10 datalogger. The datalogger scan rate is a nominal 10 seconds. The signal averaging interval is 1 minute. All data is reported in local daylight time (LDT). On a daily basis, the air quality and meteorological data is downloaded, the QC data reviewed, and ambient data subjected to initial review for completeness, reasonableness, and quality. Instrument inspection and repair will be determined from the daily QC checks.

Quality Assurance:
Dynamic zero and span (gas addition) checks are conducted for the NOy, NO₂, NO, SO₂, and CO gas measurements between the hours of 0800 and 2200 hours. The lower gas addition concentration levels are approximately the midday median concentration. Daily zero, precision, and span checks, using gas substitution techniques, are conducted between midnight and 0600 hours for O₃, NOy, NO₂, NO, SO₂, and CO.

Quality Assurance Audits:
System audits are conducted by the SOS Science Team. Performance audits, adapted to test the customized monitoring systems employed by the Level 2 stations, are conducted using independent gas sources and dilution devices. Performance audits are conducted (witnessed) by either an EPA Region IV audit team, or by Tennessee and Kentucky state audit teams before the field study.

Calibrations:
Routine instrument calibrations are conducted at the beginning and end of the intensive study period. Non-routine calibrations are conducted after instrument adjustment, repair, or replacement. Calibrations are conducted through the sampling system inlets with calibration gases traceable to NIST standards.

Data Archival:
NARSTO will archive all air quality and meteorological measurements (including all QA/QC information) from the ground based air monitoring network for the 1999 Nashville field study, following validation and submittal by TVA. The data will be available for data analysis and for use in model validation.

Description of Sampling Procedures and Instrumentation
All stations consist of environmentally controlled shelters. The local meteorological measurements are made at the same elevation as the air sampling inlets. The Nashville
site is located atop the James K. Polk Building on the corner of Fifth and Deadrick Avenues in Nashville, Tennessee at a ground elevation of 160 meters above mean sea level. The station is located within the penthouse level of the building with gas sample lines extending from the station to an elevation of 4 meters above the top of the southeast corner of the building on a fixed tower. The sample inlet elevation is 110 meters above ground level. The Dickson County site, at an elevation of 225 meters above sea level, is located on Daniel Lane off Route 48 between Charlotte and Cumberland Furnace, TN, approximately 35 miles west of Nashville in an open pasture about 100 meters from the nearest wooded area. The sample inlet elevation is 10 meters above ground level.

Air samples for O₃, SO₂, and CO are collected through a common 3/8-in OD Teflon tube running from the sampling inlet head to a manifold located in the rear of the instrument cabinet. Individual _-in OD Teflon sampling lines, equipped with 5-μm Teflon particulate filters, are used to deliver air samples to their respective monitors. The O₃ Model 49, SO₂ Model 43S, and CO Model 48S monitors are obtained from TEII. The only modification to these three instruments are the bypassing of the internal sampling pumps. The exhaust of the instruments are joined together into a common vacuum line so that the total sampling line flow is measured.

Air samples for NO/NO₂ and NOₓ are each collected separately through 1/4-in OD Teflon sampling lines. The NO/NO₂ measurement system and the NOₓ measurement system each use a TEII Model 42S. The NO/NO₂ measurement system sampling line is split into a NO and NO₂ sampling mode. The NO₂ measurement mode consists of a photolytic cell, operated at ambient pressure and instrument sampling flow (about 1 lpm), to convert NO₂ into NO. The photolytic cell is illuminated with a 300-W Xenon lamp reflected off a dichroic mirror designed to reflect 350-450 nm wavelengths. An auxiliary flow control box and associated pump is used to maintain constant flow through the photolytic cell as the Model 42S alternates between the NO and NO₂ sampling modes. The NOₓ air sampling inlet system also contains a molybdenum converter to reduce NOₓ to NO; the converter is located external to the TEII Model 42S.

QA/QC Procedures for Specific Continuous Gas Measurements

A critical element in the operation of the enhanced ground monitoring network is the Quality Assurance/Quality Control Procedure (QA/QC). The QA/QC consists of the usual zero, span, and precision checks using gas substitution techniques and also includes procedures employing gas addition techniques. Gas substitution techniques involve the dilution of a source gas with clean dry air to generate a synthetic gas concentration mixture. This gas mixture is then introduced at the sample inlet at a gas flow in excess of the sampling flow rate. Thus the ambient air is substituted (replaced) with the synthetic gas mixture. The gas addition technique involves the addition of a known flow rate of the source gas into the ambient air sampling stream at the sampling inlet. Since the sampling flow rate is monitored, the gas addition (spike) concentration can be calculated. The gas addition technique determines matrix effects in the sampling system and allows the network manager to assess the data quality.
The calibration gases, as well as the gases used for daily QA/QC activities, are EPA Protocol SO₂, CO, NO, and NO₂ gas cylinders obtained from Scott Specialty Gases. The n-propyl nitrate (NPN) gas cylinder is obtained from Scott-Marrin. For the daily QA/QC activities, a Campbell CR10 data logger is programmed to automatically control the gas selection and concentration, sampling line selection, and the execution of the gas addition or gas substitution procedure. The site is equipped with a TEII 111 Zero Air generating system and a TEII 146 Dynamic Gas Calibrator. The CO catalytic reactor from the TEII Model 111 provides CO-free ambient air for the CO monitor. The QA/QC activities for specific gases are outline in Table 5 and described in more detail in the sections below.

**Ozone:**

Measurements for O₃ were conducted according to SLAMS protocol, modified to operate the O₃ instrument on the 0.2 ppmv full scale range. The O₃ concentrations for the daily span and precision checks for all stations are 160 ppbv and 40 ppbv which are 80% and 20% of the 200 ppbv instrument range. The internal ozonator in the TEII 146 was used to provide standard concentrations for the ozone precision and span checks.

**Gas Substitution:**

The daily zero, precision, and span checks for all gases will use the gas substitution technique. The execution of standard daily zero, span, precision checks are conducted during the night using gas substitution techniques, which allows for the daily check of station operations. The span value will be conducted at 80% of full scale value for each gas monitor. The precision value, except for O₃ (see above), will be based on the midday median concentration level. The selection of the approximate midday median concentration level as the precision value allows robust statistics to be generated for the ambient concentration levels that occur most frequently. The midday median concentration level is also the more representative value for the regional concentration level that is used in diagnostic air quality models.
### Table 5. List of Nominal Concentrations for Specific QA/QC Activities

<table>
<thead>
<tr>
<th>SITE</th>
<th>NASHVILLE</th>
<th>ALL OTHER STATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OZONE</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full Scale</td>
<td>200 ppbv</td>
<td>200 ppbv</td>
</tr>
<tr>
<td>ZERO Warning Limits (WL)</td>
<td>± 2 ppbv</td>
<td>± 2 ppbv</td>
</tr>
<tr>
<td>ZERO Control Limits (CL)</td>
<td>± 3 ppbv</td>
<td>± 3 ppbv</td>
</tr>
<tr>
<td>SPAN</td>
<td>160 ppbv</td>
<td>160 ppbv</td>
</tr>
<tr>
<td>SPAN; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>4% &amp; 8%</td>
</tr>
<tr>
<td>PRECISION</td>
<td>40 ppbv</td>
<td>40 ppbv</td>
</tr>
<tr>
<td><strong>NO\textsubscript{y}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full Scale</td>
<td>200 ppbv</td>
<td>50 ppbv</td>
</tr>
<tr>
<td>ZERO Warning Limits (WL)</td>
<td>+/- 0.5 ppbv</td>
<td>+/- 0.5 ppbv</td>
</tr>
<tr>
<td>ZERO Control Limits (CL)</td>
<td>+/- 1.0 ppbv</td>
<td>+/- 0.5 ppbv</td>
</tr>
<tr>
<td>SPAN with NO</td>
<td>160 ppbv</td>
<td>40 ppbv</td>
</tr>
<tr>
<td>SPAN with NO; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>10% &amp; 15%</td>
</tr>
<tr>
<td>SPAN with NPN</td>
<td>80 ppbv</td>
<td>20 ppbv</td>
</tr>
<tr>
<td>SPAN with NPN; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>10% &amp; 15%</td>
</tr>
<tr>
<td>PRECISION with NO</td>
<td>15 ppbv</td>
<td>5 ppbv</td>
</tr>
<tr>
<td>PRECISION with NPN</td>
<td>15 ppbv</td>
<td>5 ppbv</td>
</tr>
<tr>
<td>GPT (NO\textsubscript{x})</td>
<td>190 ppbv</td>
<td>45 ppbv</td>
</tr>
<tr>
<td>GPT; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>4% &amp; 8%</td>
</tr>
<tr>
<td>ADDITION NO LOW CONC</td>
<td>15 ppbv</td>
<td>5 ppbv</td>
</tr>
<tr>
<td>ADDITION NO HIGH CONC</td>
<td>160 ppbv</td>
<td>40 ppbv</td>
</tr>
<tr>
<td>ADDITION NPN LOW CONC</td>
<td>15 ppbv</td>
<td>5 ppbv</td>
</tr>
<tr>
<td>ADDITION NPN HIGH CONC</td>
<td>160 ppbv</td>
<td>40 ppbv</td>
</tr>
<tr>
<td><strong>SO\textsubscript{2}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full Scale</td>
<td>200 ppbv</td>
<td>100 ppbv</td>
</tr>
<tr>
<td>ZERO Warning Limits (WL)</td>
<td>+/- 0.3 ppbv</td>
<td>+/- 0.3 ppbv</td>
</tr>
<tr>
<td>ZERO Control Limits (CL)</td>
<td>+/- 0.5 ppbv</td>
<td>+/- 0.5 ppbv</td>
</tr>
<tr>
<td>SPAN</td>
<td>160 ppbv</td>
<td>80 ppbv</td>
</tr>
<tr>
<td>SPAN; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>10% &amp; 15%</td>
</tr>
<tr>
<td>PRECISION</td>
<td>10 ppbv</td>
<td>4 ppbv</td>
</tr>
<tr>
<td>ADDITION LOW CONC</td>
<td>5 ppbv</td>
<td>2 ppbv</td>
</tr>
<tr>
<td>ADDITION HIGH CONC</td>
<td>50 ppbv</td>
<td>20 ppbv</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full Scale</td>
<td>5000 ppbv</td>
<td>1000 ppbv</td>
</tr>
<tr>
<td>ZERO Warning Limits (WL)</td>
<td>+/- 300 ppbv</td>
<td>+/- 100 ppbv</td>
</tr>
<tr>
<td>ZERO Control Limits (CL)</td>
<td>+/- 500 ppbv</td>
<td>+/- 200 ppbv</td>
</tr>
<tr>
<td>SPAN</td>
<td>4000 ppbv</td>
<td>800 ppbv</td>
</tr>
<tr>
<td>SPAN; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>10% &amp; 15%</td>
</tr>
<tr>
<td>ADDITION LOW CONC</td>
<td>300 ppbv</td>
<td>200 ppbv</td>
</tr>
<tr>
<td>ADDITION HIGH CONC</td>
<td>4000 ppbv</td>
<td>800 ppbv</td>
</tr>
<tr>
<td><strong>NO/NO\textsubscript{2}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full Scale</td>
<td>200 ppbv</td>
<td>20 ppbv</td>
</tr>
<tr>
<td>ZERO Warning Limits (WL)</td>
<td>+/- 0.5 ppbv</td>
<td>+/- 0.2 ppbv</td>
</tr>
<tr>
<td>ZERO Control Limits (CL)</td>
<td>+/- 1.0 ppbv</td>
<td>+/- 0.3 ppbv</td>
</tr>
<tr>
<td>SPAN</td>
<td>160 ppbv</td>
<td>20 ppbv</td>
</tr>
<tr>
<td>SPAN; WL &amp; CL</td>
<td>4% &amp; 8%</td>
<td>20% &amp; 30%</td>
</tr>
<tr>
<td>PRECISION</td>
<td>1.0 ppbv</td>
<td>0.5 ppbv</td>
</tr>
<tr>
<td>GPT (NO)</td>
<td>30 ppbv</td>
<td>7 ppbv</td>
</tr>
<tr>
<td>ADDITION LOW CONC</td>
<td>1.0 ppbv</td>
<td>0.5 ppbv</td>
</tr>
<tr>
<td>ADDITION HIGH CONC</td>
<td>15 ppbv</td>
<td>5 ppbv</td>
</tr>
</tbody>
</table>
Consistent with standard operating procedures, warning limits and control limits are established. The warning limits and control limits will be 4% and 8%, respectively, of the span value for the Downtown station and O_3 instruments. The warning limits and control limits are 10% and 15%, respectively, for all the other gas monitors at the non-urban sites. Further details are given below.

Gas Phase Titration (GPT):

The converter efficiency for the Downtown station’s NOy instrument must be tested for high levels of NO_2 due to frequent impacts from morning rush hour traffic. The NO_2 concentrations are generated by GPT techniques using NO concentrations at 190-200 ppbv and using the O_3 setting that produces 160 ppbv O_3. The lower NO_2 concentrations at the other stations are generated also by GPT techniques using NO concentrations at 45-50 ppbv and using the O_3 setting that produces 40 ppbv O_3. The GPT process titrates 80% to 90% of the NO to NO_2 at all sites. In summary, the gas phase titration (GPT) procedure will use the 40 ppbv O_3 setting for all stations except Downtown Nashville which will use the 160 ppbv O_3 setting. These values will generate NO_2 concentrations that are 80% to 90% of the full scale range of the NO_x instrument.

Gas Addition:

Gas additions are conducted at approximately the midday median concentration level for CO, SO_2, NO, NO_2, and NOy (using NPN, n-propyl nitrate). Since this value is also used in the gas substitution technique, differences in the two techniques will indicate ambient sample matrix effects. Gas additions are also conducted at the span concentration levels. The high concentration NO gas addition to the NO sampling line is a system check for losses due to chemical reactions of NO with O_3 and other oxidants in the NO sampling line.

Gas additions of NO are conducted to each of the NOy and NO/NO_2 sampling lines. The NO gas addition to the NOy and NO/NO_2 sampling line provides a system check on the monitoring instrument performance during NO_2 and NOy sampling modes. This system check is necessary to verify the results of the NO_2 conversion efficiency tests using NO_2 and also to verify the NOy converter efficiency tests using NPN gas addition under ambient conditions. The NPN is used as a surrogate for gaseous HNO_3, which is the most difficult of the nitrogen oxides to reduce to NO. Since HNO_3 can represent the major fraction of NOy during the midday period, the NOy converter efficiency is continually checked with the NPN (three times a day). Since the NOy converter system check is conducted using NPN concentrations that represent the midday median NOy values, the NO gas addition to the NOy sampling line is also conducted at this concentration level.

The SO_2 concentration measurements from only the midday hours are used to determine the regional SO_2 levels. Therefore SO_2 addition occurs during the midday hours to determine if any ambient air matrix effects exist that would bias the observed concentrations.
The CO concentration measurements from the midday hours are important in the testing of air quality models since CO is used as a tracer for urban sources of O_3 precursors. CO is also involved in photochemical reactions producing O_3. Therefore CO addition also occurs during the midday hours to determine if any ambient air matrix effects exist that would bias the observed concentrations.

A catalytic converter is used to obtain CO native-zero ambient air measurement every two hours to correct for H_2O interference and to correct for instrument baseline instability. A second CO addition is used to check converter efficiency and overlaps one of the time periods that the CO native-zero ambient air measurements occur. Since this procedure will result in a loss of 30 minutes of ambient data collection, the second CO addition occurs during the late evening hours after the evening rush hour and prior to the nightly zero, span, and precision checks.

Assessments and Response Actions

Assessments activities in this project will be limited to those for Tasks 1a and 1b: Level 2 stations (2) operated during the summer of 1999, and NO/NO_y systems (2) operated at Dickson and Hendersonville in parallel with SCISSAP particle composition monitors for a period of 2 years (assuming funding for the second year of operations). The project manager will review all operational procedures for the Level 2 stations before and once during the period of operation. Performance audits of the instrumentation at the Level 2 stations will be conducted during their period of performance as described above. The TVA quality assurance manager will review the audits and the calibration procedures during the period of operation of the Level 2 stations. Any deviations from the standard operation procedures will be reported to, and discussed with the project manager.

Data Validation and Usability

All data to be reported to other SOS scientists and to EPA through the AIRS protocols will undergo four levels of validation as described below. All rejected data will be retained in an archive file but will not be reported to other investigators or to AIRS. The data validation procedures for the 1999 SOS/Nashville Level 2 stations operating during the field intensive consist of the following:

- Level 1 data validation - elimination of data that fall outside the monitoring instrument’s range.
- Level 2 data validation - elimination of data during the time periods that fail the quality control limits.
- Level 3 data validation - data review by the principal scientist for completeness, reasonableness, and quality.
- Level 4 data validation - intensive review of the final data set by the principal scientist before submittal to SOS Science Team. The level 4 data validation is needed for the research grade data that is obtained from the level 2 stations. The research
grade data is obtained after data manipulations are conducted as directed by the principal scientist. Identical data validation protocols will be used for the NO/NO$_y$ instruments operated at Dickson and Hendersonville for the longer period paralleling that of the SCISSAP samplers.

The detailed validation scheme to be used for the data is attached in the form of a control chart as Figure 2. Since the data is research grade quality collected during a relatively short duration period of the field intensive, the data validation scheme is designed to capture as much of the data as possible. Figure 2 shows the four decision points that could result in the data elimination. The first decision point is based on the results of the daily QC checks. The QC data are gas challenges using the gas substitution technique to determine the monitoring instrument and sample line malfunctions. Note that the data are eliminated only if the QC data indicate instrument malfunction or sample line leakage. If no changes are performed on the monitoring instrument or sample line during the period of missing QC data, then the data is not eliminated and the data validation procedure proceeds. The next decision point is based on the results of the daily QA checks. The QA data are gas challenges using the gas addition technique to determine sample line matrix effects. Unlike the QC data which provide clear cut decision, the QA data results are reviewed by the principle investigator (PI) to determine whether the data is to be eliminated or adjusted. The third decision point is station log entry. Data is eliminated whenever the station log entry indicates local activity that may affect the data. Final decision point is review of final ambient data by the principle investigator. Experience with ambient gas measurements is used to determine if the data is to be eliminated or archived as good or suspicious.

The final form of the database for both Tasks 1a and 1b will reported to and discussed with the SOS Science team at data analysis workshops, the first of which is expected to be held during the late spring or summer of 2000.

Reference

Figure 2. Data Validation for Level 2 Station Gas Species

NOTES:
QC Data = Gas Substitution
QA Data = Gas Addition; none for O3
Station Log = Comments by station operator on actions affecting data quality
Ambient Data = daily plots after all QC/QA and data eliminations are executed
Eliminate = Eliminate data between verified QC/QA times