SOS99NASH LEVEL 2 STATION DESRIPTION

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A. INTRODUCTION

TVA operated two enhanced (Level 2) surface-level monitoring stations during the 1999 Nashville/Middle Tennessee Field Study. 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. High-sensitivity, short time resolved (5-minute averaged concentrations) gas measurements include sulfur dioxide (SO₂), carbon monoxide (CO), ozone (O₃), nitrogen oxide (NO), nitrogen dioxide (NO₂), and total oxides of nitrogen (NO_Y). The meteorological measurement package includes wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), and solar radiation (RAD). These stations were operated in an automatic mode similar to the Level 2 station operations during the 1995 SOS/Nashville intensive.

B. MEASUREMENTS AND DATA ACQUISITION

This document describes the Quality Assurance / Quality Control procedures employed for the ground-based air monitoring network for the 1999 SOS/Nashville field intensive.

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

Performance audits consisted 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. These procedures include gas

challenges at the sample line inlets to determine the accuracy of the entire measurement system, not only the monitoring instrument.

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 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.

Accuracy of the measurement systems are determined from the enhanced performance audits and are shown below. 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 measurement accuracy is estimated in both per cent and concentration with the higher value representing the measurement estimated accuracy.

TABLE OF MEASUREMENT ESTIMATED ACCURACY

Species	Site	Percent	Concentration
O3	NASH	5 %	5 ppbv
O3	DICK	3 %	3 ppbv
SO2	NASH	8 %	0.5 ppbv
SO2	DICK	5 %	0.3 ppbv
CO	NASH	10 %	75 ppbv
CO	DICK	5 %	50 ppbv
NO	NASH	10 %	0.5 ppbv
NO	DICK	5 %	0.2 ppbv
NO2	NASH	15 %	1 ppbv
NO2	DICK	10 %	0.5 ppbv
NOY	NASH	15 %	1 ppbv
NOY	DICK	10 %	0.5 ppbv

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 indisputable evidence when this site is 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

Standard Operating Procedures:

A full description of the Level 2 network standard operating procedures (SOPs) can be found in section B of the report, SOS 1995 Nashville/Middle Tennessee Ozone Study, Volume II, Level 2 Network Operations Manual, prepared by the Tennessee Valley Authority, Environmental Research Center, Muscle Shoals, Alabama 35660.

Data Collection:

Air quality and meteorological data is collected by a Campbell CR10 data logger. The data logger scan rate is a nominal 10 seconds. The data logger signal averaging interval is 1 minute. The reported 5-minute averages are the average of the 1-minute recorded data. The NO-NOX analyzer performs a 7-second measurement average every 30 seconds for NO and NO2 but these measurements are not concurrent. Similarly the NOY data is also a 7-second measurement average taken every 30 seconds. The O3, SO2, and CO data are each recorded as the average of six consecutive 10-second measurement averages.

Quality Assurance Procedures:

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 gas addition lower concentration challenges are approximately the midday median concentration value. Daily zero, precision, and span checks, using gas substitution techniques, are conducted between midnight and 0600 hours for O₃, NO_y, 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 a Tennessee state audit team during the field study.

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 ½-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 instruments is the bypassing of the internal sampling pumps. The exhaust of the

instruments is joined together into a common vacuum line so that the total sampling line flow is measured.

Air samples for NO/NO₂ and NO_y are each collected separately through $\frac{1}{24}$ -in OD Teflon sampling lines. The NO/NO₂ measurement system and the NO_y 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 NO_y air sampling inlet system also contains a molybdenum converter to reduce NO_y to NO; the converter is located external to the TEII Model 42S and at the sample line inlet probe.

QA/QC Procedures for Specific Continuous Gas Measurements

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 every two hours to correct for H₂O interference and to correct for instrument baseline instability.

GAS SUBSTITUTION:

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.

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 NO₂ concentration at about 160 ppbv is generated for the Downtown station by GPT techniques. Lower NO₂ concentration at about 80 ppbv is generated also by GPT techniques at the Dickson station. The GPT process titrates 80% to 90% of the NO to NO₂ at both sites.

GAS ADDITIONS:

Gas additions are conducted at approximately the midday median concentration level for CO and SO₂. Gas additions of NO, NO₂, and NPN are conducted to each of the NOy and NO/NO₂ sampling lines. The NPN is used as a surrogate for gaseous HNO₃, which is the most difficult of the nitrogen oxides to reduce to NO. Since HNO₃ 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). The SO₂ and CO gas additions occur once during the midday hours to determine if any ambient air matrix effects exist that would bias the observed concentrations. Further details are given below.

List of Nominal Concentrations for Specific QA/QC Activities

SITE	NASHVILLE	DICKSON
OZONE		
Full Scale	200 ppbv	200 ppbv
ZERO Warning Limits (WL)	± 2 ppbv	± 2 ppbv
ZERO Control Limits (CL)	± 3 ppbv	± 3 ppbv
SPAN	160 ppbv	160 ppbv
SPAN; WL & CL	4% & 8%	4% & 8%
PRECISION	40 ppbv	40 ppbv
NO_{v}		
FULL SCALE	200 ppbv	100 ppbv
ZERO Warning Limits (WL)	+/- 0.5 ppbv	+/- 0.3 ppbv
ZERO Control Limits (CL)	+/- 1.0 ppbv	+/- 0.5 ppbv
SPAN with NO	160 ppbv	80 ppbv
SPAN NO; WL & CL	4% & 8%	10% & 15%
PRECISION	10 ppbv	20 ppbv
ADDITION GAS CONC	80 ppbv	80 ppbv
SO_2		
FULL SCALE	200 ppbv	100 ppbv
ZERO Warning Limits (WL)	+/- 0.3 ppbv	+/- 0.3 ppbv
ZERO Control Limits (CL)	+/- 0.5 ppbv	+/- 0.5 ppbv
SPAN	80 ppbv	80 ppbv
SPAN; WL & CL	5% & 10%	5% & 10%
PRECISION	10 ppbv	20 ppbv
ADDITION GAS CONC	12 ppbv	12 ppbv
CO		
FULL SCALE	5000 ppbv	2000 ppbv
ZERO Warning Limits (WL)	+/- 300 ppbv	+/- 100 ppbv
ZERO Control Limits (CL)	+/- 500 ppbv	+/- 200 ppbv
SPAN	3000 ppbv	800 ppbv
SPAN; WL & CL	4% & 8%	10% & 15%
PRECISION	400 ppbv	400 ppbv
ADDITION GAS CONC	500 ppbv	200 ppbv
NO/NO2		
FULL SCALE	200 ppbv	100 ppbv
ZERO Warning Limits (WL)	+/- 0.5 ppbv	+/- 0.2 ppbv
ZERO Control Limits (CL)	+/- 1.0 ppbv	+/- 0.3 ppbv
SPAN	160 ppbv	80 ppbv
SPAN; WL & CL	4% & 8%	10% & 15%
PRECISION	10 ppbv	20 ppbv
ADDITION LOW CONC	10 ppbv	10 ppbv
ADDITION HIGH CONC	80 ppbv	80 ppbv

D. DATA VALIDATION AND USABILITY

The data validation procedures for the 1999 SOS/Nashville Level 2 stations operating during the field intensive are described in the form of a control chart as shown below. 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.

E. REFERENCE

SOS 1995 Nashville/Middle Tennessee Ozone Study, Volume II, Level 2 Network Operations Manual, prepared by the Tennessee Valley Authority, Environmental Research Center, Muscle Shoals, Alabama 35660, 1995.

