APPENDIX B

QUALITY ASSURANCE

B. QUALITY ASSURANCE

Purpose is to provide a quantitative estimate of the uncertainty of the measurements through estimates of the precision, accuracy (or bias) and validity. QA ensures that the procedures and sampling methods used in the study are well documented and are capable of producing the data which meet the specifications for the study.

Quality assurance will be under the overall direction of the QA manager who will coordinate a QA team. The team will consist of the QA manager and sponsoring agencies that have the necessary expertise. The QA manager and team will be responsible for developing a QA plan for the study, reviewing standard operating procedures, performing systems and performance audits, reviewing and validating study data processing procedures and data, and estimating the uncertainties in the data. The QA team will work closely with the data manager, the field manager, and investigators. The QA manager should be selected early and should be an integral member of the planning team. The QA manager should coordinate with and be assisted by the audit staff members of the air quality agencies in the study area to assure that measurements are based on the same standards.

Once the sampling has been completed and the investigators have provided the data management contractor with a clean data set, the QA team helps validate the data in two stages, Level 1 (univariate checks such as maxima and minima, rates of change, and diurnal variations) and Level 2 (multivariate consistency tests based on known physical, spatial, or temporal relationships). The QA team also makes the final estimates of the precision and accuracy of the data with the help of the investigators and the data manager.

Quality auditing tasks can be performed both by contractors and by the QA staff of the sponsoring organizations. The QA manager bears overall responsibility for ensuring that the quality auditing tasks are performed by members of the QA team. The major tasks are summarized below.

Overall:

- Manage the overall QA activities. Interact with the field manager and the principal investigator and provide feedback to them concerning the status of unresolved QA problems and the potential for their resolution.

Before field operations begin:

- Work with investigators to determine whether each measurement method is likely to meet its specifications for accuracy (or bias) and precision.

- Review the SOPs for each measurement and verify the assumptions on which they are based.

- Prepare systems audit procedures.

- Perform preliminary systems audits at investigators' analytical laboratories, paying particular attention to calibration methods.

- Develop performance audit procedures for measurements for either accuracy (i.e., compared to established standards) or, where that is not possible, for bias (i.e., compared to another co-equal laboratory's measurements).

- Arrange for investigators' calibration standards to be checked against EPA, ARB or other standards.

- Audit transfer standards.

- If not all field sites are to be audited, develop a priority system indicating which field sites and which laboratories should be audited during or just prior to field measurements.

- Immediately prior to field operations, carry out performance audits of the continuous gas analyzers and flow measuring instruments at the chosen field sites.

During field operations:

- Perform systems audits on field and laboratory measurements and data processing procedures. Field air quality measurement sites, sampling aircraft, upper air sites, and meteorology sites should be audited.

- Perform systems audits for the data processing and data management operations of the measurement and data management contractors.

- Coordinate performance audits on routine measurements. Arrange for or perform those audits not done by the sponsoring organizations.

After field operations:

- Prepare reports of the audits.

- Work interactively with the data management contractor in the on-going Level 1 and Level 2 validation of the data.

- Work with investigators to determine the accuracy (or bias) and precision for each measurement value and prepare a report summarizing the uncertainties in the study data.

A quality assurance plan specifies the activities associated with the CCOS quality assurance program, schedules, and responsibilities. The following sections describe elements of the Quality Assurance Plan.

B.1 Quality Assurance Overview

The primary purpose of the quality assurance (QA) tasks is to provide a quantitative estimate of the uncertainty of the measurements through estimates of the precision, accuracy (or bias), and validity. In addition, QA ensures that the procedures and sampling methods used in the study are well documented and are capable of producing data which meet the specifications of the study. Quality assurance is intimately connected with data management. Before sampling starts, the QA team assists the investigators and the data management contractor to develop the format of the database; the QA team also reviews the investigators' standard operating procedures (SOPs) and makes estimates of the precision and accuracy that might be expected from the measurement systems. Prior to or during sampling the QA team carries out quality audits and helps resolve any problems.

The quality assurance program includes two types of activities: quality control (QC), and quality auditing (QA). The QC activities are on-going activities of the measurement and data processing personnel. QC activities consist of written standard operating procedures to be followed during sample collection, sample analysis, and data processing. These procedures define schedules for periodic calibrations and performance tests (including blank and replicate analyses). They specify pre-defined tolerances which are not to be exceeded by performance tests and the actions to be taken when they are exceeded. The QC activities also include equipment maintenance, and acceptance testing, and operator training, supervision, and support.

Quality auditing consists of two components: systems audits and performance audits. Systems audits include a review of the operational and quality control (QC) procedures to assess whether they are adequate to assure valid data which meet the specified level of accuracy and precision. After reviewing the procedures, the auditor examines phases of the measurement or data processing activity to determine whether the procedures are being followed and that the operating personnel are properly trained. The system audit is a cooperative assessment resulting in improved data. Performance audits establish whether the predetermined specifications for accuracy are being achieved in practice. For measurements, the performance audit involves challenging the measurement/analysis system with a known standard sample that is traceable to a primary standard. Performance audits of data processing involve independently processing samples of raw data and comparing the results with reports generated by routine data processing. The specialized nature of some measurements (e.g., hydrocarbon speciation, carbonyl compounds, PAN, NOy, ozone lidar, upper air meteorology) preclude simple performance audits for these measurements. Intercomparison studies are typically used to assess the representativeness, accuracy, and precision of these measurements.

B.2 Data Quality Objectives

Data quality objectives should be specified prior to the study to ensure that all measured data meet the end-use requirements for air quality and meteorological model input and evaluation, data analyses, and monitoring the success of meeting data quality objectives. Precision and accuracy goals are identified for measurement variables. Many methods and procedures employed in CCOS are routinely measured variables for which expected precision and accuracy are known. Other measurements are experimental and target objectives can only be estimated.

In evaluating precision and accuracy objectives, it is important to consider the methods used to determine the values. For example, a greater deviation may occur between replicates with real samples with complex matrices than with replicates of standards in simple matrices. Synthetic mixtures of hydrocarbons that are used in the Photochemical Assessment Monitoring Station Program is an example. An ambient sample yields a more complex chromatogram and greater potential for inconsistent identification. Analysis of a standard mixture of hydrazones does not address potential sampling artifacts that may be associated with carbonyl compound measurements using the DNPH derivitization method.

Precision and accuracy targets are commonly based on relative percent differences. Precision is either based on a relative percent difference between replicates (analytical precision) or duplicate samples (method precision) as follows:

100 * (rep1 - rep2)/(rep1 + rep2)/2

The standard deviation of the average of a group of replicate (or duplicate) pairs represents the precision for a measurement parameter. For accuracy, percent difference is determined relative to a known or target value and is as follows:

100 * (observed - target)/target

The objective may be a standard of known concentration or an audit value independently obtained or prepared by the QA team. For some parameters, standards of known concentration are not easily obtained or cannot be accurately prepared for use in the field, and accuracy can only be checked against an independent method that is believed to be either without bias, has a known bias that can be accounted for, or a method that has been used historically. Accuracy determined in this manner is considered a test of equivalency and not true accuracy.

After an audit, data flags are reported immediately to the field operations manager and to the appropriate contractor to ensure rapid implementation of corrective action by the measurement group. Tasks Performed by the Quality Assurance Manager

Specify tasks to be performed by the QA manager before, during and after the field study

B.3 Systems Audits

B.3.1 Field Systems Audits for Surface Monitoring Sites

Prior to the start of the field study, the auditing team obtains pertinent forms and documents, their latest revisions, and information needed to perform the audits. These forms and documents include SOPs, instrument manuals, logbooks, chain-of-custody records, data sheets, control charts, and maintenance records. The auditor verifies that each of these forms and documents is available at the field site. If out-of-date documents are identified at the field site, recommendations for replacement are made in the systems audit report. Calibration records, performance test tracking charts, and maintenance records are examined to determine that the tasks were being performed on the schedules specified in the SOP. Contents of logbooks and checklists are examined to determine that the field documentation procedures were being

followed. The auditor examines the site description, field documentation, SOPs, spare parts, and supplies, and performs a general instrument inspection. The QA manager coordinates review of the latest revision of field SOPs and ensures that each auditor has the most recent version prior to systems audits. The auditor independently evaluates the siting of measurement platforms to document relevant characteristics that might affect the measurement at a particular location. An inspection of measurement devices and evaluation of their condition with respect to obtaining a quantitative measurement is also part of each system audit. The audit examines the relationship among different instruments and their conformity with requirements at each site. The instrument serial numbers and model numbers are compared with those recorded in the project records as being present at each site. Sample lines are examined for dirt or obstruction. Leads from each instrument to data acquisition system are examined to ensure that they are connected to the proper channels. Inconsistencies with project records are reported, and recommendations for site modification are made by the QA manager.

B.3.2 Field Systems Audits for Aircraft Platforms

Aircraft systems audits are similar to surface systems audits. A systems audit questionnaire is completed by the auditor for each aircraft. The auditor reviews the type of measurements that are actually being performed relative to those specified in the most recent work plan. The level of documentation of quality control checks, instrument logs, etc., are examined. Results of calibration records and performance tests are evaluated. The auditor records pertinent information relative to the sampling system to form an independent documentation of conditions as they existed during the audit.

B.3.3 Laboratory Systems Audits

Laboratory analysis and data processing activities are audited in this procedure. The laboratory systems audit examines the procurement and acceptance testing of sampling substrates, laboratory documentation, SOPs, laboratory instrumentation, spare parts, and supplies. A traceability audit randomly selects a single data value for each observable from a recent data report and tracks the documentation and traceability to standards associated with that value. This traceability audit determines how well each of the individual procedures was integrated to produce valid data values.

B.4 Performance Audits

B.4.1 Field Performance Audits of Surface Monitors

Quantitative transfer standards are used during field performance audits to determine the percent difference between the field measurements and the standard (i.e., to estimate the accuracy of the measurement). The difference should meet the acceptance criteria defined by the quality assurance objectives. Otherwise, reasons for exceeding acceptable levels are sought, and recommendations are made for eliminating the problem and adjusting or flagging data as necessary.

Ozone. A calibrated transfer standard with an internal ozone generator is used to generate five standard ozone concentrations and one zero level concentration to audit the

instruments. Corresponding concentrations are recorded from each instrument and compared. A linear regression of measured versus audit results is calculated to determine baseline offsets and linearity of response. The in-station performance test gases are verified against the certified NIST standards. The audit includes a comparison of values taken from the instrument display, the strip chart recorder, and the data acquisition system.

Standard and High-sensitivity NO/NOx and NO/NOy. A calibrated audit system used to challenge the standard sensitivity instruments consists of zero air, NIST-traceable NO gas in a cylinder, and an ozone generator. At least three NO concentrations and a zero are introduced to the instrument, and the response of the data acquisition system and the instrument are recorded. Audit NO2 is produced by gas-phase titration and introduced to the analyzer for at least five different concentrations. Audit versus site differences are determined, and a linear regression of site versus audit results is calculated to determine baseline offsets and linearity of response. In addition, site test gases are verified against the audit standard.

PAN and NO2. This audit involves the use of a calibrated audit system consisting of zero air and a NIST-traceable low concentration NO2 gas cylinder. These standards can be unstable with time, and precautions need to taken into account for any degradation that occurs during the audit process. At least three NO2 concentrations and a zero are introduced to the instrument, and the response of the data acquisition system and the instrument is recorded. Audit versus site differences are determined, and a linear regression of site versus audit results is calculated to determine baseline offsets and linearity of response. In addition, site test gases are verified against the audit standard. Since NIST transfer standards do not exist for PAN, collocated measurements using a gas chromatograph with electron capture detection (GC/ECD) may be used for comparison. PAN is thermally unstable, even at room temperature, and thus difficult to calibrate. This difficulty can lead to discrepancies between field measurements that are difficult to resolve without further laboratory studies. One advantage of the LPA-4 PAN analyzer is that the instrument can be calibrated in the field with NO_2 rather than the thermally unstable PAN. Level 2 validation of the PAN data includes correlation and time series of PAN values compared to NOy, NOz, and NO/NO_2 ratios.

B.4.2 Field Performance Audits for Surface Meteorological Measurements

This audit includes the variables of wind direction, wind speed, temperature, relative humidity, and solar radiation. These procedures generally are performed by both auditor and site operator, since several of these procedures require readings to be made in the instrument shelter while someone is on the meteorological tower. Safety considerations also require the presence of an additional person whenever someone ascends the tower. Audit values are compared with instrument displays (when available), stripchart output, and data acquisition system output. In this way, the entire measurement system is audited, and the causes of exceedances of the acceptance criteria can be isolated. The following paragraphs summarize the audit procedures.

Wind Direction. Distance sighting targets are determined for each site. Where possible, these targets are measured with a stable sighting compass on a nonmagnetic tripod and corrected for declination. The operator ascends or cranks down the tower and aligns the point and tail of the wind vane toward these targets while the auditor records the output in the shelter.

Differences between true and measured direction are recorded. Vane starting thresholds are checked using a starting torque watch.

Wind Speed. The anemometer cups are temporarily replaced by synchronous motors, and the equivalent wind speed displayed by the anemometer is compared with the speed corresponding to the rotation rate as supplied by the manufacturer. Anemometer starting thresholds are checked from a torque measurement using a gram scale applied at a measured distance from the axis of rotation.

Temperature. An aspirated thermometer traceable to standards from the NIST is placed adjacent to each temperature-sensing device, and the two readings are compared. The resistance of temperature-sensing units is compared to the NIST-traceable thermometer. When feasible, two sets of readings are taken to cover a wide range of readings.

Relative Humidity. An aspirated psychrometer using NIST-traceable thermometers is operated at the level of the relative humidity sensor. Relative humidity based on the psychrometer readings is determined and compared to the instrument value.

Solar Radiation. An audit pyranometer is zeroed and readings are taken with the audit instrument placed next to the station pyranometer. A comparison is made between the hourly average readings of the two instruments.

B.4.3 Field Performance Audits for Upper-Air Meteorology

Field audits for upper-air meteorological measurements form surface-based platforms are particularly challenging, and special techniques are needed. For systems, ground truthing of set-up conditions (surface wind, pressure, and temperature) is performed similar to the standard surface meteorology audit procedures described above. In addition, for Doppler acoustic sounders and radar profilers, performance audits are accomplished using collocated audit tethersondes, radiosondes, and/or instrumented aircraft (flying nearby spirals). The Quality Assurance Plan for CCOS will need to provide more specific quality assessment and data validation procedures.

B.4.4 Field Performance Audits for Aircraft Platforms

Quantitative transfer standards, similar to those used for the performance audits of the surface-based monitors, are used to challenge each measurement system aboard the aircraft platform. Results of each audit are compared to acceptance criteria and values that exceed the criteria are flagged. Immediately following the audit, the auditors provide a verbal report of the audit to the appropriate aircraft supervisor. During the verbal report, values and equipment problems are discussed in terms of possible reasons for the discrepancies and corrective action to be taken. If corrective action is implemented, the audit is repeated.

B.4.5 Laboratory Performance Audits for Chemical Analysis

Laboratory performance audits for CCOS will consist of the submission of blind performance evaluation samples of known concentrations and/or interlaboratory comparisons of samples for measurements of individual and total hydrocarbons and carbonyl compounds.

Experiences from previous field studies demonstrate that measurements of ambient hydrocarbon speciation are not routine, and that the quality and completeness of measurements vary among different laboratories using essentially the same samplers and analytical instrumentation (Fujita et al., 1994). Potential problems include: positive and negative artifacts due to effects of sampler and sampling media; incomplete resolution or loss of C_2-C_3 hydrocarbons due to introduction of excessive moisture in the column or improper sample loading and injection; underreporting of true concentrations due to selection of incorrect integration threshold; loss of material in the analytical system due to poor chromatographic technique (particularly for very light and heavy hydrocarbons) or prolonged storage in canisters prior to analysis (especially for olefins and some aromatics); incorrect or incomplete peak identification due to limitation of peak identification software, especially for compounds that exist in lower concentrations and elute in a crowded segment of the chromatogram; systematic bias due to calibration problems; and variable measurement of true total NMHC among laboratories due to variation in analytical method and data processing (e.g., use of Nafion® dryer, inclusion or exclusion of oxygenated compounds in total NMHC). Interlaboratory comparisons using ambient samples are required to fully assess these problems. Also the need to measure VOC species that are not currently quantified in the PAMS program (semi-volatile hydrocarbons and oxygenated compounds) should be evaluated with respect to the goals of CCOS. For example, MTBE is a major component of ambient VOC in areas where this compound is the primary oxygenated compound in reformulated gasoline (RFG) and higher molecular weight carbonyls are relatively more abundant in downwind receptor areas. MTBE may serve as a useful marker for motor vehicle emissions and higher carbonyls have important implications for photochemical modeling.

The sampling and analytical parameters that affect the accuracy and validity of measurements of carbonyl compounds by the 2,4-dinitrophenylhydrazine-impregnated cartridge technique (TO-11) are not completely resolved and are currently under extensive study and scrutiny by EPA and the scientific community (NARSTO-NE: field comparison in Agawam, MA, SOS: formaldehyde intercomparison at Boulder, CO, field measurement comparison in Nashville, TN). Relevant parameters include the substrate (type, DNPH loadings, blank levels, and variability), sampling conditions (ambient ozone concentrations, temperature, relative humidity, sample volume measurements, breakthrough, type of sampling line and ozone scrubber), sample storage, and handling (exposure to light and heat, type of storage and duration of storage), sample preparation and analysis (extraction efficiency and instrument calibration, peak resolution).

Each of the air pollution control districts in central California that have PAMS networks participate in performance audit programs run by the EPA and by the California Air Resources Board. Both the federal and state performance audits for hydrocarbons involve analysis of a standard mixtures of target compounds on an annual basis during the PAMS measurement season. Carbonyl audits involve laboratory analysis of standard extracts of selected hydrazones. While these audits can document possible systematic calibration biases, they do not address a number of other potential problems that can affect the accuracy of analytical results.

The following quality assessment tasks should be completed prior to the CCOS field study in order to resolve these issues.

- The ARB should conduct expanded performance audits of the district hydrocarbon measurements during the summer of 1999. In addition to the synthetic audit mixtures, the expanded performance audit should also include a set of ambient samples consisting of both urban, mobile source dominated samples and downwind, aged air samples. In addition to the ARB laboratory, one other laboratory (possibly EPA-AREAL) should participate in the interlaboratory comparison. A similar interlaboratory comparison should be conducted in 2000 prior to the CCOS episodes. This comparison should include the contractor that is selected to provide supplemental VOC measurements.

- Review and summarize the results of past EPA and ARB performance audits of the PAMS programs in southern California. Summarize the problems that were identified and corrective actions that have been taken.

- Review the results of on-going hydrocarbon interlaboratory and performance audit programs during NARSTO-Northeast and SCOS97-NARSTO

- Review recently completed and on-going laboratory evaluations and intercomparisons for carbonyl measurements by Method TO-11.

- Incorporate these tasks in the quality assurance plan for CCOS and include results in the final QA report for the CCOS field measurement program.