APPENDIX V

MATES V

FINAL REPORT

Quality Assurance and Quality Control for Monitoring and Analysis

DISCLAIMER

Any or all reference made in this Appendix to a specific product or brand name does not constitute an endorsement of that product or brand by the South Coast Air Quality Management District.

Appendix V

Quality Assurance and Quality Control for Monitoring and Analysis

V.1. INTRODUCTION

This appendix, in association with the sampling and analysis detail provided in Appendix III of this report, describes the objectives, procedures, documentation, and data review techniques that were used by the South Coast AQMD to assure that MATES V produced data that met or exceeded the accepted criteria for its intended use.

V.1.1 Quality Assurance and Quality Control Background

South Coast AQMD is committed to achieving high quality data that meets the objectives for the MATES program, as well as other environmental monitoring programs. The South Coast AQMD is designated by U.S. EPA, with primary responsibility for air monitoring and data quality under its jurisdiction.

V.1.1.1 Quality Management Plan (QMP)

The South Coast AQMD Quality Management Plan (QMP[1]), approved by U.S. EPA in 2017 (South Coast AQMD, 2016; see Section V.4, References), is the foundational document describing the agency's quality management system for air monitoring and laboratory analyses. It outlines quality assurance goals, policies, procedures, lines of authority, organizational responsibilities, evaluation, and reporting requirements. It is South Coast AQMD policy that sufficient quality assurance activities are conducted to demonstrate that data collected by and on behalf of South Coast AQMD are scientifically and legally valid for the purposes to which they are intended.

Quality Assurance (QA) encompasses all measures taken by management and staff to ensure that the quality of a finished product meets the regulations and standards of the organization and program. Major QA functions include review and oversight of most aspects of a measurement program, including planning documents, training, records, and procedures, as well as independent audits of sampling equipment, field instruments and performance tests of laboratory analyses.

Quality Control (QC) encompasses all the direct actions taken to achieve and maintain a desired level of quality for a given product. From an environmental monitoring perspective, QC includes all the measures taken by project managers and field, laboratory, and data management personnel to achieve a predetermined level of data reliability. QC is applied from the planning and design stages of the monitoring effort, through the implementation stages, to the handling, storage and reporting of accumulated data.

[1] The South Coast AQMD Quality Management Plan, Quality Assurance Project Plans (QAPPs) and related Standard Operating Procedures (SOPs) are available upon request through the South Coast AQMD Monitoring and Analysis Division, Quality Assurance Branch.

V.1.1.2 Quality Assurance Project Plans (QAPPs)

Quality Assurance Project Plans (QAPPs) describe the quality control, quality assurance, training, records management, measurement objectives, assessment activities, and other related technical activities for a project or program to ensure data is of a known and verifiable quality meeting its intended purpose. QAPPs also describe the responsibilities within the organization for carrying out each program component. They are intended to be sufficiently complete and detailed to ensure that data meet programmatic Data Quality Objectives (DQOs). The DQOs consider the program or project goals and the types of decisions that the data is intended to address by the end users. QAPPs include Standard Operating Procedures (SOPs) and Operational Assistance Guides (OAGs), which are the specific directions for performing sampling, monitoring, and analytical activities. This includes field monitoring operations, support (e.g., maintenance, repairs, calibrations), lab analyses, and independent audit activities. The QAPP documents list the QA and QC requirements for each activity and provide instructions for data review and validation, QA oversight and audits, and the corrective action process that is used to document issues that may have significant or repeated adverse impacts on data quality, completeness or safety, including the issue's resolution and recurrence minimization.

The QAPPs describe the Data Quality Indicators (DQIs) that are determined to ensure that the data is of known and defensible quality and available in a timely manner to meet the DQOs. DQIs typically include precision, accuracy/bias, completeness, representativeness, sensitivity, and comparability. Precision is a quantitative measure of how reproduceable the data are. Accuracy/bias is a quantitative measure of how well the measurements reflect what is actually in the sample. Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected. Representativeness, related to program site, instrument and method selection, is a measure of the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Comparability is a measure of the confidence with which one data set or method can be compared to another. Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of a variable of interest.

Measurement Quality Objectives (MQOs) are the acceptance or performance criteria for individual DQI's. QAPPs, along with the associated Standard Operating Procedures (SOPs) or Operational Assistance Guides (OAGs), are designed to document and control the various phases of the measurement process (e.g., preparation, sampling, and analysis) to ensure that the total measurement uncertainty is within the range prescribed by the MQOs. For MATES, the MQOs are based upon comparable measurements from ongoing federal and South Coast AQMD measurement programs, using the quality goals, QA/QC activities and procedures described in South Coast AQMD QAPPs.

The quality goals and QA requirements for gaseous and particle pollutants measured during MATES V are found in the various QAPP documents, as outlined below.

National Air Toxics Trends Stations (NATTS) Program

The MATES V quality goals and QA/QC activities for monitoring ambient levels of volatile organic compounds (VOCs), carbonyls, hexavalent chromium, and polycyclic aromatic hydrocarbons (PAHs), and some metals were adopted from the U.S. EPA National Air Toxics Trends Stations (NATTS) program. The South Coast AQMD NATTS QAPP (South Coast AQMD, 2013a) was last revised in 2013 and is currently under revision to incorporate the October 2016 U.S. EPA revised NATTS Technical Assistance Document (TAD; U.S. EPA 2016) and other recent changes to program elements that have been implemented by South Coast AQMD.

Chemical Speciation Program

The MATES V quality goals and QA/QC activities for monitoring and analyzing the components of fine particulate matter ($PM_{2.5}$), including Organic and Elemental Carbon (OC/EC), Anions and Cations, and trace metals, were adopted from the U.S. EPA CSN program. The requirements can be found in the South Coast AQMD $PM_{2.5}$ Chemical Speciation Program QAPP (South Coast AQMD, 2014), which was last approved by the U.S. EPA Region 9 in May 2014. This QAPP is also under review by staff for revision to more fully incorporate both the U.S. EPA CSN Program, where analyses are done by national contract laboratories, and the South Coast AQMD supplemental chemical speciation program, where analyses are done by the South Coast AQMD laboratory (as done for MATES).

Criteria Pollutant Monitoring Program

The MATES V quality goals and QA/QC activities for monitoring and analyzing TSP-Lead (Pb) and PM2.5 fine inhalable particle mass were adopted from the U.S. EPA Criteria Pollutant Monitoring Program. These requirements can be found in the South Coast AQMD Criteria Pollutant Monitoring Program QAPP, which, at the time of the MATES V monitoring, had been last revised in 2016. It was recently revised again in April 2020 to incorporate revised programmatic elements and guidance, including the updated U.S. EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. II, Ambient Air Quality Monitoring Program (U.S. EPA 2017a,b). This latest QAPP revision was approved by U.S. EPA Region 9 in July 2020.

Special Monitoring Program

The South Coast AQMD Special Monitoring program provides air quality measurements in response to events such as wildfires, localized air quality concerns, and pollutants from local sources which also includes rule compliance and rule development monitoring. The MATES V quality goals and QA/QC activities for monitoring and analyzing ultrafine particles (UFPs) and black carbon (BC) can be found in the South Coast AQMD Special Monitoring QAPP (South Coast AQMD, 2013b), which describes the standardized practices and procedures followed by South Coast AQMD for monitoring other "non-criteria" pollutants and performing local-scale or facility focused measurement studies. The current version of this QAPP was last revised in 2013 and reviewed by U.S. EPA in August 2014. The Special Monitoring QAPP is undergoing incorporation into a new QAPP for Special Monitoring and AB 617 Community Air Monitoring Programs. As of this writing, this QAPP is under internal review.

V.1.2 Glossary of Quality Assurance Terms

Accuracy/Bias
A determination of how closely reported data values are to true values. Annually conducted performance audits challenge the various samplers and instruments used in this program to assess their accuracy. All valid program data accepted as valid satisfy the criteria set forth in the representative QAPP and SOPs. Accuracy is expressed as "percent" deviation from true and is calculated as follows:

$$\text{Percent Deviation from True} = \frac{\text{Indicated Value - True Value}}{\text{True Value}} \times 100$$

Collocated Sampling
The process of running two identical samplers concurrently at the same location. Collocated data measures a method's precision. One of the samplers is designated *A* and is treated as the true value; while the other sampler is designated *B* and is regarded as the indicated value.

Data Completeness (DC)
The percent of valid data points actually collected out of the total number of data points possible. The data completeness objectives for the MATES V program. DC is calculated using the following formula:

$$\text{Percent DC} = \frac{\text{Total valid data points}}{\text{Total number of planned data points}} \times 100$$

Data completeness for discrete sampling of air toxics for MATES V, including VOCs and PM metals, is informed by the South Coast AQMD NATTS QAPP, along with the current NATTS TAD (U.S. EPA 2016). A valid sample is one that was collected, analyzed, and reported without null flags, including make-up samples. Note that samples below the MDL that are valid are included as complete. The measurement quality objective for air toxics for annual sample collection completeness is that ≥ 85% of the scheduled annual air samples on a 1-in-6-day sampling schedule must be valid, equivalent to 52 of the annual 61 expected samples (51 during years when there are only 60 collection events). Invalidation of data beyond this threshold triggers a corrective action process to review the cause and to improve sampling, quality control, or analysis procedures, as needed.

For MATES V continuous data (i.e., BC, UFP, meteorology), the Special Monitoring and Criteria Pollutant QAPPs specify a 75% completeness goal of all possible hourly measurements. The continuous measurements for MATES V greatly exceed the 75% goal.

Performance Evaluation
An instrument audit procedure conducted to establish individual analyzer and overall sampling and analysis accuracy. Probe audits are used to measure the integrity of both the sampling and analysis systems. Flow audits measure the accuracy of the flow metering devices that assure the sample's temporal representativeness. Gas standard audits

determine accuracy of laboratory analyzers in measuring known concentrations of toxic compounds.

Performance Test (PT)
A procedure from which data collected by execution of a particular test method to analyze samples containing a known amount of an analyte is used to assess compliance with a data quality objective. This is typically performed on but not limit to laboratory analyses performed in support of the NATTS program.

Precision
The measure of monitoring system repeatability. Precision is determined by amassing a variety of measurements of the same true value over a period of time and assessing the variability of those measurements.

Quality Assurance (QA)
The practice of establishing procedures external to the day-to-day monitoring operations that indicate whether air quality data is accurate, representative, precise, and complete enough to satisfy the needs of the data users. QA activities include, but are not limited to, system and performance evaluation audits and collocated and parallel sampling.

Quality Control (QC)
Any procedure incorporated into the internal, day-to-day operations of collection and analysis of samples to satisfy the data user's need for valid data.

Representativeness
The goal that samples are representative of both temporal and/or spatial scales at all sites. This is accomplished by conforming to 40CFR58 siting and sampling requirements.

System Audit
An inspection and review of the monitoring program, typically including training, records management, instrumentation, data flow and problems that can impact data quality or completeness.

V.2. MATES V Quality Assurance Activities

MATES V monitoring was accomplished with discrete 24-hour samples, except for the continuous black carbon (BC), Ultrafine Particles (UFP), and meteorology data. The discrete canister VOC, carbonyl, and PM-speciation samples were prepared by the laboratory staff, then sampled in the field and returned to the lab by the field operations staff with chain-of-custody (COC) documentation. The sample data and supporting information was entered into the laboratory information management system (LIMS) for the laboratory analysis and data validation. Following this, the data was submitted to the U.S. EPA AQS and the MATES V databases. The continuous data was collected onsite using data loggers and telemetered in near-real-time to the South Coast AQMD Data Management System (DMS) for further review and validation prior to inclusion in the MATES V database.

The MATES V field monitoring and laboratory instruments, performance specifications, acceptance testing, siting, operations and sampling schedules, quality control (QC) checks, calibrations, repairs, recordkeeping, and data handling are described further in the QAPPs listed above that support ongoing South Coast AQMD monitoring and analysis programs, along with the associated operations, support, QA and laboratory SOPs. Those documents also further describe analytic procedures and methods employed by the laboratory, as well as the sample handling and chain-of-custody (COC) protocols that impact both the field collection of samples and the lab analytic process. Those intersecting program documents, records, procedures and quality objectives and acceptance criteria provide the backbone for the MATES measurements and analyses. Section III.3 of Appendix III also describes canister use and cleaning, sample distribution, and the sampling media and analytic methods used for canister-sampled VOCs, carbonyls, TSP and PM2.5 filter-based samples. The filter samples are used for determination of hexavalent chromium and other metals, ions, total mass, organic carbon (OC), elemental carbon (EC) and total carbon (TC).

For MATES V, the South Coast AQMD Quality Assurance Branch conducted independent instrument performance evaluation audits on a semi-annual basis for the MATES V canister VOC, carbonyl, and filter-based PM sampling instruments at all stations. The QA Branch auditors also conducted systems audits of the program monitoring and support activities, site maintenance, and safety, including review of COC forms, maintenance sheets, work orders, and the station and instrument logbooks. Due to the overlap of MATES with the NATTS, CSN and lead (Pb) programs, laboratory analyses performance tests (PTs) were conducted during MATES V to verify acceptable levels of bias in laboratory analysis as compared to other laboratories performing the same analyses under federal programs and to known spiked samples.

Corrective Action Process

For issues that arose during MATES V with potential to impact data quality or safety, beyond the normal application of routine quality assurance checks, calibrations, repairs, and data validation, the South Coast AQMD Corrective Action Process was employed. The Quality Assurance Alert (QAA), as described in Operations Assistance Guide (OAG) QA0002, is used by staff to inform the QA Branch and relevant supervisors and managers of a potential concern. The Corrective Action Request (CAR), described in OAG QA0001, is issued by the QA Branch to document significant issues and their resolution, including those resulting from an audit finding or in response to a QAA. The closure of a CAR includes documenting the issue and its resolution along with steps taken to avoid recurrence.

V.3. MATES V Sampling Issue and Data Treatment

Sampling Issue

Sampling manifold issues occurred during the MATES V sampling period (May 2018 through April 2019), evident in VOC canister and carbonyl samples from three monitoring stations (Central Los Angeles, Rubidoux and Anaheim).[2] This was discovered during the South Coast AQMD Laboratory data validation process as staff noted anomalously high concentrations of carbonyls as compared to historic data. Lab and field operations staff informed the Quality Assurance Branch about the anomalous data with a Quality Assurance Alert (QAA), submitted near the end of MATES V. This triggered further investigation, evaluation, a data treatment plan, and other corrective actions to resolve the issue and minimize the potential for future recurrence and documented in a Corrective Action Request (CAR).

The canister VOC and carbonyl monitoring through the manifold at Central Los Angeles and Rubidoux was ongoing prior to the start of MATES V, due to sampling for NATTS and PAMS. The canister VOC and carbonyl sampling manifold and samplers at Anaheim were operational by April 2018, installed specifically for MATES V.

To identify the occurrence of manifold issues and to assess the severity and time periods of concern, the following were reviewed:

- Manifold system flow checks (flow differential measured at the inlet and after the manifold) to test for leak potential, conducted at all ten MATES V sites. Note that the routine sampler QC flow checks, flow rate verifications/calibrations, and flow rate audits were not able to identify the manifold leaks; testing of the manifold system was needed.
- Sample data for the presence of an indoor air signature potentially due to a leak (e.g., formaldehyde, acetaldehyde, etc. from shelter building materials & furnishings).
- Manifold system records (e.g., station and instrument logbooks, maintenance sheets, and chain-of-custody forms) for potential root causes and timing.
- The physical manifold configuration, fittings, connections, and instruments where leaks were suspected.

The manifold flow tests done at all ten MATES V stations indicated leaks at Rubidoux and Central Los Angeles and a relatively more severe leak at Anaheim. Through physical review of the manifolds at these sites, the cause of the manifold leakage was determined in each case to be loose fittings on the manifold ports, likely due to operator error. For the Anaheim site, a ferule was missed on the manifold inlet upon installation for MATES V. At Central LA, all the fittings

[2] Note that this sampling manifold issue also impacted other program samples on the same manifold at Central Los Angeles and Rubidoux, as follows: VOC and carbonyl sampling data for NATTS (same samples as MATES V), Photochemical Air Monitoring Stations (PAMS), and CARB Air Toxics Program (VOC canister samples only, since CARB carbonyls are not on the manifold).

were connected but, when evaluated further, staff noted that some were not completely tight. At Rubidoux, a loose cap was found on an unused manifold port.

Records, including the data, logbooks, maintenance sheets and chain-of-custody forms were reviewed and compared to the atypical shifts in the MATES V data by compound and station to evaluate the period of concern. Using the timing of the presence of an indoor air signature in the analyzed data and the manifold-related records, the timing of the leak problems was associated with field operations activities that impacted these manifolds. For Anaheim, the change from outdoor carbonyl sampling with the Xontech 924 to indoor sampling with the ATEC 8000, starting with the April 2, 2018 sample, showed elevated formaldehyde and acetaldehyde. The missing ferule at the inlet occurred at the initial installation of the manifold for MATES V and was not resolved until the end of the study. With this timing, along with laboratory analysis indicating the strong presence of indoor air for the entire sampling period, all MATES V canister VOC and carbonyl data were invalidated for Anaheim.

For Central Los Angeles and Riverside, the manifold flow checks indicated the presence of leaks, although these leaks were less severe compared to the issues at Anaheim. At Central Los Angeles, the timing of the problem was associated with a manifold cleaning procedure completed prior to the August 18, 2018 sample run that was apparently exacerbated shortly thereafter on September 25 by the replacement of a carbonyl sampler in the manifold. This issue was significantly improved by tightening the loose fittings but was not fully resolved until a large O-ring connecting two manifold parts was replaced to pass a manifold leak test in April 2019.

At Rubidoux, the signature of indoor air in the carbonyls data helped define the period of concern, after the outdoor Xontech 924 was changed to an indoor ATEC 8000 carbonyl sampler on the manifold, at the beginning of April 2018. With that change, slightly elevated carbonyls were evident. A review of manifold-related activities from the station and instrument logbooks conservatively identified the period of concern back to the prior manifold cleaning in late 2017. The later sampling data indicated that the leaks were further exasperated, starting in late July 2018, as indicated by an increased indoor air signature. This was likely associated with manifold activities that included the addition of a Picarro continuous formaldehyde instrument for testing. The leak identified at Rubidoux was a loose fitting of a cap on an unused port of the manifold. Tightening the loose fitting in February 2019 resolved this issue.

The leakages were primarily indicated by unusually elevated formaldehyde and acetaldehyde concentrations for the MATES V samples. The concentrations of these analytes were consistent with emissions from station building materials, such as flooring and wallboard. Since the leaks were associated with loose or missing fittings and not from completely disconnected sampling lines, the sampled air was still deemed to be predominantly ambient outdoor air after a thorough statistical evaluation and additional tests. To further evaluate the impact of indoor air leakage on the analyzed compounds, staff conducted indoor/outdoor concurrent VOC canister and carbonyl sampling at each location. These samples were analyzed to identify the potential for the leaks to

bias data, by analyte. This sampling also helped to discount initial concern that the elevated values might have been due a nearby ambient source. Staff also reviewed the suspect sample data as compared it to historical data, including PAMS, NATTS, CARB Toxics Program data, as well as to the current and prior MATES data to assess data outliers.

The MATES V portion of the data collected with each of the sampling manifolds included 22 canister VOC compounds and 4 carbonyl compounds. This issue did not impact $PM_{2.5}$ chemical speciation and metals monitoring, as samplers used to collect these type samples were not attached to the compromised manifolds. Criteria pollutant gases are sampled using a separate manifold which was also not compromised; hence they were not impacted.

Data Treatment Plan

Laboratory staff used statistical methods to identify effective screening tools for data outliers (i.e., false positives/negatives). The following data treatment plan was used for the South Coast AQMD samples, including those for MATES V:

- Invalidate all manifold-sampled carbonyls with a null code in the U.S. EPA Air Quality System (AQS) database (BJ= Operator Error). Overall, the indoor/outdoor samples indicate a significant indoor air bias. Routine sample data indicates significant outliers compared to historical trends.
- Invalidate VOC canister data point outliers, by species, with a null code in AQS (BJ= Operator Error), if three conditions are met: (1) indoor/outdoor samples indicate indoor air bias; (2) data points screened as outlier by statistical outlier tests; and (3) data points inconsistent with 5- or 10-year trends, with seasonal variation considered.
- Flag remaining VOC compound data points – with a qualifier code in AQS (3 = Field Issue) to inform data users of the potential issue. In this case the indoor/outdoor sampling did not indicate a significant indoor air contamination bias and the data were not determined to be outliers based on statistical tests and appeared to be consistent with historical trends.

Table V-1 shows the period of the manifold leaks at each station, along with the percentage of the MATES V data invalidated for each site. Due to the presence of significant outliers and a more significant indoor presence of these species in the indoor/outdoor sampling, all MATES V carbonyl data was invalidated during the leak period for the three stations. The invalidated analyte data was removed from the database and replaced with a null code (AQS Null Code BJ, Operator Error). When compared to historical data, the MATES V VOC canister samples for Central Los Angeles and Rubidoux did not indicate outliers for those analytes and the indoor/outdoor sampling did not indicate a significant indoor bias for these analytes; therefore, no MATES V canister data was invalidated at these sites. However, the data was flagged with a qualifier code (AQS Qualifier Code 3, Field Issue) to warn data users of potential data issues should they become evident during data analysis. Due to the more severe magnitude of the

manifold leak at Anaheim throughout the entire MATES V sampling period, all VOC data from this site was invalidated.

Table V-1. Manifold Leak Periods and Percentages of VOC and Carbonyl Data Invalidated by Site during the 1-Year MATES V Sampling Period

	Rubidoux	Central Los Angeles	Anaheim
MATES V Sampling Period (1 Year): 5/1/2018 – 4/30/2019			
MATES V Manifold Leak Period	5/1/2018 – 2 /19/2019	8/18/2018 – 4/25/2019	5/1/2018 – 4/30/2019
Percent of Invalidated VOC Samples	0% (0 of 61 samples)	0% (0 of 61 samples)	100% (61 of 61 samples)
Percent of Invalidated Carbonyl Samples	80%* (49 of 61 samples)	69% (42 of 61 samples)	100% (61 of 61 samples)

* includes 2 Rubidoux carbonyl samples that invalidated due to other sampler run issues

Corrective Actions

South Coast AQMD staff implemented corrective actions to minimize the chance of similar manifold issues occurring in the future. These actions have strengthened the sampling system operations, maintenance, calibration, and audit procedures, along with stressing the timely identification and reporting of potential sampling concerns raised during the laboratory analysis. The revised procedures enhance the periodic maintenance of the entire sampling system (i.e., inlet, manifold, and sampling instruments), including cleaning, leak tests, flow tests, blanking and known standard challenges, records review, and audits. Routine physical manifold review and manifold leak testing follows significant manifold modifications or instrument changes, manifold cleanings, or when routine laboratory analyses or the analysis from an instrument challenge test (zero air blanking and known standard challenge) indicates the distinctive signature from common indoor air analytes. Reviews of the entire manifold system are also done with the twice-annual canister VOC and carbonyl sampler flow audits by the Quality Assurance Branch.

Several manifold design and handling procedures were implemented or enhanced. The larger manifolds, used at Central Los Angeles and Rubidoux, were replaced to remove potential for leakage where two glass manifolds were joined, now using a single-piece glass manifold with fewer connection ports. Revised VOC manifold sampling system procedures now require replacing all O-rings at each cleaning. Work on the manifold systems is to be done by trained personnel, with oversight by experienced staff. The use of the VOC manifolds for testing instruments or temporary studies (other than MATES, NATTS, and PAMS) has been restricted. The CARB Air Toxics Program canister VOC sampling was recently removed from the Central Los Angeles and Rubidoux manifolds to provide routine, independently analyzed collocation samples that can be used for data comparison to help identify potential concerns.

V.4. References

South Coast AQMD (2013a). *Quality Assurance Project Plan for the National Air Toxics Trends Stations Program*, Version 2.3, September 2013. *[Copies available upon request]*

South Coast AQMD (2013b). *Quality Assurance Project Plan for Special Monitoring*, Revision 0, September 2013 (reviewed by U.S. EPA August 7, 2014 – no federal approval required). *[Copies available upon request]*

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