Quality Assurance Project Plan for the

Chevron Richmond Refinery Fence Line Air Monitoring Program

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1 Introduction

1.1 Background

On April 20, 2016, the Bay Area Air Quality Management District (BAAQMD) adopted Rule 12-15-403, which requires development of a Fence Line Air Monitoring Plan (Plan). The Plan must include procedures for implementing data quality assurance and quality control (QA/QC). The purpose of this QAPP is to fulfill the QA/QC requirements in Rule 12-15-403. In April 2016, the BAAQMD also published Air Monitoring Guidelines for Petroleum Refineries. Chevron's policy is to comply with all local and federal environmental regulations including the fence line monitoring provisions of BAAQMD Rule 12-15.

This QAPP focuses on quality assurance of equipment that will become subject to Rule 12-15 that are not already subject to quality assurance measures by another regulatory program. Sorbent tube analysis for benzene and GLMs are mentioned for informational purposes, but QA/QC of this equipment is considered outside the scope of this QAPP. Sorbent tube analyses are subject to QA/QC requirements in 40 CFR 63 Appendix A Methods 325A and 325B. GLMs are subject to QA/QC requirements in BAAQMD Manual of Procedures Volume VI.

1.2 Fence Line Monitoring Key Personnel

The Chevron Richmond Refinery Fence Line Air Monitoring Program (Program) is operated by the following key personnel.

Data Manager - The Data Manager is responsible for data review, verification, and validation.

Field Technician - The Field Technician is responsible for the day-to-day operation of the fence line monitoring system including following an equipment operation verification and maintenance schedule to assure data quality. Duties include performing work in a safe manner, completing training timely, and following all standard operating procedures associated with the Program.

Field Technician Supervisor - The Field Technician Supervisor is responsible for overseeing the day to day operation of the Program. The Supervisor ensures Standard Operating Procedures are updated and maintained.

Information Technology Manager - The Information Technology Manager supports the website and information technology infrastructure that enables the fence line monitoring data to be made available real time to the public. The Information Technology Manager also supports the system that sends alerts when monitor operating parameters are abnormal.

Program Manager - The Program Manager is responsible for maintaining and updating the Fence Line Air Monitoring Program and associated Quality Assurance Project Plan (QAPP). The Program Manager provides an initial copy of the Plans and updates to key personnel. The Program Manager finds additional resources needed to support the fence line air monitoring program when needed. If the Field Technicians and Field Technician Supervisor are contractors, the Program Manager supports the contractors.

1.3 Personnel Qualification and Training

Field Technicians and the Field Technician Supervisor will be trained in the operation, maintenance, and operation verification of the equipment as well as have resources to troubleshoot any technical issues. Training will be provided by an instructor who has undergone vendor specific training for each analyzer. It is expected that once the Field Technicians and Field Technician Supervisor gain about three years of experience with the analyzers, they have developed expertise so that they can become trainers of new Field Technicians.

1.4 Equipment Functionality

The following sections summarize equipment functionality.

1.4.1 Open-path UV DOAS

The UV-DOAS monitoring systems use a Partial Least Square (PLS) algorithm to quantify data. Each target gas has a spectral library of gases covering the concentration range of the analyzer. It also includes libraries of potential interfering gases such as oxygen and ozone. The PLS algorithm is specifically designed to minimize the influence of cross-interference.

1.4.2 Open-path Tunable Diode Laser

The Tunable Diode Laser (TDL) air monitoring system measures light in a region of the light spectra where H_2S absorbs infared light. The system then passes the light beam through an internal reference cell that contains a known concentration of hydrogen sulfide. Once the two measurements are complete, the two spectra are compared to each other using analytic software that determines the concentration of hydrogen sulfide in the field data. In addition, the software reports a correlation coefficient (R^2) between the two measurements. Higher R^2 value reflects higher confidence that the field measurement was H_2S.

1.4.3 FTIR

An open path FTIR uses an optical telescope to transmit an infrared beam through the air, monitoring compounds present in the air mass. An open path FTIR can be configured in monostatic or bistatic mode. The monostatic mode of operation has a telescope at one end of the path and one or several corner cube arrays at the other end. The bistatic mode of operation consists of a transmitter telescope at one end and a receiver telescope at the other end of the path.

An extractive or point FTIR uses an extraction line and pump that pulls the air sample through an internal cell in the accessory. An internal source emits an infrared light energy beam which is modulated. The system collects spectra of the sample, analyzes it, and provides total alkane concentration.

1.4.4 GC-PID

The North Richmond community monitor uses a gas chromatograph followed by photionization detector to measure BTEX compounds in ambient air. Sample gas flows through the gas chromatograph column and separates at different rates depending on the various chemical and physical properties. The photionization detector causes ionization of the sample using ultraviolet light. The ionization chamber exposed to the light source contains a pair of electrodes. When a positive potential is applied to one electrode, an electro-magnetic field is created in the chamber. Ions formed by the adsorption of photons are driven to a collector electrode. The current produced correlates with concentration.

1.5 Instrument Performance

The entire fence-line monitoring system is continually monitored for system performance. This includes the instruments, workstations, and internet communication hardware. If at any time an element of the system fails to meet performance criteria, a message is generated to key personnel who will begin activities to correct the problem. If an issue cannot be immediately corrected, the real-time website will be updated with a message explaining the problem. The following table lists potential problems and responses.

Table 1.1 Response to Potential Monitor Problems

Potential Problem	Response
Analyzer has low signal	Website updated with low signal message for specific analyzer. If the low signal is not due to weather conditions, a Field Technician corrects the issue.
Analyzer off-line	Website updated with analyzer off-line message. Field Technician corrects issue.
Workstation fails	Website updated with analyzer off-line message. Technician corrects the issue.
Internet communication failure	Backup Internet connection activated

1.6 Required Routine Maintenance

Routine maintenance for the UV-DOAS, TDL, FTIR, and North Richmond GC is summarized in Tables 1.2, 1.3, 1.4, and 1.5. The Castro Street GLM is maintained in accordance with BAAQMD Manual of Procedures Volume VI. In addition, maintenance checks will be performed if Data Quality Checks fail or data availability targets are not met.

Table 1.2 Schedule of Maintenance Activities for the UV-DOAS

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓	✓	✓
Inspect optics; clean if necessary.	✓	✓	✓
Confirm the alignment to verify there has not been significant physical movement. Note: this is automatically monitored as well.	✓	✓	✓
Download data from detector hard drive and delete old files to free space, if needed.	✓	✓	✓
Ensure there are no obstructions in the beam path.	✓	✓	✓
Change out the UV source.		✓	
Realign system after service.	✓	✓	✓
Check system performance indicators.		✓	✓
Perform bump test (simulates system-observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit.		✓	
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency.		✓	✓
Verify system settings.			✓

Table 1.3. Schedule of Maintenance Activities for the TDL

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓	✓	✓
Inspect optics on detector, clean if necessary.	✓	✓	✓
Check the alignment to verify there has not been significant physical movement.	✓	✓	✓
Download data from detector hard drive and delete old files to free space, if needed.	✓	✓	✓
Ensure there are no obstructions in the beam path.	✓	✓	✓
Check system performance indicators.		✓	✓
Perform bump test		✓	
Review and test light and signal levels.		✓	✓
Verify system settings.			✓

Table 1.4. Schedule of Maintenance Activities for the FTIR

Activity	Monthly	Quarterly	Annually	Five Years
Visually inspect the system.	✓	✓	✓	
Confirm the alignment to verify there has been no significant physical movement.[a]	✓	✓	✓	
Download data from detector hard drive and if needed delete old files to free space.	✓	✓	✓	
Ensure there are no obstructions between the detector and the retro-reflector.	✓	✓	✓	
Change out the IR source.				✓
Realign system after service.		✓	✓	
Check system performance indicators.		✓	✓	
Check system response (bump test).		✓		
Perform factory calibration check.			✓	
Review and test light and signal levels. Check average light intensity to establish baseline for IR source change frequency and retro-reflector wear.	✓			
Verify system settings.		✓		
Perform Cryocooler Check. Replace Cooler or swap detector module assembly if necessary.			✓	

[a] Note: this is automatically monitored as well.

Table 1.5. Schedule of Maintenance Activities for the North Richmond Community Monitor GC-PID

Activity	Quarterly	Annually	Two Years
Replace micro dust filter for sample.	✓		
Remove dust from ventilator.	✓	✓	
Clean the lamp.		✓	
Clean the PID.		✓	
Change the carrier gas filters.		✓	
Clean the diaphragm.		✓	
Renew external sample tubing.		✓	
Replace preconcentration tenax tube.		✓	
Replace cooled preconcentration trap.		✓	
Optimize hard disk.		✓	
Clean internal gas tubing.			✓
Clean lamphouse.			✓

2 Data and Measurement Quality Objectives

For all instrument/parameter combinations, data completeness requirements are provided in Table 2.1. Percent data recovery (or data capture) for 1-hr data is the percentage of valid 5-minute data values that were collected, divided by 12. Percent data recovery for the day is the number of valid 1-hr values collected divided by 24. Percent data recovery for the calendar quarter is the number of days of valid data collected divided by the total number of days in the date range. For communication purposes, the Percent Data Valid—the percentage of data values that are valid divided by the number of captured data values, corrected for weather related conditions—will also be computed. The Rule allows for omission of time periods from the completeness calculation when atmospheric conditions prevented measurement, as indicated by three instruments at the same location (UV-DOAS, TDL, and FTIR) having drops in signal simultaneously, or as indicated by a visibility sensor.

Table 2.1. Data Availability Requirements.

Completeness Requirement	Relevant to	Minimum No. of Values Needed
75% per hour 75% per day	5-minute average data 1-hr average data	9 per hour 18 per day
90% per calendar quarter	Daily data	81 days per 90-day quarter [a]

[a] The exact number of days in the quarter will be used; this example is for illustration only.

3 Quality Control

All monitoring equipment will be operated using quality assurance protocols outlined in this QAPP. This includes continuous monitoring of instrument parameters for data quality (error flags/messages from the analyzers, low signal measurements), quarterly validations, and annual servicing of the analyzers. Accuracy will be measured using the protocols listed in the Environmental Protection Agency's Environmental Technology Verification Program Generic Verification Protocol for Open-Path Monitors (ETV). The specific measurements will be made at the manufacturer's location where necessary or in the field with the system in its standard operational configuration. Where the manufacturer conducts quality assurance tests, Chevron will request a report of the tests conducted. Chevron will keep a quality assured spare analyzer in service while the manufacturer conducts quality assurance tests of the primary analyzer.

For the UV DOAS system, a bump test will be performed quarterly. In the field, a bump test is used to verify the system can detect at or below a set level of concern.

TDL calibration is typically done at the factory. In the field, a bump test will be performed quarterly. During factory calibration, a back-up instrument may be used so that measurements continue.

For an open-path FTIR, a bump test will be performed quarterly.

For factory calibrations, a certification of the standard gases used will be requested from the manufacturer. In addition, the spectra background file version number used for signal processing will be documented.

For the North Richmond Community monitor GC-PID, zero and span checks are conducted monthly. The analyzer is calibrated if the target zero value reads greater than or equal to two ppb or if the span value is greater than equal to 15%. Calibrations are also scheduled quarterly. Instrument bias is checked annually to ensure the coefficient of variance is less than 10 percent.

For the Castro Street GLMs, calibration is completed every two weeks.

Sorbent tube analyzers are calibrated in accordance with 40 CFR 63 Appendix A Method 325B requirements.

For the open-path systems, precision can be measured by evaluating the variance of pollutant concentrations during a period of low variability, when atmospheric influence on variability is assumed to be minimal. Five-minute data will be selected during periods of low variability, but when concentrations are well above the MDL. The precision can then be evaluated by calculating the coefficient of variation (CV) during the period of low variability, as shown in Equation 1.

$$\text{Precision} \approx CV = \frac{\sigma_{measured}}{\overline{[conc]}_{measured}} \times 100\% \quad \textbf{(1)}$$

Where:

$$\sigma_{measured} = \sqrt{\frac{\sum\left([conc]_{measured} - \overline{[conc]}_{measured}\right)^2}{N-1}}$$

The accuracy of the monitors will be evaluated for target gases by inserting a gas cell into the beam path with a known concentration of a target gas and comparing cell gas concentration to the concentration measured by the open-path monitor. The relative accuracy (*A*) of the monitor with respect to the reference gas is assessed using the following formula:

$$A = \frac{\left|\overline{R} - \overline{T}\right|}{\overline{R}} \times 100$$

Where:

A is the accuracy of each measurement

$\overline{R}$ is the average value of the reference gas

$\overline{T}$ Is the average value of the measurements

4 Data Management

Data quality criteria are evaluated through (1) automatic data checks conducted through a data management system and (2) data review by trained analysts.

4.1 Data Acquisition and Communications

Raw data management occurs on a real-time, monthly, quarterly, and annual basis. In near real-time, data are transferred from infield instruments through a data acquisition system (DAS) to a Data Management System (DMS). Data are also stored onsite on instrument computers. These raw data are not yet intended for the public website.

The DMS automatically quality-controls data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities will be used for continuous examination of data quality. The DMS will feed auto-screened data to the field operations website and notification system to inform/alert project and facility staff. The automatically

QC'd air quality data will be fed to the public website typically within ten minutes of data measurement.

4.2 Automated Data Review

Automated data review is conducted within the DMS upon data ingest. Automated screening checks of data feeds are used to screen out invalid data for public display identified in Table 1.1. Initial quality review, along with actions to be taken, are summarized in Table 4.1. The review concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. All review criteria (flags and rates of change) are preliminary and will be refined during the project based on actual observations. The DMS auto-review checks that will be used include

- **Range.** These checks will verify that the instrument is not reporting values outside of reasonable minimum and maximum concentrations.
- **Sticking.** If values are repeated for a number of sampling intervals, data will be reviewed for validity. Typically, four or more intervals of sticking values are a reasonable time span to indicate that investigation is needed. Sticking checks will not be applied to data below the instrument detection limit.
- **Rate of Change.** Values that change rapidly without reasonable cause will be flagged and reviewed.
- **Missing.** If data are missing, data during those time periods will be coded as missing.
- **Sensor OP codes and alarms.** If the instrument assigns operation (op) codes to data automatically (e.g., for bump tests, internal flow rate checks), the data will be reviewed, codes confirmed, and data flags checked.

Additional parameters that may be monitored as indicators of data quality include data quality values for each concentration as reported by the instrument (i.e., correlation between measured and reference spectra), and signal strength. For signal strength, if the signal is below 1,250 for the UV-DOAS or 200 for the TDL, the data are invalid. For an FTIR, data with relative intensity less than 2% are invalid. There are no a priori data quality objectives for the other parameters; objectives will need to be developed for these parameters if they prove to be useful indicators for automated data quality screening or for data validation.

Data flags identified through auto-review will be reviewed during data validation (i.e., not in real-time), and QC flags will be updated with quarterly actions. Data changes will be tracked. Raw data are preserved as well as all changes.

Table 4.1. The following checks are used for post process data review.

	MDL	Range	Checks		
			Sticking	Missing	Sensor OP Code or Alarm
Benzene (ppb)	If below MDL, flag as below MDL	If above 5 ppb, flag for review	If value is above MDL and the same value is observed for four or more intervals, flag for review	If data are missing, flag as missing	If sensor indicates malfunction or calibration, flag as appropriate
Toluene (ppb)		If above 70 ppb, flag for review			
Ethylbenzene (ppb)		If above 320 ppb, flag for review			
Total Xylene (ppb)		If above 200 ppb, flag for review			
H_2S (ppb)		If above the MDL, flag for review			
SO_2 (ppb)		If above 40 ppb, flag for review			
Methane (ppm)		If below 1,720 ppm, flag for review			
Alkanes, C2-C5 (ppb)		If above 1.6 ppm, flag for review			
N_2O (background check)		If below 270 or above 330 ppb, flag for review			

4.3 Data Verification

An automated system conducts Initial data review checks at least daily and notifies technicians and managers of the system status and any issues, if any occurred. If it appears that an instrument is not operating, or the data are missing, the field operator will conduct further investigation and corrective action.

The automated alerting system will let technicians and managers know when data have been missing for a specified period of time. Missing data may indicate a power issue, an instrument problem, or a data communication problem.

4.4 Data Validation

On a frequency of at least quarterly schedule, an experienced air quality analyst will validate data by building on the automated screening results. This process starts with an in-depth review of the data, a review that includes evaluation to ensure the data are valid for the intended end use. The QA Manager will evaluate QA/QC procedures and ensure adherence to the methods for meeting data quality objectives. Data validation activities will be reviewed and approved by the QA Manager.

Data validation activities include:

- Review of spectral features in flagged data to verify the measurement.
- Ensuring there are not several continuous 5-minute averages of the same number.
- Evaluating monthly summaries of the minimum, maximum, and average values.
- Ensuring data reasonableness by comparing to remote background concentrations and average urban concentrations.
- Ensuring the data or measurements are realistically achievable and not outside the limits of what can be measured.
- Inspecting several sampling intervals before and after data issues or instrument repairs to ensure all affected data have been properly flagged.
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on observations by site operator.
- Assessing instrument meta data to confirm reasonableness.
- Assessing weather related downtime based on two or more analyzers within the same proximity experiencing a drop in signal simultaneously

Additional QC checks for the instruments are summarized in Table 4.2. Data that fail checks will be flagged in the DMS and brought to the attention of the reviewer by color coding in the graphic summaries. Common reasons for invalidation include instrument malfunction, power failure, and bump test data that were not identified as such. As the measurements progress, we will update and refine the screening checks. Screening checks are typically specific to the site, instrument, time of day, and season and adjusted over time as more data are collected.

Table 4.2. Instrument QA/QC Checks.

QA/QC Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test (accuracy)	Quarterly and after major service	±25%
Single beam ratio test (strength of UV source)	Real-time	If peak to peak noise is less than 3 milliabsorbance units in the region for 251-254 nm
Integration time	Continuous	< 750 mS
Signal strength	Continuous	>1250 *Signal intensity below 1250 results in a warning notification; data are invalid*
TDL		
Multi-point bump test	Annually and after major service	±25%
Signal strength	Continuous	>200 *Signal intensity below 200 results in a warning notification; data are invalid*
FTIR		
Bump test	Quarterly and after major service	±25%
Comparison with approximate ambient methane concentration	Continuous	*Above 1.7 ppm*
IR single beam ratio test (background vs. sample intensity)	Real-time	*To be determined*
Relative intensity	Continuous	>5% *Signal intensity below 5 results in a warning notification*
GC-PID		
Zero and span	Monthly	Zero < 2 ppb Span <15%
Precision	Quarterly	Linear regression correlation > 96%, zero +/- 0.5 ppb
Bias	Annually	Coefficient of Variance < 10%

Data are invalidated only if a reason can be found for the anomaly or automated screening check failure. If the data are anomalous or fail screening, but no reason can be found to invalidate the data, the data are flagged. Additional analysis may be needed to deem data valid or invalid. Voided data will be flagged as invalid in the database. A summary of issues leading to invalidated data will be documented in the data file.

On at least a quarterly basis, analysts will subject the data to final QC by filling in missing records with null values, and adding Null Codes:

- Invalid data will have a Null Code, or in other words, a reason for being invalid.
- If a record is not created for a particular site/date/time/parameter combination, a null record will be created for data completeness purposes.
- Review quarterly data completeness.

All actions will be documented, which retains raw data and traceability of all actions that result in the final data.

On an annual basis, the refinery or its designated contractor will review the performance of the network by reviewing the data completeness by monitoring path, instrument, and species; by reviewing results of QA/QC tests; by analyzing the reported values in context of refinery operations; and by analyzing the data in context of the meteorology. The refinery or its designated contractor will also evaluate overall network performance to ensure it is meeting overall objectives, using analyses similar to those used to support the network design. The results will be summarized in a technical memorandum and provided to the BAAQMD upon request.

Chevron or its contractor will monitor and investigate any portion of the fence line system that fails to meet data quality objectives, measurement quality objectives, or on-stream efficiency requirements under Rule 12-15. The investigation team will include members of the fence line management team, contractors and appropriate equipment vendors. They will assess the problem and initiate corrective action. Corrective actions will be undertaken in a timely manner with the understanding that all work will be done with safety as a primary focus. In addition, improvement opportunities identified will be considered to minimize the chance for similar problems in the future.

5 Documentation and Records

All records discussed below will be retained for five years.

5.1 Fence Line Monitoring Plan and QAPP

The Program Manager will be responsible for providing initial copies and updates of the Plan including the QAPP to key personnel identified previously. The Plan and QAPP will be updated periodically and distributed to address a deficiency, improve procedural accuracy, or to make procedures more robust.

5.2 QA/QC Records

The Program Manager will retain QA/QC reports from equipment manufacturers. The Field Technician Supervisor will retain field QA/QC records.

5.3 Training Records

The Field Technician Supervisor will keep documentation of training.