# Air Monitoring Plan for the Valero Refinery in Benicia, California

Prepared for Valero Refining Company - CA Benicia Refinery Benicia, CA



September 7, 2017

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# 1. Introduction

### 1.1 Background

The Valero Refining Company (Valero) proposes to conduct air quality monitoring at its Benicia, California, refinery in response to the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15.<sup>1</sup> The monitoring will follow a facility-specific air monitoring plan consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.<sup>2</sup> Rule 12-15 requires routine monitoring near the fencelines of all San Francisco Bay Area refineries for specific air compounds, with data reported to the public.<sup>3</sup> The rule also requires that refineries submit air monitoring plans to the BAAQMD for approval. This document is Valero's submittal for its Benicia facility.

The remainder of this section gives an overview of the Monitoring Plan and outlines the steps that will be taken after the plan is approved.

## 1.2 Plan Summary

This section provides an overview of the monitoring plan. Subsequent sections provide additional plan details and associated justifications for the monitoring program design.

Rule 12-15 requires fenceline monitoring of multiple compounds using "open-path technology capable of measuring in the parts-per-billion range regardless of path length" or an alternative measurement technology.<sup>2</sup> The required compounds to be measured include benzene, toluene, ethylbenzene, xylenes (BTEX) and H<sub>2</sub>S. In addition, sulfur dioxide (SO<sub>2</sub>), alkanes, 1,3-butadiene, other organics, and ammonia should be considered for measurements.

For the Valero fenceline monitoring program, Valero proposes to use open-path instruments to measure the required compounds (BTEX and H<sub>2</sub>S) along three paths. The three measurement paths, composed of two segments each, will be implemented to cover Valero's fencelines in consideration of nearby local receptors (e.g., residences and businesses), dominant winds that blow from west to the east, and infrequent winds that blow from the northeast to the southwest to portions of populated areas in Benicia. As shown in Figure 1, the business park east of Valero is the only populated area influenced by the dominant winds; winds blow from other directions less than 10 percent of the time for 22.5 degree wind direction segments.

<sup>&</sup>lt;sup>1</sup> Petroleum Refining Emission Tracking (Rule 12-15; approved by the BAAQMD on April 20, 2016).

<sup>&</sup>lt;sup>2</sup> Bay Area Air Quality Management BAAQMD (2016) Air monitoring guidelines for petroleum refineries. April. Available at baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en.

<sup>&</sup>lt;sup>3</sup> The exact timing for the start of fenceline monitoring depends on when this monitoring plan is approved by the BAAQMD.



**Figure 1.** Areas downwind of the Valero Benicia Refinery property boundaries for wind directions that occur more than 10 percent of the time on an annual basis. The only populated area impacted by the dominant wind direction is the business park to the east of the Valero refinery.

Along all paths, BTEX and  $SO_2$  will be measured by monostatic Ultra Violet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source.  $H_2S$  will be measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instruments. These open-path instruments transmit light across a given path and detect the amount of energy absorption at a particular wavelength of light to determine the average concentration of a particular pollutant along the path. The three primary monitoring paths, composed of six total segments, are shown in Figure 2. Please note: the exact paths may need to be adjusted based on final site logistics and exact instrument capabilities, particularly in regard to the maximum path lengths needed for the instruments to reliably measure the compounds of interest.





Paths 1 and 2 cover the southwest fenceline to assess potential transport toward the city of Benicia. This transport direction is infrequent and only occurs on an occasional basis in the winter, when winds sometimes blow from the northeast toward the southwest. Over the course of a year, these northeast winds occur less than about 7% of the time. Because of terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability; therefore, the downwind areas that could be affected under these wind conditions are very narrow.

Path 3 covers the eastern fenceline to assess potential transport toward the business/commercial area east of the refinery. This transport direction is common in the spring, summer, and early fall, when winds often blow from the west toward the east. Monitoring between Path 2 and 3 is not needed, as there are no significantly populated areas downwind of this space between the

monitors. In addition, a release that might travel between Path 2 and 3 would likely be seen on Path 2 or 3 monitors because of dispersion. Also, it is not feasible to add monitors between Paths 2 and 3 because of road, railtrack, and terrain issues.

Instruments on Paths 1 and 2 will be elevated about 5 ft above ground level (agl). Instruments on Path 3 may be elevated to about 15 to 20 feet agl so that vehicle traffic will not block the openpath sensor light; the final height will be determined on the basis of site logistics. While instruments will be located at the above elevations, the distance between the ground and the light beam along the path will vary according to the terrain.

Open-path analyzers will be located at sites 1, 2, 3', and 3". Sites 1 and 2 will each have two UV-DOAS and two TDLAS analyzers. Each pair of analyzers at each site will point roughly 180 degrees from each other. The remaining numbered sites (1', 1", 2', 2", and 3) will have retro reflectors (i.e., mirrors). This setup will provide maximum spatial coverage along the critical paths.

Visibility instruments will be placed at sites 1 and 3' to measure visibility conditions at different locations and elevations. The visibility measurements will be used as evidence of low visibility conditions that cause missing measurements from the open-path instruments. Two sites have been selected because visibility can vary spatially across the refinery. In addition, these locations were selected for ease of access.

All instruments will be installed and operated following manufacturers specifications, including necessary bump tests. A bump test challenges an instrument using known gas concentrations to confirm accurate instrument response.

Instruments will be operated to strive for a minimum of 75% completeness by hour and day, and 90% completeness by annual quarters. Appropriate completeness criteria will be calculated after removing time periods when atmospheric conditions prevented measurement.

Measurements will be collected at a time resolution of 5 minutes or less.

Data from the fence line monitors will be transmitted to an internet website where the near-real-time results can be viewed by the public.

Data generated by the fenceline monitoring equipment undergoes review throughout the measurement and reporting process. Included in this process is automated QA/QC checks that occur before data is reported on the real-time website. Under normal circumstances, a 5-minute average measurement will appear on the website within 10 minutes of the end of the measurement period. However, the data uploaded may be impacted by internet traffic. An automated system conducts the Quality Assurance checks before the data is reported to the website. The website will also make available a rolling 24-hour trend of the 5-minute data for each gas reported.

Once QA/QC of the final data is completed within 60 days after the end of each calendar quarter, the refinery will provide one-hour average concentration data in tabular format through a comma

separated value data file to the BAAQMD. The BAAQMD may make the one-hour average data available to the public through a BAAQMD website or through public records request. The refinery will make data available to BAAQMD upon request prior to the report submittal.

The website will also provide a mechanism for public comment, which will be monitored by Valero or a designated consultant.

All data will be retained by the facility for a period of five years, consistent with Regulation 12-15-302.

### 1.3 Next Steps to Implement the Fenceline Monitoring

Once BAAQMD approves this Monitoring Plan, Valero or its designated consultant(s) will:

- Acquire instruments and supporting equipment.
- Finalize the Quality Assurance Project Plan (QAPP) based on the acquired instruments.
- Develop instrument infrastructure, including power, concrete pads, shelters, security fences, access paths, and communications.
- Install the instruments.
- Develop the data management system.
- Develop the public data-display website for displaying data in real time.
- Operate and maintain instruments following manufacturer's specifications.
- Operate and maintain the public website.

# 2. Monitoring Plan Design Considerations

This Monitoring Plan was developed in consideration of the following elements.

- Rule 12-15 and related guidance.
- Monitoring objectives, which were established in consideration of Rule 12-15 and related guidance.
- The findings of a scoping study, which involved assessments of (1) the geographic setting around Valero's Benicia Refinery, (2) the relevant meteorological conditions, and (3) air quality monitoring and dispersion modeling results.
- Technical and engineering feasibility related to available monitoring technologies and instrument siting.
- Data management and QA/QC requirements.

Details on each of these elements are provided in the following subsections.

### 2.1 Key Elements of Rule 12-15 and Guidance

According to the BAAQMD's April 2016 guidelines, the main goals of fenceline monitoring are to:

- "Provide continuous air quality concentration information on a short enough time scale to address changes in fence-line concentrations of compounds associated with refinery operations;
- "Provide data of sufficient accuracy to identify when concentrations of compounds associated with refinery operations are elevated as compared to other monitoring locations throughout the Bay Area;
- "Potentially aid in identifying corrective actions that will lower emissions."

Key guidance provided in the Guidance Document for designing a monitoring plan to address BAAQMD goals is summarized below.

• Conduct "fenceline" measurements of BTEX and H<sub>2</sub>S. Consider measuring other compounds, including SO<sub>2</sub>, alkanes, 1,3-butadiene, other organics, and ammonia. The term "fenceline" in the guidance refers to a general boundary between refinery property and areas outside the refinery property, not necessarily to an actual fence.

- Conduct measurements in areas where emissions from the refinery could impact populated areas on a frequent basis. Specifically,
  - "Measurements must cover populated areas within one mile of the refinery fence-line likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10 percent of the time, or greater, based on the most representative meteorological measurements for sources likely to emit the compounds listed above at the refinery."
  - In addition, "Meteorological measurements should also be used and addressed in the Air Monitoring Plan to ensure proper siting of fence-line systems, looking at long-term measurements such as annual average wind rose, but also taking into account more seasonal and recurring short term meteorological events."
- Provide measurements of the compounds at the ppb level or as technology allows.
- Conduct measurements using open-path instruments or an appropriate alternative.
- Provide rationale for the compounds to be measured and not measured.
- Provide rationale for the locations for the measurements.
- Provide rationale for the instruments to be used.
- Collect the measurements every five minutes.
- Process the data and display the data in near-real time to a public website.
- Meet data recovery and completeness criteria.
- Develop a QAPP for the measurement program and follow the QAPP.

## 2.2 Scoping Study

#### 2.2.1 Assessment of the Geographic Study Setting

Valero's Benicia Refinery is located at 3400 East 2nd Street in the eastern part of the City of Benicia, Solano County, California (see Figure 3). The refinery is bounded by Suisun Bay and by the Carquinez Strait on the east and south sides of the property. Low coastal hills rise to elevations of 400 to 1,000 feet on the west and north sides of the refinery. Valero's 800-acre property is largely undeveloped and provides a useful area for air monitoring. Valero's Refinery operations occupy approximately 330 acres, including a 46-acre process block that lies between East 2nd Street and Park Road and a 50-acre crude oil tank farm that lies between Park Road and Interstate 680 (see Figure 4). The Shell Martinez and Tesoro Golden Eagle refineries are located to the south and southeast across the Carquinez Strait.



Figure 3. Geographic setting of the Valero Benicia Refinery.



**Figure 4.** Layout of the Valero Benicia Refinery (Source of information: Valero Improvement Project Environmental Impact Report, June 2008).

Residential areas are located to the southwest, west, and northwest of the facility and most are at least 1,500 feet from the refinery plant and storage tanks. Businesses are located east and northeast of the refinery, and the business/commercial area begins a short distance from the refinery property. Interstate 680 is adjacent to the eastern side of the refinery and Interstate 780 is located to the south; there are residences between Interstate 780 and the refinery. The nearby public-access areas—e.g., residences, businesses, and public roadways—represent air quality "receptors" that are nearest and at times downwind from Valero's Benicia Refinery. The positions of these receptors received careful consideration during the design of this air quality monitoring plan.

#### 2.2.2 Assessment of Valero Processes

Valero's Benicia Refinery is a petroleum refinery producing fuel products, such as liquefied petroleum gas (LPG), gasoline, jet fuels, diesel fuels, and residual fuel oils through distillation of crude oil, including cracking, alkylation, and reforming. In light of Valero's products, processes, and associated potential emissions, the following rationales in Table 1 were used to determine which compounds need to be measured or not measured. Additional details are provided following Table 1.

- 1. Benzene measurements are a good qualitative indicator for other Hazardous Air Pollutant (HAP) emissions<sup>4</sup>
- 2. Not a HAP (this is not the sole reason for exclusion, but is provided for completeness)
- 3. Emissions are low compared to background concentrations
- 4. Already measured by existing ground level monitors (GLM)
- 5. Alerting systems already in place at the refinery
- 6. Not manufactured as a product of the refinery and not used in routine processing.

 Table 1. Compounds and the rationale for their exclusion from the fenceline monitoring program.

Compound	Required by the BAAQMD	To Be Measured	Rationale for Exclusion
Benzene	Yes	Yes	NA
Toluene	Yes	Yes	NA
Ethylbenzene	Yes	Yes	NA
Xylenes	Yes	Yes	NA
Hydrogen sulfide	Yes	Yes	NA
SO <sub>2</sub>	No, if justified	Yes	NA
Alkanes	No, if justified	No	1 (for hexane) 2 (except for hexane) 5
1,3-Butadiene	No, if justified	No	6
Other organics	No, if justified	No	1
Ammonia	No, if justified	No	5, 6

**Exclusion of alkanes.** Valero will not include alkanes in its fenceline monitoring program. During normal operations, there is no potential for alkanes to be released at the fenceline without a corresponding benzene release, and as noted in Table 1 above, benzene is included in the fenceline

<sup>&</sup>lt;sup>4</sup> Background section of Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards.

monitoring program. Alkanes are used within the refinery process units; however, the Benicia refinery is unique in its design of integrated process units. This design, intended to maximize energy efficiency and minimize the storage of intermediate products, essentially causes the entire refinery to function as one integrated unit. This means that a release of alkanes from a process unit that *does not* emit BTEX compounds would coincide with a release from a process unit that *does* emit BTEX compounds. Therefore, the proposed fenceline BTEX monitoring would serve as the alert in the event of a release of alkanes used in the process units.

The only location where alkanes could potentially be released without a corresponding benzene release is at tank storage (liquefied petroleum gas [LPG] spheres, one pressurized tank, and two LPG loading racks). However, fenceline monitoring of these alkanes would not serve as a first alert of an alkane leak: any release from one of these sources would be a significant event with refinery alarms that would activate refinery emergency response procedures and evacuation of people downwind. The LPG storage area, including the loading racks, has open-path total hydrocarbon detectors that alarm in the Control House in the event of a release. The pressurized tank is equipped with pressure relief valves (PRVs). These existing open-path analyzers and PRVs serve as the first alert for an alkane release that would activate emergency response procedures; a fenceline monitor would not be used as a first alert of a release in this situation.

**Exclusion of 1,3-butadiene.** Valero will not include measurements of 1,3-butadiene in its fenceline monitoring program. This is because 1,3-butadiene is not manufactured as an intermediate product or end product of the refinery and is only present in trace quantities.

**Exclusion of other organics**. Valero will not include measurements of other organics in its fenceline monitoring program. Other organics, with the exception of alkanes, are coincident with BTEX; therefore, the BTEX measurements serve as an excellent surrogate for other organics. The exclusion of alkanes is discussed above.

**Exclusion of anhydrous ammonia.** Valero will not include measurements of anhydrous ammonia in its fenceline monitoring program because anhydrous ammonia is used in air pollution control devices and is not used in routine processing at the refinery. Anhydrous ammonia is present in only one location, in two 3.5' x 14' drums that have high temp/pressure/level alarms for detection of release at the source. There are also excess flow shutoff valves on the drum, fixed fire monitors around the perimeter, and bollards and elevated foundations to protect the drums.

#### 2.2.3 Assessment of Local Meteorology

Valero's Benicia Refinery is positioned in a wind flow corridor between the San Francisco Bay and the Sacramento Valley. Wind flow through the corridor is driven by seasonally variable regional temperature gradients and large-scale meteorological systems.

To characterize meteorological processes, measurements of wind, mixing height, and visibility were collected and assessed at several sites (see Figure 5). Items investigated included the monthly, annual, seasonal, and spatial patterns of winds; the low-level vertical structure of winds and how that structure might impact the transport of elevated sources versus surface sources; and the presence of fog and low clouds (as related to the ability of open-path sensors to obtain measurements). The primary data used in this analysis included:

- Routine surface winds collected at the Valero's Administration building and an offsite warehouse in 2007–2016.
- Special-study surface winds collected at MRU Bunker in 2015.
- Special-study 1-minute visibility measurements collected using a Belfort visibility instrument at the facility's Equipment Storage site (ES) location from January 14 through July 9, 2015.

Surface wind data collected at the special-study Buffer Property site (BP) in winter 2015 were compared to data from the Administration site. It was determined that the wind data collected at BP were very similar to the data collected at the Administration site; thus, the BP data were not included in the detailed analysis summarized in this report. Also, the Administration meteorological site is appropriate for understanding movement of air from the refinery to Benicia because (1) it is located between the refinery and the community to the west and thus better represents transport directions to the community; (2) it is at an elevation that is more representative of winds that blow into the community; and (3) it is not influenced by nearby buildings.

General meteorological patterns were also discussed with experts in meteorological processes in the North Bay Area.

For this analysis, seasons were defined as follows: winter is December, January, February; spring is March, April, May; summer is June, July, August; and fall is September, October, November.



Figure 5. Meteorological monitoring locations.

#### **General Flow Patterns**

**Figure 6** illustrates the predominant wind flow patterns (1) winds blowing from the northwest and west to the east and southeast (onshore flow, most often occurring in spring, summer, and early fall); and (2) winds blowing from northeast to southwest (regional offshore flow, most often occurring in winter).



Figure 6. Typical wind flows around Valero's Benicia Refinery.

#### Wind Roses

Wind roses were created to determine the frequency of wind speed and direction for various time periods. To evaluate the actual winds against the wind direction requirement stated in the BAAQMD Guidance document, wind roses showing annual mean wind direction in 22.5 degree segments were created and reviewed. To evaluate seasonal and recurring short-term meteorological events, seasonal and monthly wind roses were created.

The petals of a wind rose show the direction from which the wind is blowing. The wind roses show that:

- **Onshore winds** Winds blowing from northwest to southeast, west to east, and southwest to northeast are in excess of 10% per year (see Figure 7). Winds from these directions are most common in spring, summer, and early fall.
- Offshore winds Winds blowing from the refinery toward the city of Benicia (i.e., winds blowing from northeast to southwest) are infrequent and occur on an occasional basis less than 7% of the time throughout the year (Figures 8 and 9). Although the northeasterly winds occur less than 10% of the time annually, they are included for consideration in this Monitoring Plan because portions of the city of Benicia are downwind of the refinery under these conditions and the winds may occur more than 10% of the time *during the winter season only*. Winds from other directions occur a negligible amount of the time.

To better illustrate the downwind areas impacted by the onshore and offshore winds, maps that highlight the areas downwind of the Valero Benicia Refinery property were created. For offshore winds, more precise modeling was performed because this wind direction is from the refinery toward the residences of Benicia. Details on the modeling are discussed in Section 2.2.4. The downwind areas of influence for onshore flow and offshore flow are shown in Figure 1 and Figure 10, respectively. These analyses show that:

- During dominant onshore (southwest through northwest) winds, the main area downwind of the refinery is the business/commercial area just to the east.
- During infrequent offshore (northeasterly) winds, the main area downwind of the refinery is the city of Benicia, excluding west and northwest Benicia. The offshore wind direction is well defined and has little directional variability (because of terrain effects and the orientation of the Carquinez Strait). Therefore the downwind areas that could be affected under these conditions are very narrow.

The results of the wind and modeling analyses indicate that air quality measurements are needed along the southwest fenceline (Paths 1 and 2) and eastern fenceline (Path 3) of the Valero Benicia Refinery (see Figure 2). Monitoring between Paths 2 and 3 is not feasible because of road, railtrack, and terrain issues. However, monitoring between Paths 2 and 3 is not needed, as there are no significantly populated areas downwind of this space between the monitors. Monitoring north of Path 1 is not needed because it is outside of the area of influence.



**Figure 7.** Wind rose for Administration site showing near-surface wind directions for data collected from 2007 through 2016.



Figure 8. Wind roses at the Administration building (surface winds) by season for data collected from 2007 through 2016.



Figure 9. Wind roses at MRU Bunker for January 2015.



**Figure 10.** Areas downwind of the Valero Benicia Refinery property boundaries during offshore (northeast to southwest) winds.

#### 2.2.4 Winter Offshore-Flow Dispersion Modeling

Because of terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability; therefore, the downwind areas that could be affected under these wind conditions are very narrow. To provide further evidence that monitoring Paths 1 and 2 upwind of Benicia during winter months are in the correct locations to capture the narrow area of the offshore flow, air pollutant dispersion modeling was performed using the American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD [Version 15181]).<sup>5</sup> AERMOD is a steady-state Gaussian plume dispersion model. The advantage of dispersion modeling over wind rose analysis is that it combines winds, topography, atmospheric stability, emissions, and dispersion processes to estimate areas of peak concentrations across the entire downwind area. Importantly, dispersion modeling accounts for the time variability in

<sup>&</sup>lt;sup>5</sup> https://www3.epa.gov/scram001/dispersion\_prefrec.htm.

meteorology to create a more accurate assessment of the locations where fenceline monitoring is needed.

AERMOD uses hourly meteorological data to assess the dispersion of emission plumes from several point, area, or volume sources in flat and complex terrain.

Special meteorological measurements were conducted from January 15, 2015, through late spring of 2015, to support the development of this monitoring plan. The data collected during this study were used to support the air pollutant dispersion modeling. Due to the infrequent nature of northeasterly wind events (the meteorological conditions of importance for transport to Benicia and the focus of the modeling), there were only a few days to model; these days included January 24, 2015, January 25, 2015, and January 26, 2015. Meteorological data collected on these days used in the model included sodar winds (continuous winds from about 20 m to 600 m above ground level), ceilometer mixing heights (roughly the height to which any emissions will mix), and surface winds.

Sources of benzene emissions at Valero's Benicia Refinery<sup>6</sup> were identified, and dispersion was modeled for three representative case-study days. Benzene measurement is a reasonable surrogate for other HAP emissions.<sup>7</sup> Maps of the 24-hr accumulative concentrations of benzene were produced for each of the days.

**Figures 11 through 13** provide the model results for these case study days. The results predict very low benzene levels downwind of the refinery. The concentrations fields provide further evidence that the monitoring paths (Paths 1 and 2) upwind of the city of Benicia are in the correct location and that monitoring along the western/northwestern fenceline is not required. Any emission that would pass just north of Path 1 would also be captured by Path 1 monitors, because of pollutant dispersion.

Because the east boundary that is upwind of the business/commercial area is covered by Monitoring Path 3, we did not perform modeling for the onshore, westerly wind events.

As noted in Figure 2, there is a small gap in coverage between monitoring Paths 1 and 2 over 2<sup>nd</sup> Street because it was not logistically feasible to measure in this area. However, the horizontal dispersion of any material released from the refinery would create a wide enough plume by the time the plume reached this gap, such that monitoring along both Paths 1 and 2 would measure any material.

<sup>&</sup>lt;sup>6</sup> Based on 2010 EPA ICR data adjusted for the flue gas scrubber.

<sup>&</sup>lt;sup>7</sup> Background section of Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards.



**Figure 11.** Dispersion modeling results using meteorological data from January 24, 2015, showing predicted 24-hr average benzene concentrations ( $\mu$ g/m<sup>3</sup>). Note: 1 ppb = 3.2  $\mu$ g/m<sup>3</sup> for benzene at 20°C and 1013 mb.



**Figure 12.** Dispersion modeling results using meteorological data from January 25, 2015, showing predicted 24-hr average benzene concentrations ( $\mu$ g/m<sup>3</sup>). Note: 1 ppb = 3.2  $\mu$ g/m<sup>3</sup> for benzene at 20°C and 1013 mb.



**Figure 13.** Dispersion modeling results using meteorological data from January 26, 2015, showing predicted 24-hr average benzene concentrations ( $\mu$ g/m<sup>3</sup>). Note: 1 ppb = 3.2  $\mu$ g/m<sup>3</sup> for benzene at 20°C and 1013 mb.

#### 2.2.5 Visibility Conditions

Tule fog forms when there is high relative humidity (typically after rain), light wind, and rapid cooling. Tule fogs typically form in the California Central Valley, extending into the marshlands along the Sacramento and San Joaquin Rivers and into the Carquinez Straits, especially during the rainy season of late fall through early spring. Heavy fog may entirely block the signal from an open-path instrument and prevent data collection; however, even light fog can absorb the signal partially and interfere with measurements. Tule fogs may occur during periods when pollutant measurements are most critical because (1) the stable atmospheric conditions associated with Tule fogs are unfavorable for pollutant dispersal, and (2) they are most likely to occur during northeasterly wind events when residential receptors in Benicia are downwind from the refinery. Figure 14 shows an example of the Tule fog at the refinery. To investigate visibility, a visibility monitor was operated at the refinery from January 14 through July 9, 2015.



Figure 14. Example of tule fog at the Valero Benicia refinery.

**Figure 15** shows that 617 five-minute periods were recorded with visibility below 500 meters, and 839 periods were recorded with visibility below 1,000 meters. While the exact relationship between visibility and open-path measurements is not established, the expectation is that there would be no measurements when visibility is less than the twice the path lengths (two times the path lengths is used because the open-path sensor light travels to the mirror and back to the analyzer). Assuming that the frequency of low visibility observed during mid-January to mid-July is representative of visibility from mid-July through mid-January, and that 2015 is representative of other years, we expect fog to preclude open-path measurements only about 1% of the time over the course of a year. Rule 12-15 allows for this missing data, but only if supported by visibility measurements. For this reason, visibility measurements will be taken as part of the measurement program.





#### 2.2.6 Instrument Selection

Literature reviews, site surveys, and interviews with instrument manufacturers were performed to determine the instruments needed to meet Rule 12-15 requirements. Both fixed-site and open-path instruments were investigated. Based on the distances that need to be covered by measurements (hundreds of meters), data time-resolution requirements (5 minutes), and current measurement technology, open-path instruments were selected.

Open-path instruments transmit light or infrared energy across a long path; the signal is either detected remotely by a targeted detector, or reflected by a targeted mirror ("retroreflector") for detection elsewhere—usually by a combined transmitter/detector at the original point of transmission. Energy absorption at different wavelengths is measured and recorded by the detector. Energy absorption relates to the average concentrations of gases of interest along the light path, according to Beer-Lambert's absorption law, with individual gases having characteristic wavelengths at which they absorb most effectively. Therefore, measurements of energy absorption between the transmitter and detector can be used to infer average concentrations across the length of the path for species of interest. Figure 16 illustrates the basic concepts of open-path measurements. Note that open-path measurements cannot distinguish between a widely dispersed, low-concentration plume and a narrow, high-concentration plume; they detect average concentrations across the entire distance from transmitter to detectors.



**Figure 16**. Basic premise for open-path instrument operation. Image from CEREX Sentry-MS monitoring brochure.

Along all paths, BTEX and SO<sub>2</sub> will be measured using a monostatic UV-DOAS with a xenon light source. The xenon light is required to achieve measurements over paths that are about 300 to 600 meters long and to achieve the minimum detection limits (MDL) for BTEX. H<sub>2</sub>S will be measured using monostatic TDLAS instruments. The basic principle of TDLAS is to measure the absorption of a single absorption line for the target pollutant. A tunable diode laser can emit light at a very specific wavelength, which allows the measurement to avoid potential interferents. For H<sub>2</sub>S, manufacturers report that the TDLAS has detection limits on the order of 200 ppb for path lengths of about 500 meters; however, its actual minimum detection limit will depend on atmospheric conditions and on the specific instrument used. In theory, one can monitor H<sub>2</sub>S using UV-DOAS, but its absorption spectra overlaps with BTEX and will generate false positives. While Fourier Transform Infrared Technology spectroscopy (FTIR) technology was considered for measurements of BTEX and H<sub>2</sub>S, instrument manufacturers informed Valero that FTIR is not suitable for these compounds because of poor detection limits and overlap in absorption with other compounds (such as carbon dioxide with benzene).

Table 2 summarizes the MDL and upper detection limit (UDL) for each species by instrument for each measurement path, as provided by instrument manufacturers. The detection limits are for the average species concentration along a path; narrow plumes that only cover a portion of the path would need to have a higher concentration than the MDL to be detected.

Table 2. Open-path instruments and approximate detection limits by pollutant and path. Actual limits will be different and will depend on ambient conditions and final instrument vendor. TDLAS MDLs for H<sub>2</sub>S is less certain; thus, only a rough MDL is provided.

Path			1-1'		1-1"		2-2''		2-2'		3-3'		3-3"
Distance (meters)			321		523		598		572		574		527
Technology	Compound	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)						
TDLAS	Hydrogen Sulfide	200	15600	200	95600	200	83600	200	87400	200	87100	200	94900
	Benzene	0.4	23900	0.3	14700	0.2	12800	0.2	13400	0.2	13400	0.3	14600
	Toluene	4	13600	2	8300	2	7300	2	7600	2	7600	2	8300
UV-DOAS (Xenon )	Ethylbenzene	9	2900	5	1800	5	1600	5	1600	5	1600	5	1800
(,	Total Xylene	22	7300	13	4500	12	3900	12	4100	12	4100	13	4400
	Sulfur Dioxide	10	6800	6	4200	6	3600	6	3800	6	3800	6	4100
Monostatic (as opposed to bistatic) instruments use mirrors to reflect sensor light; monostatic instruments have been selected to reduce the need for substantial power at the mirror sites and to improve MDL by increasing effective path lengths. Power, communications, and shelter are required at the light-source/detector end of the monitoring path only. The retro-reflector needs only to be aligned for maximum performance at the other end of the path and to be cleaned regularly. An example of a UV-DOAS analyzer and receiver in a shelter is shown in Figure 17. The retro-reflector is shown in Figure 18. We anticipate a very similar setup for Path 1 and Path 2. For Path 3, the instruments and retroreflector may be placed on an elevated platform to avoid interference with passing vehicles (see the example in Figure 19).



Figure 17. Example of a UV-DOAS analyzer installation.



Figure 18. Example of a UV-DOAS retroreflector installation.



Figure 19. Example of a UV-DOAS analyzer installation on an elevated platform.

### 2.3 Data Management Requirements

### 2.3.1 Data Recovery

BAAQMD guidance for open-path measurement data recovery requirements are shown in Table 3. Because open-path measurements are affected by atmospheric conditions such as dense fog, missing data during low-visibility conditions do not count against completeness requirements. Visibility measurements will be made using a forward scattering optical visibility sensor to document the time periods of reduced visibility. The threshold for impairment of the open-path measurements is not well established. For example, for a path length of 500 meters to the mirror, the effective path length is 1,000 meters; therefore, visibility less than 1,000 meters will likely affect data quality. We will refine this threshold based on final instrument selection, path length, manufacturer specifications, and review of the actual data signal (e.g., signal to noise ratio) once the equipment is installed and operating. Visibility measurements will be made at least every five minutes to coincide with the open-path measurements.

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

#### Table 3. Data recovery requirements.

<sup>a</sup> The exact number of days in the quarter will be used; this example is for illustration only.

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 that were collected divided by 24. Percent data recovery for the calendar quarter is the number of valid daily values that were collected divided by the total number of days in the date range (e.g., 90 days in the quarter). The 1-hr values must meet the 75% data completeness requirement to be included in the computation for quarterly completeness. 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 low-visibility conditions—will also be computed.

Other factors that affect data availability include instrument bump test (approximately every quarter for a few hours), other maintenance (e.g., replacement of UV bulbs for the UV-DOAS after every 2,000 hours of use, roughly quarterly), and annual maintenance. For the TDLAS, a backup system will be used when each of the primary TDLAS instruments is returned to the manufacturer for maintenance. Regular maintenance and careful, responsive operation will minimize instrument downtime.

### 2.3.2 Data Quality Assurance/Quality Control (QA/QC)

A key goal of the QA/QC plan is to ensure high-quality data that are representative and defensible. Clear definitions and procedures for QA/QC are also necessary to inform the public on why some data are missing, flagged as questionable, or invalid. Data review will consist of the following types of actions.

An air quality specialist will review bump test data, instrument field setup, and instrument functionality. Initial bump test data, data processing calculations (i.e., conversion of instrument signal to concentration), data file formats, and data transfer will be verified. Throughout operations, the project QA manager will ensure that Standard Operating Procedures (SOPs) are being followed, operators are documenting field operations in field data sheets and logbooks, instrument performance checks are being conducted, and instruments are passing the performance checks.

Additional checks will focus on internal consistency of the data. Both automatic screening and manual visual review of data streams will be conducted. An air quality specialist will perform daily review of data to ensure proper operation of field equipment and provide feedback to the field operators when potential problems are identified. By keeping monitoring equipment operational, higher data completeness can be achieved.

Details regarding the QA/QC process can be found in Section 3.2.1 and in the QAPP (Appendix A).

# 3. Routine Operations

Use of six UV-DOAS, six TDLAS, and two visibility instruments are proposed. Instrument operations, maintenance, and bump tests include daily checks to ensure that data are flowing from all instruments, as well as monthly, quarterly, and annual maintenance activities. Further details are provided in the following sections, which describe routine instrument and data management operations. Full details and documentation are included in the QAPP, which is provided in Appendix A.

### 3.1 Instrument Operations

### 3.1.1 UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. Table 4 summarizes typical UV-DOAS maintenance activities as recommended by the manufacturer. Preventive maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms will alert operators to specific issues needing to be addressed.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	$\checkmark$	$\checkmark$	$\checkmark$
Inspect optics on detector and retro-reflector; clean if necessary.	~	✓	~
Inspect system filters.	$\checkmark$	$\checkmark$	$\checkmark$
Confirm the alignment to verify there has not been significant physical movement. This is automatically monitored as well.	$\checkmark$	$\checkmark$	$\checkmark$
Download data from detector hard drive and delete old files to free space, if needed.	~	$\checkmark$	~
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	√	✓	V
Change out the UV source.		$\checkmark$	
Replace ventilation exit and intake filters.		$\checkmark$	
Clean optics on detector and retro-reflector.		$\checkmark$	
Realign system after service.		$\checkmark$	$\checkmark$
Check system performance indicators.		$\checkmark$	$\checkmark$
Check system response (bump test).		$\checkmark$	
Perform bump test to verify the system can detect at or below a lower alarm limit.			$\checkmark$
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency.		$\checkmark$	$\checkmark$
Verify system settings.			$\checkmark$

Table 4. Schedule of maintenance activities for the UV-DOAS.

### 3.1.2 TDLAS

The TDLAS has similar maintenance activities to the UV-DOAS. The TDLAS system is also designed to require only modest service and maintenance. Table 5 summarizes TDLAS maintenance activities, as recommended by the manufacturer. Preventative maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed. Calibration is typically done at the factory, and field calibration is not required because these instruments do not suffer span drift; however, bump tests will be performed.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	$\checkmark$	$\checkmark$	$\checkmark$
Inspect optics on detector, clean if necessary.	$\checkmark$	$\checkmark$	$\checkmark$
Check the alignment to verify there has not been significant physical movement.	$\checkmark$	$\checkmark$	$\checkmark$
Download data from detector hard drive and delete old files to free space, if needed.	✓	✓	$\checkmark$
Ensure there are no obstructions between the detector and the retroreflector (such as equipment, vegetation, vehicles).	✓	✓	✓
Check system performance indicators.		$\checkmark$	$\checkmark$
Perform bump test.		$\checkmark$	$\checkmark$
Review and test light and signal levels.		$\checkmark$	$\checkmark$
Verify system settings.			$\checkmark$

Table 5. Schedule of maintenance activities for the TDLAS.

### 3.1.3 Visibility Instruments

For the visibility instruments, monthly maintenance includes inspecting the sensor for dirt, spider webs, birds' nests, or other obstructions. If the sensor is dirty, the glass windows can be cleaned with glass cleaner. There are no serviceable components in the sensor.

The sensors are calibrated in the field using a manufacturer-specific calibration kit. A calibration kit consists of a blocking plate or block for checking the sensor zero and a scatter plate for checking the sensor span. The calibration fixture is assigned a factory-traceable extinction coefficient (EXCO) used to calculate the expected values during calibrations. Calibrations will be performed every six months or as specified by a manufacturer.

### 3.2 Data Management Operations

Data management occurs on a sub-daily, quarterly, and annual basis. On a sub-daily basis, data are transferred from infield instruments through a data acquisition system (DAS) to the Data Management System (DMS) using cell modem in near-real time. Data are also stored onsite on instrument computers in case of cell modem failure. The DMS uses a Microsoft SQL relational database with stored procedures. These raw data are not yet intended for the public website.

DMS can handle the large volumes of data that will be generated in this project. DMS will be used to automatically quality control data, detect outliers and problems, generate reports, and create 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 project and facility staff. The operations website will show time series plots of BTEX, H<sub>2</sub>S, SO<sub>2</sub>, winds, and visibility data. The automatically QC'd air quality data will be fed to the public website (see Section 3.2.2) in near-real time. The DMS data will be backed up on a daily basis. Backup media will be moved weekly to a secure offsite facility.

### 3.2.1 QA/QC

All data values that are not associated with bump tests, other instrument maintenance, or instrument problems will be displayed to the public in near-real time. If data are subsequently proven to be invalid, they will be removed from the public display.

A non-public field operations website will be used for daily graphical review of the data (see example at Figure 20). Common problems include flat signal/constant values, no signal/missing data, extremely noisy signal, rapid changes (spikes or dips), and negative concentrations (see annotated Figure 21 for some examples). An initial review, typically of a three- to five-day running time-series plot of selected parameters for each instrument, allows the analyst to see common problems and verify instruments are operational. If it appears that an instrument is not operating, or the data are missing, the field operator will be notified and further investigation and corrective action, if needed, will be taken.



Figure 20. Example of non-public field operations website used for daily review of instrument operations.





Once it is clear that instruments are operational, the next step will be to review whether the pollutant concentration patterns are reasonable with respect to the time of day, season, meteorology, and concentrations are expected and observed at other sites. If anomalies are observed, additional analysis will be conducted to determine if there is an instrument malfunction or the data are truly anomalous, but explainable and valid.

Visual review of data will be augmented by automated data screening within the DMS upon data ingest. Automated screening checks of data feeds are helpful to focus the analyst's efforts on the data that need the most attention and are used to screen out invalid data for public display. Initial screening checks, along with actions to be taken, are summarized in Table 6. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. All screening criteria (flags and rates of change) are preliminary and will be refined during the project based on actual observations. In summary, the DMS auto-screening checks that will be used include:

- Range These checks will ensure 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 QC checks for the instruments are summarized in Table 7. 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. Data are invalidated only if a known 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. 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.

In addition to auto-screening and daily visual checks, data will be subjected to more in-depth review on a quarterly basis and when data fail screening. Final data sets will be compiled quarterly, 60 days after each quarter, and provided to the BAAQMD.

On a quarterly basis, validation checks will include:

- Looking for statistical anomalies and outliers in the data
- Inspecting several sampling intervals before and after data issues or instrument tests or repairs
- Evaluating monthly summaries of minimum, maximum, and average values
- Ensuring data reasonableness by comparing to remote background concentrations and average urban concentrations
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on observations by site operator
- Ensuring that data are realistically achievable, i.e., not outside the limits of what can be measured by the instrument
- Confirming that bump tests were conducted and were within specifications

These in-depth analyses typically require data that are not available in real time and ensure that final data sets are fully validated.

On a quarterly basis, to ensure all the daily QC tasks are complete, analysts will:

- Review any instrument bump test results.
- Verify that daily instrument checks were acceptable

- Review manual changes to operations/data, and verify that the changes were logged and appropriately flagged
- Ensure that daily instrument checks have the appropriate QC codes applied

On a quarterly basis, analysts will subject the data to final QC by:

- Filling in missing records with null values, and add Null Codes
  - If a record is not created for a particular site/date/time/parameter combination, a null record will be created for data completeness purposes.
  - Invalid data will have a Null Code, or in other words, a reason for being invalid.
  - Inspect data consistency over three months.
  - Review ranges of values for consistency—ranges should remain consistent over months of monitoring.
  - Check bump test values for consistency.
  - Review quarterly data completeness.

All actions will be documented in the DMS, which retains raw data and traceability of all actions that result in the final data. Additional details on the final QC process are provided in the QAPP.

On an annual basis, Valero 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 bump tests; by analyzing the reported values in the context of refinery operations; and by analyzing the data in the context of the meteorology. The results will be summarized in an internal technical memorandum and provided to the BAAQMD upon request.

**Table 6.** Initial screening checks for 5-minute data. All valid and flagged data values will be displayed to the public in real time. If they are invalid, they will not be included in the public display. All screening values below (flags and rates of change) are preliminary and will be refined during the project.

Management			Checks						
(units)	MDL	Range	Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility		
Benzene (ppb)		If above <u>24 ppb</u> , flag data and conduct investigation on validity		If value changes by more than 12 ppb, flag data and conduct investigation on validity	If data are missing, code as missing and investigate cause	If sensor indicates malfunction or bump test data, code as appropriate and do not display data	If visibility is less than 1,000 m and data are missing, code as missing due to low visibility		
Toluene (ppb)	If below MDL, flag	If above <u>100 ppb</u> , flag data and conduct investigation on validity	If same value observed for four or more intervals, flag	If value changes by more than 50 ppb, flag data and conduct investigation on validity					
Ethylbenzene (ppb)	as below MDL	below DL If above <u>100 ppb</u> , flag data and conduct investigation on validity If above <u>100 ppb</u> , flag data and conduct investigation on validity	data and conduct investigation on validity	If value changes by more than 50 ppb, flag data and conduct investigation on validity					
Total Xylene (ppb)				If value changes by more than 50 ppb, flag data and conduct investigation on validity					

		Range	Checks						
(units)	MDL		Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility		
H <sub>2</sub> S (ppb)	If below MDL, flag	If value above If same value <u>30 ppb or the MDL</u> , observed for flag data and four or more conduct intervals, flat w investigation on as suspect validity and conduct w	If same value observed for four or more intervals, flag as suspect and conduct	If value changes by more than 15 ppb, flag data and conduct investigation on validity	If data are missing, flag as missing and investigate cause (SAME FOR ALL POLLUTANTS)	data are If sensor ssing, flag indicates missing malfunction or d bump test data, vestigate flag as use (SAME appropriate PR ALL (SAME FOR ALL DLLUTANTS) POLILITANTS)	If visibility is less than 1,000 m and data are missing, flag as		
SO <sub>2</sub>	as below MDL	If value above <u>37.5</u> <u>ppb</u> , flag as suspect and conduct investigation on validity	investigation on validity (SAME FOR ALL POLLUTANTS)	If value changes by more than 19 ppb, flag as suspect and conduct investigation on validity			appropriate (SAME FOR ALL POLLUTANTS)		
Visibility (meters)	If value less than 0, flag data		Not applicable	Not applicable	POLLUIANTS)		Not applicable		

QA/QC Checks	Frequency	Acceptance Criteria
Baseline stability	Continuous	
Single beam ratio test (strength of UV source)	Real-time	
Bump tests in field	Quarterly	±20%
Measurement quality – R2	Continuous	0.7 to 1.0
Integration time	Continuous	80-200 mS 400 mS integration time results in a warning notification
Signal intensity	Continuous	>30% Signal intensity below 30 results in a warning notification
	TDLAS	
Bump tests	Quarterly	

### Table 7. Instrument QA/QC checks.

Auto-screening checks were discussed in Section 3.2.1. Data flagged through auto-screening will be graphically reviewed, and QC flags will be updated with daily and quarterly actions (see Figure 22). DMS keeps track of data changes in its chain of custody feature—i.e., raw data are preserved as well as all changes.



Figure 22. Screenshot of DMS showing winds and pollutant concentrations.

### 3.2.2 Public Data Availability and Display

Data are screened in real time upon ingest into the DMS, as described in previous sections. Automated procedures will be used to ensure that data are properly ingested, stored, processed, and quality-assured, and that products are delivered to a public-facing website in real time, defined here as 10 minutes or less after data collection.

For the public website, key components include visual display of data in real time, context for the public to better understand the concentrations displayed, and a mechanism for feedback on the website.

The preliminary QC'd data will be presented in a time series of benzene, toluene, ethylbenzene, total xylenes, SO<sub>2</sub> and H<sub>2</sub>S concentrations, and visibility, wind speed, and wind direction. Data will be provided as 5-minute running averages. Data will be color-coded and annotated for quality (valid,

invalid, flagged, missing). An example of a public-facing website that allows users to explore data is shown in Figure 23.

In the event that high concentration levels occur, Valero will follow its existing event protocol and the City of Benicia will decide when it is appropriate to activate its emergency alert program. Episodic data will be provided to the BAAQMD upon request, consistent with other regulatory measurements.

Once QA/QC of the final data is completed within 60 days after the end of each calendar quarter, the refinery will provide one-hour average concentration data in tabular format through a comma separated value data file to the BAAQMD. The BAAQMD may make the one-hour average data available to the public through a BAAQMD website or through public records request. The refinery will make data available to BAAQMD upon request prior to the report submittal.

All data will be retained by the facility for a period of five years, consistent with Regulation 12-15-502.



Figure 23. Example of a public-facing web page.

The data to be collected are high time resolution, spatially variable, and chemically complex. To provide context to this complex data set for the public, the following information will be included through a combination of links, graphics, or captions:

- Information about the species measured and the measurement techniques.
- Context of what fenceline measurements represent as compared to other regional air quality measurements and as outlined by BAAQMD.
- Health data provided on the webpage will be sourced from OEHHA official information.
- Discussion of non-refinery sources that could affect the measured concentrations
- Definitions of abbreviations
- Discussion of data below detection
- Definition of data QC flags and their meaning
- Frequently asked questions (FAQs; to be developed over time)
- Quality procedures

Information will be written at a public-friendly level. Clarity and thoroughness will help to reduce the number of questions that arise.

To facilitate public feedback, a feedback button will be provided on the web page. When a user clicks on the button, an email form will pop up for the user to submit comments about the website. The email will be delivered to a Valero contact or a designated consultant responsible for deciding how to respond to the public comments. The emails received through the website will be archived. Although not all comments have to be addressed, all comments will be made available to BAAQMD upon request. Some of the comments will aid in the creation of FAQs.

# Appendix A: Quality Assurance Project Plan

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# 1. Project Background and Management

### 1.1 Background

### 1.1.1 Purpose

The Valero Refining Company (Valero) proposes to conduct air quality monitoring at its Benicia, California, refinery in response to the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15.<sup>1</sup> The monitoring will follow a facility-specific air monitoring plan consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.<sup>2</sup> Rule 12-15 requires routine monitoring near the fencelines of all San Francisco Bay Area refineries for specific air compounds, with data reported to the public.<sup>3</sup>

### 1.1.2 Rationale

Rule 12-15 requires fenceline monitoring of multiple compounds using "open-path technology capable of measuring in the parts-per-billion range regardless of path length" or an alternative measurement technology.<sup>2</sup> Valero has proposed to conduct open path pollutant monitoring, in addition to visibility and meteorological measurements to meet the regulations.

This document is a quality assurance project plan (QAPP), which documents the measures that the project team will take to ensure that the data collected are of the highest quality.

## 1.2 Roles and Responsibilities

This project combines refinery staff, contractors, and quality assurance, field, and website personnel. Figure 1 shows an organization chart for the project.

<sup>&</sup>lt;sup>1</sup> Petroleum Refining Emission Tracking (Rule 12-15; approved by the BAAQMD on April 20, 2016).

<sup>&</sup>lt;sup>2</sup> Bay Area Air Quality Management BAQMD (2016) Air monitoring guidelines for petroleum refineries. April. Available at baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en.

<sup>&</sup>lt;sup>3</sup> The exact timing for the start of fenceline monitoring depends on when this monitoring plan is approved by the BAAQMD.



Figure 1. Organizational chart for this project.

The overall project will be run by a **Project Manager** appointed by the refinery. This PM acts as the central point of contact for the BAAQMD and the QA manager. The PM is responsible for overseeing the project and reporting directly to the BAAQMD.

The QA Manager is responsible for ensuring the quality of data collected in this project. The QA Manager oversees data collection and review, provides QA oversight during the study, and oversees and reports on QA activities to the Refinery PM and BAAQMD QA Manager. The QA Manager oversees daily data review and data management; works with the Field Staff Manager to ensure any data issues are addressed by the field technicians promptly; and works with the Website Manager to ensure that data provided to the public are of high quality.

The Field Staff Manager ensures that field technicians (site operators) are meeting the requirements of the project. The Field Staff Manager coordinates staff coverage and serves as a technical resource for site measurements.

Field Technicians/Site Operators perform instrument maintenance. The technicians ensure that all measurements are collected in accordance with SOPs, standard methods, and regulations, where applicable. Technicians perform the required quality checks on instruments and document all work in site logs.

The Instrument Contractors provide technical support for the instruments deployed in the field.

The Data Manager is responsible for ensuring that daily data review is conducted, data that fail autoscreening are inspected, and data validation follows the proper schedule and procedures. The Data Manager is also responsible for delivering the validated data to the PM.

Daily data review and data validation are conducted by experienced air quality analysts. The Data Reviewers communicate with the Data Manager when there are issues and may also interact with the Field Technicians when they notice an issue that needs to be addressed.

The Website/Data System Manager is responsible for properly displaying data on the website, managing inquiries from the public, and ensuring that validated data are available for download on a quarterly basis. Automated alerting will notify the Website/Data System Manager when the real-time data are not available on the website. This manager will be responsible for assessing and fixing data communication and other information technology–related issues concerning the website and data system.

## 2. Measurements

### 2.1 Instrument Selection and Descriptions

The required compounds to be measured are benzene, toluene, ethylbenzene, xylenes (BTEX), and hydrogen sulfide (H<sub>2</sub>S). These compounds will be measured at a 5-minute resolution. Because of the distances that need to be covered by measurements (hundreds of meters), data time-resolution requirements (5 minutes), and current measurement technology, open-path instruments (UV-DOAS and TDLAS) were selected.

Along all measurement paths (see Section 2.2.1), BTEX and SO<sub>2</sub> will be measured by monostatic Ultra Violet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. The xenon light is required to achieve measurements over paths that are about 300 to 600 meters long and to achieve the minimum detection limits (MDL) for BTEX. The analyzer records the intensity of light at discrete wavelengths. Any UV-absorbing gas that is present in the beam absorbs at a specific wavelength of light. Each species of gas has a unique absorbance fingerprint (i.e., the ratios between the absorbance at several different wavelengths are unique to that gas). The analyzer compares regions within the sample absorbance spectra to the same regions within the reference absorbance spectra. The analyzer uses a classical least squares regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files. Beer's Law is used to report gas concentrations. Though not written specifically for UV-DOAS, this approach is the same as that specified in the Environmental Protection Agency's TO-16 Methodology.<sup>4</sup> Closeness of fit is indicated by the correlation coefficient  $(R^2)$  of agreement between the measured spectra and the reference spectra. The R<sup>2</sup> is provided with each concentration so that interference can be detected if it is present. Selection of regions of analysis that are free of absorbance due to other gases within the sample is the primary means of avoiding cross-interference. Spectral subtraction is used in cases with overlapping absorbance features; the subtraction technique is proprietary to the instrument manufacturer.

Along all measurement paths, H<sub>2</sub>S will be measured by monostatic *Tunable Diode Laser Absorption Spectroscopy (TDLAS)* instruments. A tunable diode laser emits light at one very specific wavelength, which allows the measurement to avoid potential interferents. For H<sub>2</sub>S, manufacturers report that the TDLAS has detection limits on the order of 200 ppb for path lengths of about 500 meters; however, its actual minimum detection limit will depend on atmospheric conditions and on the specific instrument used.

Heavy fog may entirely block the signal from an open-path instrument and prevent data collection; however, even light fog can absorb the signal partially and interfere with measurements. Tule fog forms when there is high relative humidity (typically after rain), light wind, and rapid cooling. Tule

<sup>&</sup>lt;sup>4</sup> Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-16. Long-Path Open-Path Fourier Transform Infrared Monitoring Of Atmospheric Gases (1999) EPA/625/R-96/010b.

fogs typically form in the California Central Valley, extending into the marshlands along the Sacramento and San Joaquin Rivers and into the Carquinez Strait, especially during the rainy season of late fall through early spring. Tule fogs may occur during periods when pollutant measurements are most critical because (1) the stable atmospheric conditions associated with tule fogs are unfavorable for pollutant dispersal, and (2) tule fogs are most likely to occur during northeasterly wind events when residential receptors in Benicia are downwind from the refinery. Visibility measurements will be made at two locations and used as evidence of low-visibility conditions that cause missing measurements from the open-path instruments.

**Table 1** summarizes the method detection limit (MDL) and upper detection limit (UDL) for each species by instrument for each measurement path, as provided by instrument manufacturers. The MDL is the lowest concentration that can be measured at the path length. The UDL is the highest concentration that can be measured at that path length. The detection limits are for the average species concentration along a path; when a narrow plume covers only a portion of the path, a higher concentration than the MDL is needed for the species to be detected.

Table 1. Open-path instruments and approximate detection limits by pollutant and path. Actual limits will be different and will depend on ambient conditions, final path length, and final instrument vendor. TDLAS MDLs for  $H_2S$  are less certain; thus, only a rough MDL is provided.

Path		1-1'		1-1"		2-2''		2-2'		3-3'		3-3"	
Distance (meters)		321		523		598		572		574		527	
Technology	Compound	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)						
TDLAS	Hydrogen Sulfide	200	15600	200	95600	200	83600	200	87400	200	87100	200	94900
	Benzene	0.4	23900	0.3	14700	0.2	12800	0.2	13400	0.2	13400	0.3	14600
	Toluene	4	13600	2	8300	2	7300	2	7600	2	7600	2	8300
UV-DOAS (Xenon )	Ethylbenzene	9	2900	5	1800	5	1600	5	1600	5	1600	5	1800
	Total Xylene	22	7300	13	4500	12	3900	12	4100	12	4100	13	4400
	Sulfur Dioxide	10	6800	6	4200	6	3600	6	3800	6	3800	6	4100

## 2.2 Monitor Siting Overview

### 2.2.1 Rationale

For the fenceline monitoring program, Valero proposes to use open-path instruments to measure the required compounds BTEX, SO<sub>2</sub>, and H<sub>2</sub>S along three paths. The three measurement paths, composed of two segments each, will be implemented to cover Valero's fencelines in consideration of nearby local receptors (e.g., residences and businesses), dominant winds that blow from west to the east, and infrequent winds that blow from the northeast to the southwest to portions of populated areas in Benicia.

The three primary monitoring paths, composed of six total segments, are shown in Figure 2.

- Paths 1 and 2 cover the southwest fenceline to assess potential transport toward the city of Benicia. This transport direction is infrequent and only occurs on an occasional basis in the winter, when winds sometimes blow from the northeast toward the southwest. Over the course of a year, these northeast winds occur less than about 7% of the time. Because of terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability; therefore, the downwind areas that could be affected under these wind conditions are very narrow.
- Path 3 covers the eastern fenceline to assess potential transport toward the business/commercial area east of the refinery. This transport direction is common in the spring, summer, and early fall, when winds often blow from the west toward the east.
- Instruments on Paths 1 and 2 will be elevated about 5 ft above ground level (agl).
   Instruments on Path 3 may be elevated to about 15 to 20 feet agl so that vehicle traffic will not block the open-path sensor light; the final height will be determined based on site logistics.

Open-path analyzers will be located at Sites 1, 2, 3', and 3". Sites 1 and 2 will each have two UV-DOAS and two TDLAS analyzers. Each pair of analyzers at each site will point roughly 180 degrees from each other. The remaining numbered sites (1', 1", 2', 2", and 3) will have retro reflectors (i.e., mirrors). This setup will provide maximum spatial coverage along the critical paths.





Visibility instruments will be placed at Sites 1 and 3' to measure visibility conditions at different locations and elevations. Two sites have been selected because visibility can vary spatially across the refinery.

### 2.3 Instrument Operations and Maintenance

Three instrument systems are included in this project: UV-DOAS, TDLAS, and visibility measurements. Other meteorological data will be obtained from existing measurements at the refinery. Quality assurance is built into operations and maintenance. For all instruments, scheduled maintenance will occur monthly, quarterly, and/or annually. Emergency maintenance will occur as needed when problems are identified during daily data review and auto-screening of real-time data.

### 2.3.1 UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. Table 2 summarizes typical UV-DOAS maintenance activities as recommended by the manufacturer. These actions help ensure data integrity and maximize up-time.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓	✓	$\checkmark$
Inspect optics on detector and retro-reflector; clean if necessary.	$\checkmark$	$\checkmark$	$\checkmark$
Inspect system filters.	$\checkmark$	$\checkmark$	$\checkmark$
Confirm the alignment to verify there has not been significant physical movement. This is automatically monitored as well.	$\checkmark$	$\checkmark$	$\checkmark$
Download data from detector hard drive and delete old files to free space, if needed.	$\checkmark$	$\checkmark$	$\checkmark$
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	$\checkmark$	$\checkmark$	$\checkmark$
Change out the UV source.		$\checkmark$	
Replace ventilation exit and intake filters.		$\checkmark$	
Clean optics on detector and retro-reflector.		$\checkmark$	
Realign system after service.		$\checkmark$	$\checkmark$
Check system performance indicators.		$\checkmark$	$\checkmark$
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.		$\checkmark$	$\checkmark$
Verify system settings.			$\checkmark$

Table 2. Schedule of maintenance activities for the UV-DOAS.

### 2.3.2 TDLAS

Maintenance activities for the TDLAS and the UV-DOAS are similar. The TDLAS system is also designed to require only modest service and maintenance. Table 3 summarizes TDLAS maintenance activities, as recommended by the manufacturer. Depending on TDLAS brand, bi-annual calibration at the factory may be performed.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	$\checkmark$	$\checkmark$	$\checkmark$
Inspect optics on detector, clean if necessary.	$\checkmark$	$\checkmark$	$\checkmark$
Check the alignment to verify there has not been significant physical movement.	$\checkmark$	$\checkmark$	$\checkmark$
Download data from detector hard drive and delete old files to free space, if needed.	✓	√	~
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	√	1	~
Check system performance indicators.		$\checkmark$	$\checkmark$
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.		V	
Review and test light and signal levels.		$\checkmark$	$\checkmark$
Verify system settings.			$\checkmark$

### Table 3. Schedule of maintenance activities for the TDLAS.

### 2.3.3 Visibility

For the visibility instruments, monthly maintenance includes inspecting the sensor for dirt, spiderwebs, birds' nests, or other obstructions. If the sensor is dirty, the glass windows are cleaned with glass cleaner. There are no serviceable components in the sensor. Calibration will be performed semi-annually.

## 2.4 Sampling System Corrective Actions

Corrective action will be taken to ensure that data quality objectives are met. Table 4 lists the types of issues that require corrective actions. (This table is not all-inclusive; additional checks may be added as the project progresses.) The daily data reviewers will review data to identify issues and will work with the field technicians and instrument contractors to resolve issues that need to be addressed on site.

Item	Problem	Action	Notification	Person Responsible
Erratic data	Possible instrument malfunction	Contact Field Manager and Instrument Contractor	Document in logbook, notify Field Manager	Field technician
Power	Power interruptions	Check line voltage, reset or restart instruments	Document in logbook, notify Field Manager	Field technician
Data downloading	Data will not transfer to the DMS	Contact Field Manager and Instrument Contractor	Document in logbook, notify Field Manager and Website/Data System Manager	Field technician
Supplies and consumables	Essential supplies run out	Contact Field Manager	Document in logbook, notify Field Manager	Field technician
Access to sites	Technician cannot access the sites	Contact Project Manager	Document in logbook, notify Project Manager	Field technician
Instrument Light level	A low light level alert is observed	Contact Instrument Manufacturer; Replace bulb	Document in logbook, notify Field Manager	Field Technician
Website	Website is down	Contact Website/Data System Manager	Notify Project Manager	Website/Data System Manager

### Table 4. Potential sampling and data reporting problems and corrective actions.
# 3. Quality Objectives and Criteria

## 3.1 Data and Measurement Quality Objectives

### 3.1.1 Discussion

To ensure success of field measurements, measurement performance or acceptance criteria are established as part of the monitoring design. These criteria specify the data quality needed to minimize decision errors based on the data. Data quality is defined in terms of the degree of precision, accuracy, representativeness, comparability, and completeness needed for the monitoring. Of these five data quality indicators, precision and accuracy are quantitative measures, representativeness and comparability are qualitative, and completeness is a combination of quantitative and qualitative.

To ensure appropriate spatial coverage of measurements, a thorough meteorological analysis was performed, as documented in the monitoring plan. Comparability among measurements is addressed by using one manufacturer for each system (UV-DOAS, TDLAS, visibility) so that hardware and software are consistent among sites.

For all instrument/parameter combinations, data completeness requirements are provided in Table 5. 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 low-visibility conditions—will also be computed. The Rule allows for omission of time periods from the completeness calculation when atmospheric conditions prevented measurement, as proven using an independent measure of visibility.

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

Table 5. Data recovery requirements.

<sup>a</sup> The exact number of days in the quarter will be used; this example is for illustration only.

Other factors that affect data availability include instrument calibrations or bump tests (approximately every quarter for a few hours), annual maintenance, and other maintenance (e.g., replacement of UV bulbs for the UV-DOAS after every 2,000 hours of use, roughly quarterly). For the TDLAS, a backup system may be used (depending on brand) when each of the primary TDLAS instruments is returned to the manufacturer for factory calibration. Regular maintenance and careful, responsive operation will minimize instrument downtime.

## 3.2 Precision Checks, Bump Test, and Verification

For the UV-DOAS system, a bump test will be performed quarterly the first year and semi-annually in later years as high-quality, reliable system performance is confirmed. In the field, a bump test is used to verify the system can detect at or below a set level of concern.

TDLAS 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 the visibility instruments, the sensors are calibrated in the field using a manufacturer-specific calibration kit. A calibration kit consists of a blocking plate or block for checking the sensor zero and a scatter plate for checking the sensor span. The calibration fixture is assigned a factory-traceable extinction coefficient (EXCO) used to calculate the expected values during calibrations. Calibrations will be performed every six months or as specified by a manufacturer.

For the open-path systems, precision will 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 will then be evaluated by calculating the coefficient of variation (CV) during the period of low variability, as shown in Equation 1. If there are no periods of low variability with concentrations above the MDL, bump test data will be used to calculate precision.

$$Pr \ ecision \approx CV = \frac{\sigma_{measured}}{[conc]_{measured}} \times 100\%$$
(1)

where:

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

#### 3.2.1 Instrument or Standards Certifications

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

## 4. Data Management

Data quality criteria are evaluated through (1) automatic data checks conducted through the data management system and (2) data review by trained analysts (daily data review and periodic, more thorough validation).

## 4.1 Data Acquisition and Communications

Raw data management occurs on a real-time, daily, 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) using a cell modem. Data are also stored onsite on instrument computers in case of cell modem failure. The DMS uses a Microsoft SQL relational database with stored procedures. 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 operations website will show maps and time series plots of BTEX, SO<sub>2</sub>, H<sub>2</sub>S, winds, and visibility data.

The automatically QC'd air quality data will be fed to the public website ten minutes after data collection.

## 4.2 Automated Data Screening

Automated data screening is conducted within the DMS upon data ingest. Automated screening checks of data feeds are used to screen out invalid data for public display, and are helpful to focus the data reviewer's efforts on the data that need the most attention. Initial screening checks, along with actions to be taken, are summarized in Table 6. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. All screening criteria (flags and rates of change) are preliminary and will be refined during the project based on actual observations. The DMS auto-screening 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.
- Visibility impairment. While the exact relationship between visibility and open-path measurements is not established, the expectation is that there would be no measurements when visibility is less than the twice the path length (two times the path length is used because the open-path sensor light travels to the mirror and back to the analyzer).

Additional parameters that may be monitored as indicators of data quality include a data quality value for each concentration as reported by the instrument (i.e., correlation between measured and reference spectra), signal strength, wavelength versus intensity, and visual review of peaks. There are no previously set data quality objectives for these parameters; we will need to develop objectives for these parameters if we find that they are useful indicators for automated data quality screening or for data validation.

Data flags identified through auto-screening will be graphically reviewed during data validation (i.e., not in real time), and QC flags will be updated with daily and quarterly actions. DMS keeps track of data changes in its chain-of-custody feature—i.e., raw data are preserved as well as all changes.

**Table 6.** Initial screening checks for 5-minute data. All valid and flagged data values will be displayed to the public in real time. If data are invalid, they will not be included in the public display. All screening values below (flags and rates of change) are preliminary and will be refined during the project. During data validation, flagged data will be further investigated.

Measurement (units)	MDL	Range	Checks				
			Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility
Benzene (ppb)		If above <u>24 ppb</u> , flag data and conduct investigation on validity	If same value observed for four or more intervals, flag data and conduct investigation on validity	If value changes by more than 12 ppb, flag data and conduct investigation on validity	If data are missing, code as missing and investigate cause	If sensor indicates malfunction or bump test data, code as appropriate and do not display data	If visibility is less than 1,000 m and data are missing, code as missing due to low visibility
Toluene (ppb)	If below MDL, flag	If above <u>100 ppb</u> , flag data and conduct pelow investigation on DL, flag validity		If value changes by more than 50 ppb, flag data and conduct investigation on validity			
Ethylbenzene (ppb)	as below If MDL fl cd ir Va If fl cd ir va va	If above <u>100 ppb</u> , flag data and conduct investigation on validity		If value changes by more than 50 ppb, flag data and conduct investigation on validity			
Total Xylene (ppb)		If above <u>100 ppb</u> , flag data and conduct investigation on validity		If value changes by more than 50 ppb, flag data and conduct investigation on validity			

Measurement (units)	MDL	Range	Checks				
			Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility
H <sub>2</sub> S (ppb)	If below MDL, flag	If value above <u>30 ppb or the MDL</u> , flag data and conduct investigation on validity	If same value observed for four or more intervals, flag as suspect and conduct investigation on validity (SAME FOR ALL POLLUTANTS)	If value changes by more than 15 ppb, flag data and conduct investigation on validity	If data are missing, flag	If sensor indicates	If visibility is less than 1,000 m and data are missing, flag as
SO <sub>2</sub>	as below MDL	If value above <u>37.5</u> <u>ppb</u> , flag as suspect and conduct investigation on validity		investigation on validity (SAME FOR ALL POLLUTANTS)	If value changes by more than 19 ppb, flag as suspect and conduct investigation on validity	as missing and investigate cause (SAME FOR ALL POLLUTANTS)	malfunction or bump test data, flag as appropriate (SAME FOR ALL POLITITANTS)
Visibility (meters)	If value less than 0, flag data		Not applicable	Not applicable	POLLOIANTS, POLLOIANTS,		Not applicable

<sup>a</sup> If the MDL is higher than 30 ppb, the MDL will be used as the screening criterion.

## 4.3 Data Verification

### 4.3.1 Confirm Daily Operation

Operationally, data are reviewed daily by a data reviewer to assess instrument operation. This initial review, typically of a three- to five-day time-series plot of selected parameters for each instrument, allows the analyst to see common problems and verify instruments are operational. If it appears that an instrument is not operating, or the data are missing, the field operator will be notified and further investigation and corrective action, if needed, will be taken.

In addition to daily checks of the field website, an 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. The time period allowed for missing data will likely be adjusted as the project proceeds to reduce false or excessive alerting. The alerting will likely be set initially for 6 to 12 missing 5-minute values (i.e., 30 to 60 minutes).

#### 4.3.2 Assess Data Reasonableness

Also operationally, the data reviewer quickly assesses whether the pollutant concentrations are reasonable with respect to the time of day, season, meteorology, and concentrations expected and observed along other paths. If anomalies are observed, additional analysis will be conducted to determine whether there is an instrument malfunction or the data are truly anomalous but valid. Data reasonableness is also assessed more thoroughly later during the data validation process.

## 4.4 Data Validation

### 4.4.1 Approach

On a monthly (at first) to 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 statistical tests 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:

- Looking for statistical anomalies and outliers in the data and investigating them
- Ensuring there are not several continuous 5-minute averages of the same number

- Evaluating monthly summaries of the minimum, maximum, and average values
- Ensuring the data are not biased by exceptional conditions or events occurring off refinery property
- 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<sup>5</sup>
- Inspecting several sampling intervals before and after data issues or instrument bump tests or 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 metadata (e.g., light intensity, operation codes) to confirm reasonableness
- Assessing visibility measurements to ensure adequate signal was obtained to quantify pollutant concentrations
- Confirming that bump tests or factory calibrations were conducted and were within specifications

General criteria for suspecting or invalidating data include:

- Monitor appears to have malfunctioned (acting erratic, spiking, or showing other evidence of questionable operation)
- Data are outside of plausible values (indicating a calculation error, averaging error, or instrument malfunction)

Additional QC checks for the instruments are summarized in Table 7. 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.

<sup>&</sup>lt;sup>5</sup> Measurements below the method detection limit will be flagged in the DMS for review by an analyst.

QA/QC Checks	Frequency	Acceptance Criteria				
UV-DOAS						
Bump test (accuracy)	Quarterly and after major service	±20%				
Baseline stability	Continuous	±5%				
Single beam ratio test (strength of UV source)	Real-time	To be determined				
Measurement quality – $R^2$	Continuous	0.7 to 1.0				
Integration time	Continuous	80-200 mS 400 mS integration time results in a warning notification				
Signal intensity	Continuous	>30% Signal intensity below 30 results in a warning notification				
	TDLAS					
Bump test	Quarterly	±20%				

#### Table 7. Instrument QA/QC checks.

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 a quarterly basis, to ensure all the daily QC tasks are complete, analysts will:

- Review any instrument bump test results.
- Verify that daily instrument checks were acceptable.
- Review manual changes to operations/data, and verify that the changes were logged and appropriately flagged.
- Ensure that instrument checks have the appropriate QC codes applied.

On 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.
- Inspect data consistency over three months.
- Review ranges of values for consistency—ranges should remain consistent over months of monitoring.
- Check bump test values for consistency.
- Review quarterly data completeness.

All actions will be documented in the DMS, 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 bump test; by analyzing the reported values in context of refinery operations; and by analyzing the data in context of the meteorology. The 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. An internal technical memorandum will be prepared. The results of the network performance will also be summarized in a technical memorandum and provided to the BAAQMD upon request.

## 4.5 Data Storage and Processing

The DMS data will be backed up on a daily basis. Backup media will be moved weekly to a secure offsite facility. The data will be stored for a period of five years after sampling.

## 4.6 Data Delivery

Final data sets will be compiled quarterly, 60 days after each quarter and provided to the BAAQMD.

## 4.7 Data Flow to Website

### 4.7.1 Auto-Screening and Alert Review

All data values that are not associated with bump tests, other instrument maintenance, or instrument problems will be displayed to the public in near-real time. If data are subsequently proven to be invalid, they will be removed from the public display.

A non-public field operations website will be used for daily graphical review of the data. Common problems include flat signal/constant values, no signal/missing data, extremely noisy signal, rapid

changes (spikes or dips), and negative values. An initial review, typically of a three- to five-day timeseries plot of selected parameters for each instrument, allows the analyst to see common problems and verify instruments are operational. If it appears that an instrument is not operating, or the data are missing, the field operator will be notified and further investigation and corrective action, if needed, will be taken.

Data are screened in real time upon ingest into the DMS, as described in previous sections. Automated procedures will be used to ensure that data are properly ingested, stored, processed, and quality-assured, and that products are delivered to a public-facing website in real time, defined here as 10 minutes or less after the data are collected.

The preliminary QC'd data will be presented in a time series of benzene, toluene, ethylbenzene, total xylenes, SO<sub>2</sub>, and H<sub>2</sub>S concentrations; and visibility, wind speed, and wind direction. Data will be provided as 5-minute averages. Data will be color-coded and annotated for quality (valid, invalid, flagged, missing).

#### 4.7.2 Data Backfill Process and Schedule

Prescreened, raw data will be replaced with validated data files within 60 days after the calendar quarter. All data, raw and validated, will be retained in the DMS.

## 5. Standard Operating Procedures

Instrument-specific SOPs will be provided after instrument selection.