Rule 4460

Petroleum Refinery Fence-line Air Monitoring Plan Assistance Documentation

San Joaquin Valley Air Pollution Control District

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1. Background

On October 8, 2017, the California State Legislature and Governor Jerry Brown passed Assembly Bill (AB) 1647[1]. As a part of the California Health and Safety Code §42705.6, this legislation requires the following: (1) the District design, develop, install, operate, and maintain a refinery-related community air monitoring system; 2) petroleum refinery owners and operators develop, install, operate, and maintain a fence-line monitoring system, per guidance developed by the District; 3) the District and petroleum refinery owners and operators collect real-time data from the refinery-related community air monitoring system and the fence-line monitoring system and the data be provided to the public as quickly as possible in a publicly accessible format; and 4) petroleum refinery owner and operators be responsible for the costs associated with implementing a refinery-related community air monitoring system.

Through extensive research and a robust public outreach process, the District developed Rules 4460 (Petroleum Refinery Fence-line Air Monitoring) and 3200 (Petroleum Refinery Community Air Monitoring Fees) that take into account the unique characteristics of locally-owned Valley petroleum refining operations, while still requiring publicly-accessible monitoring data to be collected at refinery fence-lines and in nearby communities. In accordance with requirements of AB 1647, Rule 4460 requires that petroleum refinery owners and operators install, operate, and maintain fence-line air monitoring systems and make data collected by these systems publicly available. Rule 3200 requires that owners and operators of petroleum refineries operating in the Valley pay an initial fee to support the implementation of refinery-related community air monitoring by the District, and also requires the payment of an annual operations and maintenance fee to support community air monitoring system maintenance and associated District staff time. The District Governing Board adopted both rules on December 19, 2019.

Rule 4460 requires the submittal and approval of a fence-line air monitoring plan (plan) for a specified list of air pollutants. The plan must provide detailed information about the fence-line air monitoring system, including siting, instrument choices, wind data collection, maintenance procedures, measures in case of failures, quality assurance and auditing, and data reporting methods. Further, the rule sets forth requirements for the plan review process, notifications, and recordkeeping. The plan review process includes a public review period of no less than thirty (30) days prior to approval by the District. In order to provide clarity for petroleum refineries and consistency in submitted air monitoring plans, the District is providing this written assistance document to Valley petroleum refineries regarding required elements of the air monitoring plans to be submitted.

2. Air Monitoring Plan

District staff recognizes the need for flexibility when designing a fence-line air monitoring plan. Each plan will be evaluated on a case-by-case basis, and should be

[1] (Muratsuchi, 2017)

tailored to each facility's characteristics, including size, emissions, and location. An approvable fence-line air monitoring plan should provide detailed information about the installation, operation and maintenance of the fence-line air monitoring system. The proposed fence-line monitoring system should be capable of measuring routine emissions from refineries, as well as unplanned releases from refinery equipment and other sources of refinery-related emissions.

Developing an air monitoring plan requires three important steps:

1. Identification of emissions sources and affected communities
2. Development of a fence-line air monitoring system that can provide real-time information about specific air pollutant levels
3. Effective communication of this information to the public and other interested parties.

Per District Rule 4460, a fence-line air monitoring plan must include detailed information for the following:

1. <u>Equipment to be used to continuously monitor, record, and report air pollutant concentrations for the pollutants in real-time, at or near the property boundary of the petroleum refinery</u>

2. <u>Siting and equipment specifications</u>
   a. Distance from facility to closest sensitive receptor(s)
   b. Location of impacted communities
   c. Refinery air pollutant distribution in those communities
   d. Description of how the monitoring system will cover identified impacted communities
   e. Specifications for the fence-line instruments (i.e., detection limits, time resolution, etc.)
   f. Locations where equipment will be sited (e.g., GIS coordinates) and measurement pathways for open-path monitoring equipment if proposed

3. <u>Equipment to be used to measure and continuously record wind speed and wind direction data within the boundaries of the petroleum refinery</u>

4. <u>Procedures for air monitoring equipment maintenance and failures must be addressed in the plan, including:</u>
   a. Routine maintenance requirements and timelines for performing required periodic maintenance on the fence-line air monitoring equipment;
   b. Length of time that fence-line air monitoring equipment will not be operating during routine maintenance activities; and
   c. Temporary air monitoring measures that will be implemented in the event of an equipment failure or during routine maintenance activities and used until the fence-line air monitoring system is restored to normal operating conditions.

5. <u>Procedures for implementing quality assurance by a qualified independent party, including quality control and audits of the fence-line air monitoring systems</u>

   a. Quality assurance procedures for data generated by the fenceline air monitoring system (e.g. procedures for assessment, verification, and validation data)
   b. Standard operating procedures (SOPs) for all measurement equipment
   c. Routine equipment and data audits

6. Procedures for implementing the fence-line air monitoring plan, including, information pertaining to the installation, operation, maintenance, and quality assurance, for the fence-line air monitoring system
   a. Timeline for implementation

7. Methods and timeframe for dissemination of data collected by the monitoring equipment to the public, local response agencies, and the District
   a. Real-time current and historical air pollutant and meteorological data
   b. Educational material that describes the objectives and capabilities of the fence-line air monitoring system
   c. Description of all pollutants measured and measurement techniques
   d. Procedures to upload the data and ensure quality control
   e. Definition of QC flags
   f. Archived data that with data quality flags, explains changes due to QA/QC and provides chain of custody information
   g. Quarterly data summary reports, including relationship to health thresholds, data completeness, instrument issues, and quality control efforts
   h. Notifications for activities that could affect the fenceline air monitoring system (e.g., planned maintenance activities or equipment failures)
   i. Communication methods for notifications, such as, website, mobile applications, automated emails/text messages and social media

3. Pollutants to be Monitored

Pollutants to be considered in the fence-line air monitoring plan must include pollutants specified below in Table 1. Should a petroleum refinery propose to exclude measuring any of the pollutants required in Rule 4460, this proposal must be accompanied with sufficient justification. For example, in certain instances a petroleum refinery may propose to exclude monitoring for specific compounds that are not likely to be measured at or above the detection limits of the selected fenceline air monitoring equipment. In this case, the petroleum refinery would be required to provide an alternative measurement methodology, or evidence, such as historical air monitoring data or operational information, to support the proposed exclusion.

Table 1: Air Pollutants to be Considered in Fence-line Air Monitoring Plan

Petroleum Refinery Capacity (barrels per day)	Pollutants to be Considered in Monitoring Plan
Less than 40,000	Sulfur dioxide, hydrogen sulfide, BTEX compounds (benzene, toluene, ethylbenzene and xylene)
40,000 or greater	Sulfur dioxide, nitrogen oxides, total VOCs, BTEX compounds (benzene, toluene, ethylbenzene and xylene), formaldehyde, acetaldehyde, acrolein, 1,3 butadiene, styrene, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, hydrogen fluoride, black carbon

Below are descriptions of some of these pollutants:

Sulfur Dioxide

Sulfur Dioxide (SO2) is a colorless gas, with a pungent odor akin to a struck match. Inhalation of SO2 can produce adverse health effects, and difficulty breathing. Sulfur dioxide is produced largely by fossil fuel combustion.

Hydrogen Sulfide

Hydrogen sulfide (H2S) is a colorless gas characterized by its foul odor of rotten eggs and can be smelled at low concentrations. It is poisonous, corrosive, and flammable, and exposure at high concentrations can cause irritation, unconsciousness, and death. Hydrogen sulfide is often produced from the breakdown of organic matter in the absence of oxygen gas, such as in swamps, sewers, and in the crude oil extraction / refining process.

BTEX Compounds (Benzene, Toluene, Ethylbenzene, and Xylenes)

BTEX is a specified subset of aromatic hydrocarbons compounds containing benzene, toluene, ethylbenzene and xylene. These chemicals appear naturally in crude oil and can be associated with emissions from refineries as they are released partly due to incomplete combustion of natural gas as well as emissions from petroleum and storage and transfer. In addition, other combustion sources such as wood burning and fossil fuel combustion also contribute to BTEX emissions. The negative health effects associated with BTEX exposure include neurological impairment and cancer.

Nitrogen Oxides

Nitrogen oxides (NOx) are chemical compounds formed by the combination of nitrogen and oxygen. NO2 is a greenhouse gas that is largely produced by high temperature combustions of hydrocarbons in the presence of nitrogen and oxygen. There is scientific evidence that correlates NOx exposure and negative respiratory effects. Measuring NOx formation near refineries for elevated concentrations would help identify the input of these facilities into the surrounding area.

Aldehydes

Aldehydes are compounds characterized by the inclusion of a carbon with a double bonded oxygen and single bond hydrogen associated with it. Due to the wide array of aldehydes, their properties are typically based on the remainder of the molecule and can range from being water soluble to volatile. Formaldehyde and acetaldehyde are two of the most common aldehydes produced in industry. Formaldehyde is a colorless volatile compound and can cause irritation to the eyes, skin, and respiratory pathways. Chronic exposure to formaldehyde can have lasting negative health effects. Formaldehyde is produced in various portions of industrial processes. Acetaldehyde can be used in either the liquid or gaseous form depending on the process. Exposure to acetaldehyde can cause irritation to the eyes, skin, and respiratory pathways and prolonged exposure can have lasting health effects. Acetaldehyde is produced by facilities that burn fossil fuels, wood, trash, as well a gas extraction facilities, refineries, and paper mills. A more detailed list of possible aldehydes and their health effects is provided by OEHHA.

Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are carbon chained compounds that vaporize in ambient conditions. Among these compounds include but, are not limited to, BTEX, 1,3-butadiene, PAH, aldehydes, naphthalene, and diethanolamine. These compounds are typically emitted from products such as paints, inks, organic solvents, petroleum products as well as vehicle use. The health effects of these compounds vary but, long term exposure can have lasting adverse health effects. A more detailed list of possible VOCs and their health effects is provided by OEHHA.

Ammonia

While the main sources of ammonia are natural, primarily from the decay of organic matter, petroleum refineries can also emit ammonia, particularly from catalyst regenerator vent releases. Ammonia gas is colorless, pungent-smelling, and corrosive. Exposure to high concentrations may induce adverse health impacts.

4. Fence-line Air Monitoring Technologies

There are two main types of technologies available for monitoring petroleum refinery emissions, open path and point air monitoring systems. Open path air monitoring systems utilize light and reflectors to measure levels of a variety of gaseous compounds along industrial facility fence-lines, and can be configured to detect the origination point of increased pollution concentration levels. These systems range in cost, depending on the number of units needed to adequately cover a fence-line, with system equipment and installation costs as high as $2 to $4.2 million. Point air monitors are installed in a stationary location and measure concentrations of criteria pollutants, toxics, and particulate matter, depending on the configuration selected for the system, at a single location. This equipment also ranges significantly in cost depending on the number of pollutants that can be measured by the platform, with potential costs up to $750,000 for a comprehensive system that is capable of providing fully speciated emissions data.

Open Path Systems

Open path systems use a light signal, projected along a straight unobstructed path, to continuously detect and measure concentrations of chemical compounds along the distance covered by the light signal in real-time. The light source emits light towards a detector either at the opposite end of the light path (bi-static configuration) or co-located with the light source (mono-static configuration) if the light is reflected back by a reflector, providing path-averaged concentrations of multiple pollutants, simultaneously. Some of the optical technologies used in these systems include the following:

- **Ultra Violet Differential Optical Absorption Spectroscopy**: Ultra Violet Differential Optical Absorption Spectroscopy (UV-DOAS) system utilizes a high powered UV light to measure the absorption spectra as opposed to a signal produced by a single wavelength. By doing so, this separates the absorption data of multiple target analytes. By using a software as well as a predetermined subset of known gases, the Open-Path UV DOAS is able to quantify multiple target gases.

- **Tunable Diode Laser Absorption Spectroscopy**: Tunable Diode Laser Absorption Spectroscopy (TDLAS) utilizes a laser tuned to be within a strict frequency range. This range is typically exclusive to the target gas in question. The laser is then tuned to match the desired frequency of the target gas, primarily Hydrogen Sulfide (H2S). From this the absorption of at a particular wavelength, the concentration of the target gas at that wavelength can be determined.

- **Fourier Transform Infrared**: Fourier Transform Infrared (FTIR) system utilizes a beam of infrared light to measure the absorption spectra of the infrared spectrum. Infrared light is emitted from the light source, which is then directed at retroreflectors or another unit, the returning light is received by a detector.

The change in intensity, frequency, and wave length is then used to calculate the concentration of various target gases in the atmosphere. With this sampling method it is possible to measure a total alkane concentration.

Point Monitors

Point monitors extract ambient air at a specific location and performs the measurement within the system. They are the primary instrument types used in EPA approved methodologies for measuring air pollutants. These type of monitors use a variety of technologies, including the following:

- **Gas Monitoring**: In addition to the open path options for monitors, there are also single point monitors that can measure a range of target gases by utilizing methods such as chemiluminescence, UV – fluorescence, and gas chromatography. These instruments and their methods are widely used throughout multiple regulatory air monitoring networks and are accepted by both the EPA and CARB for the measurement of gases such as NO2, H2S, and SO2.

- **Particulate Matter Monitoring**: There are point monitors for particulate matter as well, which employ methods such as beta attenuation, light scattering/absorption, and tapered element oscillating microbalance. These instruments range from hourly to minute averages and cover a range of PM types including PM1.0, PM2.5, PM10, and speciated particulate matter. The previously mentioned instruments and methods are in use throughout regulatory air monitoring networks and are accepted by EPA and CARB for the criteria pollutants.

- **Total VOC Monitoring**: Photoionization Detector (PID) takes Volatile Organic Compounds (VOCs) and charges the compounds with a large amount of high energy photons which energizes the sample compounds. The energized compounds then pass by the photoionization detector which subjects the positively charged compounds to a magnetic field and forces them to a collector electrode to determine the concentration of total VOCs. Flame Ionization Detector (FID) is similar to the PID but utilizes a flame, typically fueled by hydrogen, to ionize the sample before the signal is read by the detector to determine the concentration of total VOCs.

- **Gas Chromatography - Mass Spectrometry (GC-MS)**: Gas Chromatography (GC) is paired with Mass Spectrometry (MS) as the secondary detector. The sample will pass through a GC utilizing a PID or FID as the primary detector, which will separate the sample based on retention time. The sample then passes to the mass spectrometer which will ionize and separate the sample by its mass to charge ratio. The advantage of this technique is the utilization of multiple separation methods for analysis which can supplement instances in which certain compounds will output similar spectra using GC, despite being vastly different chemically.

District staff recognize the need for flexibility when designing an air monitoring system. Each system will be evaluated on a case-by-case basis, and should be tailored to each facility's characteristics, including size, emissions, and location. The proposed fence-line monitoring system should be capable of measuring routine emissions from refineries, as well as unplanned releases from refinery equipment and other sources of refinery-related emissions. The type of air monitoring technologies required will depend on the petroleum refinery capacity as detailed in Table 2 below.

Table 2: Equipment be Considered in Fence-line Air Monitoring Plan

Petroleum Refinery Capacity (barrels per day)	Equipment for Fence-line Air Monitoring System
Less than 40,000	Point monitoring or open path system
40,000 or greater	Open path system and point monitoring as needed

5. Quality Assurance and Quality Control (QA/QC)

The air monitoring plan should address quality assurance and quality control, including training of personnel, development and maintenance of proper documentation (i.e., instrument manuals, SOPs, a Quality Assurance Project Plan (QAPP), routine maintenance and calibration checks, technical audits, data verification and validation, and data quality assessment. A QAPP should outline the QA/QC plan, following EPA guidelines. The QAPP provides a blueprint for conducting air monitoring that produces quality results and must outline the specific goals of the monitoring and instrumentation, the data quality that is required and how that relates to when data generated by the instrumentation is accepted, and how the data will be reviewed and managed by the refineries. The QAPP should provide clear definitions and procedures for QA/QC that are necessary to indicate why some data may be missing, suspect, or invalid.

The critical functions to be addressed in the QAPP are summarized below:

- **Project background and management:** The QAPP should provide background information and the general goals of the fence-line air monitoring system, quality objectives and acceptance criteria for measurement data, and plans for documentation, record keeping, and data dissemination.
- **Technical Approach:** The QAPP should demonstrate that the appropriate approaches and methodologies are employed for performing measurements, data handling, and quality control.
- **Assessment/Oversight:** The QAPP should offer appropriate QA/QC steps for ensuring the effectiveness of the monitoring, covering representativeness of the

data, instrument operation and data acquisition, calibration check procedures, data quality indicators, and independent systems and performance audits.
- **Data Validation and Usability:** The QAPP should describe what steps will be taken to ensure that the individual data elements conform to the criteria specified in the QAPP.

Air monitors should continuously measure with a frequency of at least once every five minutes. If this is not feasible, refinery operators must provide a rationale in the air monitoring plan detailing equipment or other operational limitations. Instrumentation should aim to meet a minimum of 75 percent completeness among all hourly values on a daily basis, and 90 percent complete among daily values for each quarter of the year. Atmospheric conditions beyond the control of the refinery that affects accurate measurements, such as dense fog on open-path systems, should not be counted against data completeness requirements as long as appropriate meteorological measurements document time periods when these conditions exist.

The real-time and near-real-time disseminated measurement data should not be considered final, but it is important that the preliminary real-time measurement data distributed to the public be of an acceptable quality. It is important to ensure that instrument failures are detected quickly, with automated screening where feasible, to prevent grossly invalid data from being presented to the public. This can be accomplished by utilizing built-in status flags on the instrument operational parameters and by providing real-time data screening for outliers, impossible values, stuck values, negative values, rates of change, excessive short-term noise, etc.

All monitoring data should be collected, managed and archived in a standard electronic format after necessary data processing and validation. Processing the data involves collecting the data, assuring its quality, storing the data in a standardized format, and interpreting the data for communication to the public. The most critical steps in this process include:

- Automatically retrieving data from the fence-line monitors containing the measured levels of each air pollutant along with meteorological parameters;
- Validating data file completeness and integrity;
- Transferring file contents to a database;
- Flagging data that do not meet pre-defined quality control limits;
- Copying quality assured data and indices into a database for use by data display and dissemination program;
- Generating and recording logs to monitor system operation;
- Notifications, as appropriate, when measured concentrations are above pre-defined concentrations limits.

To ensure that the collected data meets the highest quality possible, each piece of monitoring equipment should be operated in strict accordance with an in-depth operating protocol. To achieve the appropriate level of detail and standardization, and to consequently ensure that the monitoring equipment provides high quality data, SOPs should be prepared for each specific measurement method. The SOPs should be informed by general operating instructions that are typically provided by the manufacturers of equipment, by operational experience and audits, and by general operational guidelines and performance specifications that are available for EPA and State approved methods. The SOPs should address specific topics such as calibration procedures and quality control procedures (indicating standards and checks, acceptance criteria and schedule), as well as data reduction (indicating validation procedures, reporting and schedule).

The refinery operators shall submit to the District quarterly data reports of data collected through the fence-line air monitoring system. The quarterly report shall include the time and date of each period during which the fence-line air monitoring system was inoperative and the nature of system repairs and adjustments. The report is due by the 30th calendar day following the end of the calendar quarter.

6. Data Display

The air monitoring plan should identify how the data will be provided to the public through a website. The website for displaying the data should include the current real-time measurements, historical data, and quarterly data reports. The air monitoring data should be provided in a manner that the public can readily access and understand. The websites should use data visualization tools to graphically depict information using maps and time series plots of measured pollutants and wind data. The website should include the following:

- Information regarding the species measured and the measurement techniques;
- Discussion of levels of concern for each measured species;
- Definition of data QC flags;
- When a monitor or system is offline, a flag/notification should be identified online explaining the loss of data;
- Links to additional sources of information as necessary;
- Details of how the public can report experiences and provide comments and feedback for improvement of the website and other data dissemination tools and the monitoring activities in general.

The air monitoring plan should also identify alternative methods of accessing periodic reports for those members of the community who may not have internet access (e.g., automated phone systems for dial-in information, public displays, hard copies of periodic reports in libraries or community centers, etc.). Based on the needs of the communities, providing information in other languages should be considered.

Some other examples of methods for communicating the data to the public include the following:

- Mobile application;
- Automated email/fax/text notification system;
- Social media feeds;
- Public data displays in community locations;

- Automated call-in phone system;
- Television and radio reports; and
- Published quarterly data summary reports.

7. Notification System

The website should offer an opt-in notification system that is integrated with the data collected by the air monitors that automatically generates and issues notifications to subscribers when each of the pollutant levels exceed corresponding thresholds pursuant to the approved air monitoring plan. Resources for establishment of potential thresholds include the National Ambient Air Quality Standards (NAAQS), California Ambient Air Quality Standards (CAAQS), and the acute, chronic or carcinogenic Reference Exposure Levels (RELs) as assessed by California Office of Environmental Hazard Assessment (OEHHA).

The notification system could be designed to provide information to the public via email, text message or other communication venues to be notified regarding: (1) data availability and release of periodic reports; (2) exceedances of thresholds established in approved fence-line air monitoring plans; and (3) monitoring system status. The timely notifications will inform the public when certain pollutants exceed those concentration thresholds or may pose a potential health concern, allowing the public to consider further actions to protect their health. The notifications could also serve to provide information to refinery operators to rapidly identify and mitigate any undetected and/or accidental emissions.

8. Plan Review Process

Rule 4460 requires that no later than July 1, 2020, the owner or operator of a petroleum refinery must submit to the APCO a written fence-line air monitoring plan for establishing and operating a real-time fence-line air monitoring system.

If disapproved, the owner or operator must revise and resubmit the fence-line and air monitoring plan within thirty (30) calendar days after notification of disapproval of the plan. The resubmitted plan must include all information necessary to address deficiencies identified in the disapproval letter.

The District will either approve the revised and resubmitted fence-line air monitoring plan or modify the plan and approve it as modified. A fence-line air monitoring plan will be made available, by the District, for public review no less than thirty (30) days prior to approval.

9. Implementation Timeline

The owner or operator of an existing petroleum refinery must complete the installation and begin the operation of a real-time fence-line air monitoring system within 365 days of District’s approval of a proposed monitoring plan.

The owner or operator of a refinery with the capacity to process less than 40,000 barrels per day that subsequently increases processing capacity to greater than or equal to 40,000 barrels per day must submit an amended fence-line air monitoring plan at least six (6) months prior to increasing processing capacity. The owner or operator of the facility must complete installation and begin operation of a real-time fence-line air monitoring system in accordance with the approved fence-line air monitoring plan prior to increasing petroleum processing activities.

The owner or operator of a refinery not currently engaged in refining crude oil must submit a proposed fence-line air monitoring plan at least six (6) months prior to planned recommencement of refining operations. The owner or operator of the facility must complete installation and begin operation of a real-time fence-line air monitoring system in accordance with the approved fence-line air monitoring plan prior to recommencement of petroleum refining activities.

10. Updates to Air Monitoring Plans

The owner or operator of a petroleum refinery must submit an updated fence-line air monitoring plan to the District as follows:

- Ten (10) calendar days after the date of any unplanned facility, equipment, process or administrative modification that could result in changes to an approved fence-line air monitoring plan.

- Forty-five (45) calendar days before the date of implementation of any planned facility, equipment, process or administrative modification that could result in changes to an approved fence-line air monitoring plan.

- Sixty (60) calendar days after the date of receiving information that an approved fence-line air monitoring plan does not adequately measure one or more pollutant(s) identified in Table 1 that are emitted from the petroleum refinery.

Failure to comply with these requirements outlined above will result in revocation of an approved fence-line air monitoring plan. Thirty days (30) after revocation of an approved fence-line air monitoring plan, the owner or operator of a petroleum refinery must submit a new fence-line air monitoring plan to the APCO pursuant to Sections 6.2 and 6.3 of Rule 4460. An updated implementation schedule subject to approval by the APCO must be included in the new fence-line air monitoring plan but in no case shall implementation exceed 180 calendar days.