



**BAY AREA
AIR QUALITY
MANAGEMENT
DISTRICT**

October 19, 2023

Jennifer Ahlskog
Environmental Team Leader
Phillips 66
San Francisco Refinery
1380 San Pablo Avenue
Rodeo, CA 94572

RE: Disapproval of Regulation 12, Rule 15 Fenceline Air Monitoring Plan and Quality Assurance Project Plan

Dear Ms. Ahlskog:

On September 5, 2023, Phillips 66 submitted a revised fenceline air monitoring plan (AMP) and quality assurance project plan (QAPP) to the Bay Area Air Quality Management District (Air District). Phillips 66 submitted the AMP and QAPP in response to the Air District's July 19, 2023 Notice of Deficiency (NOD), as required by Air District Regulation 12-15-404.4.

Having reviewed the AMP and QAPP, the Air District has determined that Phillips 66 failed to correct several deficiencies with respect to Regulation 12-15 or the Air Monitoring Guidelines for Petroleum Refineries, which the Air District identified in the NOD; the specific deficiencies Phillips 66 failed to correct are discussed in Attachment 1 to this letter. These remaining deficiencies are fundamental to compliance with Regulation 12-15. As a result, the AMP and QAPP do not meet the requirements in Section 12-15-403. Therefore, pursuant to Section 12-15-404.4, the Air District hereby disapproves Phillips 66's AMP and QAPP.

Phillips 66 must develop an approvable AMP and QAPP that complies with Regulation 12-15; the Air District looks forward to working with you on that effort. If you have any questions regarding this notification, please contact me at jbovee@baaqmd.gov.

Sincerely,

Jerry Bovee, P.E., QSTI
Air Quality Engineering Manager

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Attachment 1 - Basis for Disapproval of Phillips 66's Fenceline Air Monitoring Plan and Quality Assurance Project Plan

1. With regard to quality assurance and quality control (QA/QC), the Air Monitoring Guidelines for Petroleum Refineries (Guidelines; p. 10) established pursuant to District Regulation 12-15-406 in April 2016 require the air monitoring plan (AMP) to include a quality assurance project plan (QAPP) that follows EPA guidelines and specifies methodologies for ensuring appropriate levels of QA/QC, data acceptance criteria, levels of data quality, data management issues and procedures, and data review and validation procedures. The Air District's July 19, 2023 Notice of Deficiency (NOD) stated that the AMP, QAPP, and associated appendices contained an insufficient level of detail regarding the methods, procedures, equations, and calculations that will be used to carry out these activities.¹ The NOD also stated that the AMP and QAPP are unclear and ambiguous about how data are validated and what data are displayed to the public.² To address these deficiencies, the NOD stated that Phillips 66 must provide standard operating procedures (SOPs) or other documentation to more fully describe these activities. Specifically, the NOD stated that Phillips 66 must:
 - a. attach to the QAPP detailed SOPs for all performance indicator checks, corrective actions, maintenance activities, QA/QC activities, data management activities, and reporting activities;
 - b. for each performance indicator check, corrective action, maintenance activity, QA/QC activity, data management activity, or reporting activity identified in the AMP or QAPP, provide references to the relevant SOPs;
 - c. include in the QAPP a detailed process flow diagram depicting the end-to-end data handling, review, and management process, from the moment of data acquisition to the quarterly submittal of final quality-controlled data to the Air District;
 - d. revise the narrative descriptions of the data handling, review, and management process in the AMP and QAPP to clearly and fully describe the step-by-step process depicted in the flow diagram;
 - e. articulate all decision rules used to automatically or manually screen data; and
 - f. illustrate the application of all auto-screening rules using real data and screen shots depicting how the auto-screened data are depicted on the public website.³

While the AMP (p. 19) and QAPP (p. 15) refer to the existence of SOPs, Phillips 66's September 5, 2023, submittal included only one related to hydrogen sulfide monitoring (i.e., Appendix C to the QAPP - *Unisearch LasIR Tunable Diode Laser System (TDLAS) Maintenance and Audit Procedure*). Furthermore, this SOP states that it is a, "working draft" for initial system validation and that it must be reviewed for compliance with local safety and quality assurance practices. Additionally, Phillips 66 failed to reference it throughout the QAPP, as stated in the NOD. Aside from relatively minor edits to the QAPP (e.g., to remove references to "an evolving checklist" of system performance indicators), Phillips 66 did not substantively address these issues identified in the NOD; many activities and the procedures for performing them remain poorly described in the AMP and QAPP. For example:

- With regard to maintenance of the tunable diode laser (TDL), page 22 of the AMP states that on an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed. It is unclear what system status checks are referred to, why they are enabled on an "as-

¹ See Attachment 1 to the July 19, 2023 NOD, issue number 4, pp. 2-3

² See Attachment 1 to the July 19, 2023 NOD, issue number 18, pp. 7-8

³ The Air District's July 19, 2023 NOD additionally stated that Phillips 66 should improve transparency about the data on its website by providing alternative views that show invalidated data. In discussions with Phillips 66's contractor following issuance of the NOD, the Air District stated that such changes to the website need not be addressed at this time.

needed” basis, under what circumstances they are enabled, how operators are alerted, and what actions are taken in response to each alarm.

- Table 4 of the AMP and Table 4 of the QAPP identify several maintenance activities for the TDL including:
 - visually inspecting the system,
 - inspecting the optics on the detectors and cleaning them if necessary,
 - checking the alignment to verify there has not been significant physical movement,
 - downloading data older than 12 months from the analyzer hard drive, moving the data to a permanent archive, and deleting old files from the analyzer;
 - checking long term trends in the signal intensity to evaluate the health of the optical components, the effects of cleaning optical components, and the noise characteristics of the spectral data;
 - ensuring there are no obstructions between the detector and the retro-reflector, and
 - inspecting all electrical and optical cables for wear and replacing them as necessary.

The AMP and QAPP are unclear about the following information, which should be included in SOPs according to guidance from the US Environmental Protection Agency:⁴

- the scope of these activities,
 - the step-by-step procedures for carrying out the activities,
 - what personnel qualifications are needed to perform the activities,
 - what equipment and supplies are necessary,
 - the availability of spare parts and equipment,
 - what health and safety warnings must be followed to prevent personal injury,
 - and what other precautions must be followed to prevent equipment damage.
- With respect to maintenance of the visibility instruments, page 25 of the AMP and page 13 of the QAPP state that the instrument will be visually inspected on a monthly basis, the optics will be inspected and cleaned as necessary on a monthly basis, and that the instrument calibration will be checked annually. Table 11 of the QAPP additionally states that the acceptance threshold for the percent error of the instrument is $\pm 25\%$. The AMP and QAPP are unclear about the details for performing these activities (e.g., scope, step-by-step procedures, personnel qualifications, equipment and supplies, availability of parts and equipment, health and safety warnings, and other precautions).
 - With regard to QA/QC, pages 27 and 31 of the AMP and page 28 of the QAPP state that as measurements progress, data screening checks and criteria are updated and refined based on actual observations. The AMP and QAPP are unclear about the process by which the screening checks are evaluated and updated.
 - With regard to quarterly data validation, page 27 of the QAPP states that statistical tests are used to ensure the data are valid for the intended end use. Additionally, page 31 of the AMP and page 27 of the QAPP state that the data are validated by looking for statistical anomalies and outliers. The AMP and QAPP are unclear about what statistical tests are applied and how they are used to

⁴ United States Environmental Protection Agency, (2007). Guidance for Preparing Standard Operating Procedures (SOPs) [QA/G-6]. Available at <https://www.epa.gov/quality/agency-wide-quality-program-documents>.

validate the data. The AMP and QAPP are also unclear about how outliers are defined and identified in the data, and about what is done with them.

- With regard to quarterly data validation, page 31 of the AMP and page 27 of the QAPP state that the reasonableness of the data are ensured by comparing them to remote background and average urban concentrations. It is unclear how this is performed, what data are used, and what is done with the results of this comparison.
- With regard to quarterly data validation, page 27 of the QAPP states that data validation activities include ensuring the data are not biased by exceptional conditions or events occurring off refinery property. It is unclear how this is accomplished, what information is used, and what is done with the results of the assessment.
- With regard to quarterly data validation, page 27 of the QAPP states that the QA Manager evaluates QA and QC procedures and ensures adherence to the methods for meeting data quality objectives. It is unclear in the QAPP how both of these activities are carried out.
- Page 5 of the QAPP explains that because the Unisearch TDL operates in a wavelength range that also contains an absorbance feature for water vapor and carbon dioxide, the correlation coefficient of these gases can be used as a performance metric. It goes on to say that if the water vapor correlation drops below a threshold value, the carbon dioxide correlation is examined and if that is also below a threshold value the data are flagged as invalid. While Table 7 of the AMP and Table 11 of the QAPP state that the water vapor correlation is measured continuously with an acceptance threshold of ≥ 0.95 , these tables do not similarly identify an instrument check and corresponding acceptance threshold for the carbon dioxide correlation coefficient. These checks are also not discussed in detail in the section of the QAPP pertaining to data validation, and it is unclear when and how these checks are applied to the data.
- Page 17 of the QAPP states that the automated data QC process flags any data with poor spectral matches to reference libraries. The QAPP lacks detail about the reference libraries and how they are applied and maintained.
- Page 16 of the AMP and page 6 of the QAPP state that data with real-time MDL values greater than 25 ppb are flagged for additional review. However, the flagging and review of MDL values greater than 25 ppb are not otherwise discussed in the sections of the AMP and QAPP pertaining to automated data screening or subsequent data validation. In addition, while Table 6 of the AMP and Table 10 of the QAPP indicate that measured concentrations below the MDL are flagged, they do not indicate that MDL values themselves are checked and flagged. Similarly, while Table 9 of the QAPP includes an operational code for values below the MDL, there is no clear code for flagging values when the MDL is outside of the required range. It is thus unclear in the AMP and QAPP when and how this check is applied and what follow-up actions are taken.
- To the extent flagged measurements appear on the public website, the AMP and QAPP are unclear about an acceptable time frame for resolving the flags.
- With respect to measuring the system precision and accuracy, page 20 of the QAPP states that during these tests a number (N) of replicated measurements of a standard reference material of known magnitude will be measured and various statistics will be calculated. The QAPP states that an acceptable number of trials is defined as $7 \leq N \leq 15$, and that a subset of test data will be used for the subsequent calculations. The QAPP is unclear as to why a subset of the test data will be used and how it will be selected.

As the AMP and the QAPP continue to lack sufficient detail regarding the procedures for maintenance activities, QA/QC activities, and data management, review, and validation, they are deficient. For guidance on the development of an adequate QAPP and SOPs, see EPA guidance document QA/G-5,

2. With regard to assessment of the TDL's accuracy and precision during monthly bump tests, the NOD stated that the AMP and QAPP were inconsistent with the requirement that the TDL have a measurement accuracy within 15% of the reference standard and a coefficient of variation (CV) not greater than 15%. To address this issue, the NOD stated the AMP, QAPP, and any SOPs must clearly state that the system's accuracy (as % Error) and precision (as % CV) will be assessed during each bump test, with acceptance criteria of $\leq 15\%$ for both performance indicators.⁵

While Phillips 66 revised Table 7 of the AMP (p. 32) and Table 11 of the QAPP (p. 29) to add acceptance criteria of $\pm 15\%$, both tables include a footnote, which states that the accuracy and repeatability specifications will be treated as objectives to become requirements at some future time, once it has been proven they can be reliably met for all seasons and atmospheric conditions.

At a meeting with representatives from Phillips 66 and other refineries on September 19, 2023, the Air District and refinery representatives discussed the need for the plans to lay out a pathway for meeting the performance specifications if they cannot be met at the present time. As currently written, Phillips 66's plan treats the accuracy and repeatability specifications as future requirements, but lacks sufficient detail for approval by the Air District. Phillips 66 must elaborate on the process it would use to prove the specifications can be met under varying conditions, suggest a time frame for making such a demonstration, or suggest a process by which the "objectives" would become actual requirements. The Air District can approve an adequately detailed plan for meeting the accuracy and precision specifications, but in their current form, the AMP and QAPP remain deficient.

3. With regard to assessment of the TDL's accuracy and precision during quarterly 3-point calibration checks, the NOD stated that the AMP and QAPP were inconsistent with the requirement that the TDL have a measurement accuracy within 15% of the reference standard and CV not greater than 15%. To address this issue, the NOD stated that the AMP, QAPP, and any SOPs must clearly state that both accuracy (as % Error) and precision (as %CV) will be assessed during each 3-point calibration check, with acceptance criteria of $\leq 15\%$ for both performance indicators at each calibration point.⁶

While Phillips 66 revised Table 7 of the AMP (p. 32) and Table 11 of the QAPP (p. 29) to include acceptance criteria of $\pm 15\%$, both tables reference the same footnote discussed above regarding the acceptance criteria for the monthly bump tests. For the same reasons stated above regarding the bump tests, the revised AMP and QAPP remain deficient with respect to the acceptance criteria for the quarterly 3-point calibration checks.

4. With regard to the detection capabilities of the TDL, the Air District's December 22, 2022 letter stated that a TDL system used to monitor hydrogen sulfide must have a limit of quantitation (LOQ), which ranges from 3 to 25 ppb depending on environmental and operational conditions. The NOD stated that the AMP and QAPP were inconsistent with this requirement and that Phillips 66 must revise the AMP and QAPP to reflect that the LOQ must be between 3 and 25 ppb.⁷

⁵ See Attachment 1 to the July 19, 2023 NOD, issue number 6, pp. 3-4

⁶ See Attachment 1 to the July 19, 2023 NOD, issue number 8, pp. 4-5

⁷ See Attachment 1 to the July 19, 2023 NOD, issue number 12, p. 5-6

In response to this issue in the NOD, Phillips 66 revised the AMP and QAPP to state that the LOQ is considered to be equivalent to the MDL. While we are not taking issue with that approach per se, the AMP and QAPP contain multiple definitions of the LOQ. For example, page 16 of the AMP states that it is calculated as twice the standard deviation of the last seven 5-minute average concentration values containing no measurable analyte. However, page 30 of the AMP states that the LOQ is calculated as twice the standard deviation of a blank sample. While it is not necessarily inappropriate to use various approaches for quantifying the detection capabilities of the monitoring equipment, the AMP and QAPP must be clear about when, how, and for what purpose those approaches are used. Because of the lack of clarity in the AMP and QAPP, they remain deficient in this regard.