

Attachment 1 - Basis for Determination That Phillips 66's Revised Fenceline Air Monitoring Plan and Quality Assurance Project Plan (Submitted February 10, 2023) Do Not Meet District Regulation 12-15-403

1. According to the Air Monitoring Guidelines for Petroleum Refineries (Guidelines) established pursuant to District Regulation 12-15-406 in April 2016, fenceline measurements must be continuously measured with a time resolution of five minutes, and instrumentation must meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters (p. 5). The air monitoring plan (AMP) and quality assurance project plan (QAPP) contain an insufficient level of detail regarding how compliance with this requirement is demonstrated. For example, the QAPP must contain information such as:
 - codes used to flag data as valid, invalid, or under review,
 - operational codes used to explain why measurements are invalid (e.g., instrument malfunction, planned maintenance, poor visibility, etc.), and
 - formulas used to determine the completeness of the data and other related statistics.

This issue is among several others previously identified in a notice of deficiency sent to Phillips 66 on August 25, 2022. To aid in resolving this deficiency, Attachment 3 to our December 22, 2022 letter interpreting Regulation 12-15 and the associated Guidelines (12/22/2022 letter) outlined detailed procedures Phillips 66 must use to demonstrate compliance with the data completeness requirement. The problem nevertheless remains unresolved. Phillips 66 must incorporate the content of Attachment 3 to our 12/22/2022 letter interpreting the Guidelines into the AMP and QAPP.

2. With regard to data completeness, page 18 of the AMP and page 8 of the QAPP state that when an instrument's signal drops below a predetermined level, coincident measurements of optical visibility will be used to identify and flag atmospheric conditions beyond the control of the refinery. However, visibility measurements are not among the data elements Phillips 66 says, elsewhere in that plan, that it will use to confirm weather-related events:

"Data from the meteorological station including wind speed and direction, temperature, and relative humidity will be used to confirm weather-related events where applicable." (AMP, p. 18; QAPP, p. 8.)

Phillips 66 must revise the AMP and QAPP to state that visibility measurements will be among the data used to confirm weather-related events.

In addition, the AMP and QAPP lack information about the equipment that will be used to measure visibility, its operation, and its maintenance. This information must also be incorporated into the AMP and QAPP.

3. Page 17 of the AMP and page 19 of the QAPP state that Phillips 66 will provide one-hour average concentration data to the Air District in a comma separated value (CSV) file that also includes the minimum detection limit (MDL) and the measured light signal for each instrument. These provisions are inconsistent with our 12/22/2022 letter. In particular, attachments 2 and 3 to the letter:
 - stated that quarterly reports must be submitted to the Air District within 60 days following the end of each calendar quarter;
 - stated that all fenceline monitoring concentration data should be provided as 5-minute averages;

- identified several required data elements;
- specified formats for the required data elements;
- specified procedures for reporting missing data;
- specified reporting procedures for bump tests and calibration checks;
- specified reporting procedures for quarterly data completeness; and
- required the use of templates provided by the Air District.

These provisions are either missing or inadequately specified in the AMP and QAPP. The content of attachments 2 and 3 to our 12/22/2022 letter must be included in the AMP and QAPP.

4. With regard to quality assurance and quality control, the Guidelines require the AMP to include a 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 (p. 10).

Section 3 of the QAPP includes information about steps that will be taken to verify instrument operation and ensure data quality. As a general matter, the QAPP contains an insufficient level of detail regarding the methods, procedures, equations, and calculations that will be used to perform these actions as required by the Guidelines. Specific examples of deficiencies include the following:

- a. Table 5 of the QAPP states that “an evolving checklist” of system performance indicators will be checked on a quarterly basis. It is unclear what indicators will be checked, how they will be checked, and what acceptance criteria will be used.
- b. Page 13 of the QAPP states that operational performance of the tunable diode laser (TDL) will be validated by assessing measurement robustness. It is unclear what this refers to, how measurement robustness will be determined, how frequently it will be checked, and what acceptance criteria will be used.
- c. Page 13 of the QAPP states that operational performance of the TDL will be validated by assessing measurement linearity. It is unclear how this will be assessed, how frequently it will be assessed, and what acceptance criteria will be used.
- d. Page 13 of the QAPP states that operational performance of the TDL will be validated by performing ambient gas validation checks. While Table 6 of the QAPP states that CO₂ measurements will be checked continuously, the stated acceptance criterion is that it “[t]racks [m]easurements made by FTIR.” It is unclear how this will be assessed and what specific criteria will be used to accept or reject the level of agreement between the measurements.
- e. Page 16 of the QAPP states that measurement quality objective (MQO) #9 will be considered to have been met if all operational performance checks provided in Tables 3 and 6 are met. This is confusing because page 13 of the QAPP states that Table 3 presents operational specifications provided by the instrument manufacturer, not performance checks.
- f. Phillips 66 failed to provide standard operating procedures (SOPs) for any quality control or maintenance activities.

Phillips 66 must revise Section 3 of the QAPP so it lays out a comprehensive suite of maintenance and QC activities and is clear about how the activities will be performed, how frequently they will be performed, and what acceptance criteria will be used. In addition, Phillips 66 must do the following:

- attach to the QAPP detailed SOPs for all performance indicator checks, corrective actions, maintenance activities, QA/QC activities, data management activities, and reporting activities; and
- 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.

Note that this is among the issues discussed in our August 25, 2022 and 12/22/2022 letters that Phillips 66 has failed to resolve. Also note that the SOPs will become part of the publicly-available QAPP. As a result, if an SOP contains confidential information, two copies must be submitted - one that has the confidential information redacted and that can be made available to the public, and another unredacted copy for internal Air District reference. Finally note that by submitting a confidential redacted version, Phillips 66 represents to the District that it includes information recognized as trade secret under California law.

5. Section 3 of the QAPP outlines procedures for subjecting measurements to precision and accuracy tests. Accuracy and precision are defined on page 15 of the QAPP as follows:

$$\%Accuracy = \frac{\bar{x} - x_{std}}{x_{std}} \times 100\%$$

$$Precision \equiv \%CV = \frac{\sigma}{\bar{x}} \times 100\%$$

The term “accuracy” is generally understood in the scientific community to refer to the closeness of agreement between a measured quantity and its true value, such that a higher accuracy represents greater agreement. However, as it is defined above, higher values of “accuracy” actually reflect less agreement between the measured quantity and its true value because the formula represents error in the measurements rather than accuracy. This convention may be confusing or misleading to casual readers of the AMP and QAPP, and because they are public documents, it is important that they be clear and understandable, and use plain language to the extent possible. To improve clarity, Phillips 66 must modify the formulas as shown below, and revise the AMP, QAPP, and any attachments as necessary to accommodate the revised definitions (e.g., if the QAPP currently states that corrective action will be taken if percent accuracy is more than 15%, it should be revised to state that corrective action will be taken if the percent error exceeds 15%).

$$\% Error = \left| \frac{\bar{x} - x_{std}}{x_{std}} \right| \times 100\%$$

$$\% CV = \frac{\sigma}{\bar{x}} \times 100\%$$

6. With regard to bump tests:

- Table 5 of the QAPP (p. 15) states that a bump test will be performed monthly, and corrective action will be taken if % accuracy is more than 25%; and
- Table 6 of the QPP (p. 16) states that a bump test will be performed monthly with an acceptance criterion of ±25%.

The Air District has the following comments regarding these provisions:

- a. The Air District’s 12/22/2022 letter stated that the hydrogen sulfide (H₂S) TDL must have a measurement accuracy within 15% of the reference standard, and a coefficient of variation (CV) not greater than 15%. The accuracy and precision specifications must be met for each monthly bump test. None of the tables referenced above reflect the precision requirement, and they incorrectly state the accuracy requirement as 25%.¹ The AMP, QAPP, and any SOPs must clearly state that both accuracy (as % Error) and precision (as % CV) will be assessed during each bump test, with acceptance criteria of ≤15% for both performance indicators.
- b. The Air District’s 12/22/2022 letter stated that the H₂S TDL must meet the accuracy and precision specifications for each bump test at a unique concentration between 50 and 100 ppb, which differs from the concentrations used in the 3-point calibration checks. Table 4 of the QAPP states the concentration for the validation cell will be between 266 ppb and 532 ppb, which is the same range provided for one of the cells used in the calibration checks. The QAPP must be revised to state that the concentration used for the bump tests will differ from those used in the 3-point calibration checks.

Furthermore, it is unclear if the concentrations listed in Table 4 refer to the cell gas concentrations, the path integrated concentrations, or the path average concentrations. Phillips 66 must revise the QAPP to clarify this, and include in the QAPP or the attached SOPs a demonstration that the specified cell concentrations result in a path average concentration between 50 ppb and 100 ppb.

- 7. Table 4 of the QAPP provides a range of 266 ppb to 532 ppb for the validation cell. However, Table 6 states that the bump test will be conducted with a concentration of approximately 125 ppb. Please note this discrepancy and correct it when addressing the other issues related to bump tests.
- 8. With regard to 3-point calibration checks, Tables 5 and 6 of the QAPP state the following:

Table 5. Schedule of maintenance activities for the TDL

Activity	Monthly	Quarterly
3-point calibration check. Take corrective action if outside of acceptance criteria.		✓

¹ The acceptance criterion of ±25% in Table 6 is unlabeled but based on the text of the QAPP it is assumed to refer to accuracy. The acceptance criteria in all tables must be clearly labeled so their meaning is clear and unambiguous.

Table 6 - Quality control checks, frequency, and acceptance criteria for TDLAS analyzers

QA/QC Checks	Frequency	Acceptance Criteria
Bump test (H ₂ S) at approx. 125 ppb	Monthly	±25%
3-point calibration	Quarterly	±25% for [H ₂ S] ≤ 2,000 ppm ±10% for [H ₂ S] > 2,000 ppm
Signal Strength	Continuous	Greater than 400 micro watts or a SignalPower of 0.4*
CO ₂	Continuous	Tracks Measurements made by FTIR
H ₂ O correlation (r)	Continuous	≥0.95

The Air District’s 12/22/2022 letter stated that the H₂S TDL must have a measurement accuracy within 15% of the reference standard, and a coefficient of variation not greater than 15%. These specifications must be met at each calibration point. The AMP and QAPP do not satisfy these requirements, and are deficient in this regard. 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 ≤15% for both performance indicators at each calibration point.

9. With regard to the required 3-point calibration checks and bump tests, the Air District’s 12/22/2022 letter stated that a failure to meet the stated accuracy and precision specifications must trigger repair, maintenance, and root cause analysis, followed by repeat calibration checks or bump tests, until a passing check or test is completed. The letter also stated that all steps in this process, including the results of each passing and failed calibration check and bump test, and the monitor response or calibration adjustments, must be fully documented in the quarterly report submitted to the Air District. The AMP and QAPP are deficient, as these requirements are not reflected in either document. The AMP and QAPP must be revised to include these requirements.

10. With regard to the established precision and accuracy specifications, the Air District’s 12/22/2022 letter stated that a failure to meet the specifications during two or more bump tests in any quarter, or four bump tests in any 12-month period, will result in a violation of the accuracy or precision specifications (as applicable) and QAPP requirements. The letter further stated that such occurrences will invalidate all data prior to the failed bump test, going back to the last passing bump test, and that invalidated data will count against data completeness requirements. These requirements and procedures cannot be found in the QAPP and must be added.

11. Page 16 of the QAPP states that precision is assessed by evaluating %CV during periods where concentrations are above the MDL and relatively consistent. It goes on to say that bump test data *can* be used to calculate precision. As stated in our 12/22/2022 letter interpreting the Guidelines, the accuracy and precision specifications of 15% must be met during each bump test. The QAPP must therefore state that bump test and 3-point calibration data will be used to calculate the %CV.

12. With regard to the detection capabilities of the H₂S monitoring equipment, our 12/22/2022 letter stated that a TDL system used to monitor H₂S must have a limit of quantitation (LOQ), which ranges from 3 to 25 ppb depending on environmental and operational conditions. In comparison to this requirement:

- a. page 14 of the AMP states that the required lower detection limit (LDL) for the TDL is less than or equal 25 ppb;
- b. page 15 of the AMP states that the detection limit for the open-path H₂S air monitoring system is between 3 ppb and 25 ppb under normal operating conditions;
- c. Table 3 of the QAPP states that the typical real-time lower detection limit for the TDL is less than or equal to 25 ppb, and that the gas quantification limit is 125 ppb;
- d. Table 4-5 of the QAPP states that a value of less than or equal to 25 ppb is the acceptance criterion for the 5-minute MDL;
- e. footnote 3 to Table 3 states that the TDL's detection limit is calculated as three times the standard deviation of the seven most recent 5-minute average concentration values having no analyte in detection; and
- f. footnote 4 to Table 3 states the limit of quantitation (LOQ) is typically calculated based on at least 5 times the method detection limit, and that optimal precision and accuracy cannot be expected below this limit.

The AMP and QAPP are deficient with respect to this requirement, as they are inconsistent with the specifications in our 12/22/2022 letter. Phillips 66 must revise the AMP and QAPP to reflect the requirement that the LOQ (not MDL) of the H₂S system be between 3 and 25 ppb.

13. Page 16 of the QAPP states that the TDL can quantify gases if the measured light intensity is greater than 400 micro watts, and that any data collected with a light intensity below this level will be flagged as invalid and not reported to the community website in real time. Accordingly, Table 6 of the QAPP states that the signal strength of the TDL will be monitored continuously, with an acceptance threshold of greater than 400 micro watts or a signal power of 0.4. Tables 3 and 5 have similar information about the signal level and power. At the same time, footnote 1 to Table 6 states that a signal power of 0.4 corresponds to a percent transmission of about 3% to 5%.

The provisions in the QAPP fail to satisfy the requirement in our October 6, 2021, and 12/22/2022 letters interpreting the Guidelines that the system have specified detection capabilities at a light transmission of 1% or less. Phillips 66 must revise the AMP and QAPP to reflect the required performance specification.

14. Page 19 of the QAPP states, "Once QA/QC of the final data is completed within 60 days after the end of each calendar quarter, the refinery will provide...data in tabular format...to the BAAQMD." This language is unclear about whether the 60-day deadline pertains to QA/QC of the data or its submittal to the Air District.

The AMP is similarly unclear about the timeline for submittal of quarterly reports: "...following QA/QC of recorded monitoring data, Phillips 66 will provide...data in a tabular format to the BAAQMD" (p. 18).

The AMP and QAPP must be revised to clearly state that quarterly reports will be submitted to the Air District no later than 60 days after the end of each calendar quarter.

15. While the QAPP contains quality control measures to verify proper operation of the air monitoring equipment, it lacks additional measures to ensure proper operation of other supporting systems, such as those used for data management and public reporting. For example, the QAPP must describe system checks and other procedures in place to ensure the website, data management system, data processing pipeline, and other related systems are functional.

16. While Section 4.3 of the QAPP is dedicated to corrective actions that will be taken if the systems do not perform as intended, the information provided in that section has an inadequate level of detail, and the QAPP is deficient in this regard. Information that should be provided in this section includes the following:

- a. a description of the response team or teams that will address problems with the monitoring equipment or supporting information technology systems;
- b. the coverage provided by the response teams;
- c. identification of typical problems that may reasonably be expected to occur (e.g., website goes down, power is interrupted, data are erratic), the role of the person who is responsible for initiating the response, and the preliminary actions that will be taken;
- d. a description of how quality control parameters or other performance indicators are monitored (e.g., manually or automatically) and how frequently that occurs;
- e. a description of how the response team is alerted and activated when issues arise (e.g., automatic alerts or manual communications);
- f. how quickly the response team is expected to act in the event of a problem;
- g. what records are maintained to document issues and the associated responses; and
- h. the availability of spare equipment in the event a long-term problem arises.

17. Page 18 states that data from the fence line system will be reviewed and validated monthly, with the results stored in a separate portion of the monitoring database from the raw data. In addition to those procedures, Phillips 66 must document all changes to the data so that all actions resulting in the final data are traceable. The systems and procedures in place to do this must be documented in the QAPP.

18. The AMP and QAPP are unclear and ambiguous about how data are validated, and about what data are displayed to the public in real time and subsequently submitted to the Air District. For example, a statement on page 18 of the AMP says that data on the community website will be filtered in real time whenever real-time data quality indicators point to the potential of poor data quality. Page 17 of the QAPP similarly states that automated QA/QC checks occur before data are reported on the real-time website. Presumably this means that if a measurement is flagged by an automated QA/QC check, it may be invalidated and never make it to the public website. This is particularly troubling given that the real-time data checks include one for high detections of data above unspecified thresholds.

In another instance, page 15 of the AMP states that detection limits for the data generated by the equipment are normally set to be at least two times the manufacturer's MDL, to minimize the occurrence of false detections being reported to the public. If the real-time MDL for H₂S is 20 ppb at a particular time, this apparently means values below 40 ppb would not be posted. If this is indeed Phillips 66's practice, it is unacceptable. Any valid concentration above an instrument's MDL must be reported to the public website as measured.

In addition, page 18 of the QAPP states that data from the fence line system will be reviewed and validated monthly during post-processing, and will be flagged as valid or invalid. As a result, it appears that legitimate measurements may be concealed or mislabeled on the public website for weeks at a time, which runs counter to the purpose of making real-time (or near real-time) data available, as required by the Guidelines (p. 5). Furthermore, Table 8 of the QAPP summarizes the data validation process, and states on multiple occasions that flagged data, "will be excluded from future reporting." It is unclear what

reporting this statement pertains to, but note that all data – both valid and invalid – must be included in the quarterly reports submitted to the Air District, and this must be made clear in the AMP and QAPP.

To resolve these issues, Phillips 66 must:

- a. 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;
- b. 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;
- c. articulate all decision rules used to automatically or manually screen data;
- d. 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; and
- e. improve transparency about the data that has been invalidated by revising the website to allow members of the public to see two alternative views of the data – one view with invalid data removed, and another view showing all data (valid and invalid). Invalid data displayed on the website must be flagged as such and the reason for invalidation must be indicated on the website alongside the corresponding invalid data.

19. With regard to the quarterly reports provided to the Air District, page 18 of the AMP and page 19 of the QAPP state that the Air District may make one-hour average data available to the public through an Air District Website or a public records request. The AMP should instead state that the Air District may make publicly available any of the data routinely submitted in a quarterly report.

20. The QAPP refers to supplemental documents, which were not provided to the Air District with the revised AMP and QAPP. Provide the Air District with the following documents:

- a. the “TAS Data Accumulator Quality Assurance Parameters Unisearch Open Path H₂S, Feb 2020” document referenced in the footnotes to Table 3 of the QAPP; and
- b. the operating manuals referenced in Section 5 of the QAPP.

21. Page 19 of the QAPP states that Phillips 66 is allowed to upgrade the system without prior consultation with other parties. This language must be stricken from the QAPP, since any change in the AMP or QAPP requires prior Air District approval.