Sample Quality Assurance Project Plan for the Collection and Analysis of Pesticide Ambient Air Monitoring Data

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Air Program

California Department of Pesticide Regulation

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1 Introduction

Data generated from pesticide ambient air monitoring projects must meet stringent quality assurance/quality control standards if it is to be used for regulatory purposes. The entire process, from sampling design, sample quality assurance, chemical analysis, and reporting of results, must follow approved protocols in order to maintain the integrity of the collected sample data.

This document is intended to provide guidance for the development of effective community air monitoring programs. The included study elements in this guide are only applicable to pesticide air monitoring studies and should be considered additional to the 14 planning elements established by CARB for air districts, communities, and others to include in community-specific air monitoring plans developed under the Program.

2 Pesticide Ambient Air Monitoring Study Elements

This section should include information about study personnel, a detailed study definition and background, study quality objectives and criteria for data measurement, training requirements, and record keeping requirements. Additionally, it should include the names of the personnel that are to approve the Quality Assurance Project Plan (QAPP).

2.1 Study Personnel

This section of the study's QAPP should list the personnel responsible for ensuring the monitoring study is executed according to the guidelines provided in the final approved QAPP.

At a minimum, the person responsible for the quality control of the monitoring study should be included. The personnel may include but is not limited to monitoring project lead, quality system personnel, lead analytical laboratory personnel, and oversight organization designee. All key personnel and any organizations that will be involved in the program should be clearly identified.

Table 1 provides a sample Table of Responsibilities, where personnel titles and specific roles should be listed.

Table 1. Sample Table of Responsibilities.

Title	Responsibilities	Name	Phone No. and Email

2.2 Study Definition and Background

Begin this section with a written account that clearly summarizes the problem or situation that the proposed ambient air monitoring project is designed to address. Briefly summarize background information on the environmental issue the project will focus on and briefly review any previous studies

or data gaps that justify why this project is needed. Explain how the air monitoring data collected from this project will be used and who might use it.

2.3 Study Description

Describe the work to be included in the project, who will perform that work, and when and where it will take place. List what kinds of air samples will be taken and which pesticide(s) is to be measured from those samples. Describe how the results will be evaluated. Also, be sure to include an overall project timetable that defines the beginning and ending dates for the project as well as the dates of specific events during the project. The timetable should include sampling dates and frequency, laboratory analysis schedules, and when results are to be reported.

2.3.1 Pesticide Selection Considerations

This section should include background information about the pesticide targets in the monitoring study, including historical use information. For this purpose, the Department of Pesticide Regulation's (DPR's) Pesticide Use Report (PUR) database, which contains a comprehensive statewide record of pesticide applications in California, can be a valuable resource. The PUR database can be used to determine the time of year when the selected pesticide is applied and historical use amounts near target communities that are to be included in the monitoring study. When determining which pesticides to include in the monitoring, volatile pesticides make good candidates for ambient air monitoring whereas low- or non-volatile pesticides may prove difficult to monitor for via air sampling.

Pesticide use should be carefully reviewed to determine periods of peak use throughout the year to best use monitoring resources and funds. If pesticide use is seasonal, monitoring should be conducted several weeks before, during, and several weeks after peak use. For long-term monitoring studies, monitoring should be conducted every week for the study duration.

2.3.2 Sampling Site Locations

For effective monitoring results, proper site selection should be conducted as part of any community air monitoring study. If more than one site is to be selected, weather pattern data can be used to prioritize the monitoring site locations that are downwind of high use areas.

Additionally, the selected sampling sites should meet the following:

- Sampling sites should be placed in the exterior or on roofs of buildings.
- The sites should be accessible to sampling personnel during time of sampling.
- The sites should have access to electrical outlets.
- Sampling sites should preferably be located on the edge of the community and/or adjacent to agricultural fields.

All air samplers at sampling sites also must meet the following United States Environmental Protection Agency's (U.S. EPA) ambient air siting criteria:

- Inlet must be 2 to 15 meters above ground
- Must be at least 1 meter horizontal and vertical distance from supporting structure

- Should be at least 20 meters from trees
- Must be at a distance from obstacles that is at least twice the obstacle height
- Must have unobstructed air flow for 270°.

2.3.3 Sampling Logistics

Once all sampling site locations are selected for monitoring, at each sampling site, at least one 24-hour sample should be collected one day per week of the predetermined duration of the study. The 24-hour sampling period should begin each week on a randomly chosen day over the full seven-day week, including weekends.

If possible, conduct more frequent monitoring for air monitoring of pesticides during peak use (i.e., during high use periods). In order to capture peak concentrations, monitoring can also be conducted for several three to four consecutive 24-hour periods per week. Additionally, 12-hour sampling can also be conducted to obtain day/night concentrations.

In addition to the primary samples, quality control samples including co-located duplicates and trip blank samples should be collected at a rate of at least 10% of the primary samples collected during the sampling period. Co-located duplicate samples should be collected under the same environmental (e.g., temperature, humidity, and exposure to sunlight) and monitoring conditions (e.g., airflow rates, sample transportation, and storage) as the primary samples.

Collected air samples must be analyzed by an analytical laboratory that has established and validated protocols for the measurement of pesticides in the matrix used for monitoring. This may include private laboratories, public/private universities, and public agencies with the necessary analytical equipment and trained staff. The laboratory should be accredited and certified by authorized entities (i.e., International Organization for Standardization [ISO], Good laboratory practice [(GLP], etc.) A contract or memorandum of understanding (MOU) must be created in order to ensure all parties involved understand the scope of the work and the requirements that must be met in order to generate quality data.

2.4 Quality Objectives and Criteria for Measurement Data

Data quality objectives and acceptability criteria detail the steps necessary to produce data with known and acceptable precision and accuracy. A strategic approach should be used to ensure that the type, quantity, and quality of pesticide air monitoring data collected is acceptable for the intended use while ensuring that resources are not wasted collecting unnecessary or redundant data.

In this section, provide information regarding the planned sample collection and the steps that will be systematically taken to assess the study's sample collection precision, accuracy, representativeness, and completeness. Additionally, if any changes to the study are to be made after study commencement, include a detailed procedure that is to be followed here as well.

2.4.1 Field Sampling Quality Control for Air Monitoring

The following types of studies should be included as part of any pesticide air sampling program. These studies are meant to ensure the integrity and representativeness of any collected pesticide air sample.

1. **Trapping efficiency study**
   This study is conducted to determine the appropriate sample media, duration of sampling, and the volume of air needed. This study helps determine the ability to trap the pesticide of interest in the selected sampling media and provides confidence in the resulting concentrations for a study. See DPR's SOP FSAI003.OO for additional information regarding pesticide trapping efficiency studies (DPR, 2003).

2. **Storage stability study**
   This study is conducted to determine the stability of collected residues during sample storage prior to analysis. A storage stability study may validate the residue's rate of decomposition in a representative matrix. See DPR's SOP QAQC001.OO for additional information regarding pesticide storage stability studies (DPR, 1995).

Additionally, the following types of quality control samples should be taken during sample collection and sample analysis as part of any well-structured pesticide air monitoring study.

3. **Laboratory blank**
   An analyte-free matrix sample that is used by the analyzing laboratory along with prepared standards to calibrate the analytical instrument and to evaluate instrument contamination.

4. **Laboratory fortified matrix spike**
   A laboratory sample to which a known quantity of pesticide has been added. It is used to assess whether the sample matrix contributes bias to the analytical results and helps evaluate analyte recovery in a sample. This sample is not exposed to field conditions.

5. **Field blank**
   A sample that contains no pesticide residue. It is used to assess potential field and laboratory contamination issues.

6. **Co-located duplicate**
   A sample that is collected adjacent to the primary air sample under the same conditions. It is used to assess for field measurement precision and analytical measurements.

An appropriate study flow rate should be set as determined by the trapping efficiency study conducted prior to sample collection. Samples should be set to the targeted flow rate and pesticide residue data should be considered valid if it is collected from an air sampler measured with less than a ± 10% difference in starting and ending flow rates. Manufacturer-certified primary gas flow calibrators should be used to measure the air sampler pump flow rate (manufacturer of primary gas flow calibrators should be ISO 17025-accredited).

Ideally, to avoid possible media contamination, manufacturer pre-packed sealed sorbent tubes should be used for most of the pesticide air samples, with the possible exception of some fumigant samples as these samples may also be collected via SUMMA air canisters. If pre-packed sealed sorbent tubes are to be used for ambient air monitoring, to avoid off gassing of collected air samples, the glass tubes should be broken only immediately prior to scheduled sampling and sealed with endcaps immediately after sampling has concluded.

All samples, with the exception of vacuum-sealed air canisters, should be immediately placed in dry ice storage following collection to prevent the outgassing and/or degradation of pesticide residues. Samples may be placed in freezer storage (approximately -20°C or -4°F) until they are analyzed by the laboratory. However, under no circumstances should the collected sample be exposed to ambient temperatures following sample collection; doing do will seriously affect the validity of the collected sample. Storage stability tests must be conducted by the analytical laboratory to determine the maximum holding time between sample collection and analysis. See DPR's SOP QAQC001.OO for additional information regarding pesticide storage stability studies.

If air canisters are to be used, canisters should be cleaned and evacuated according to U.S. EPA's Method TO-15 (U.S. EPA, 1999). Canister valves should only be opened at the beginning of sampling and closed before the input line is disconnected. Canisters should never be directly open to the atmosphere and must be controlled by a regulator or canister sampler. Canisters do not need to be stored below ambient temperature before, during, or after sample collection. To prevent sample degradation, canisters should not be in direct sunlight or exposed to elevated temperatures. Storage stability tests also must be conducted for canister sampling of ambient air.

2.4.2 Quality Assurance

The analytical laboratory chosen to analyze samples for pesticide residues must meet established laboratory quality control procedures. The laboratory should be accredited and certified by authorized entities (i.e., ISO, GLP, etc.) The laboratory must have a validated method for the determination of the pesticide(s) of interest (For additional information, see DPR [1995]) for additional information). The laboratory must have conducted trapping efficiency tests to ensure breakthrough of the sorbent tubes being used for monitoring does not occur.

Sorbent tubes used for monitoring must be certified clean by the manufacturer, who can provide certificates of registration to various manufacturing standards and certificates of quality for their products. Methods and results of storage stability tests must be provided with the reporting of data.

2.5 Training

List any specialized training or certification requirements air sampling personnel will need to successfully complete their tasks. Summarize how you will provide such training, who will conduct the training, and how the performance of personnel will be evaluated.

2.5.1 Training Requirements

Ambient air monitoring personnel should be fully trained in conducting air monitoring, sample collection, and record keeping and transport. Prior experience in air monitoring, particularly with the equipment to be used, is highly recommended.

2.6 Documents and Records

Identify the field and laboratory information and records needed for the project. Records will include raw data, field data sheets (logs and chain of custody [COC] forms), laboratory forms and other documentation generated or used in the study. Indicate for how long (e.g., 5 years) and where records

will be maintained.

2.6.1 List of Forms and Filing Procedures for Paper Files and Records

Prior to sampling, all personnel involved in the study should receive the most current approved version of the study's QAPP.

When air sampling commences at each monitoring site, the sample tracking number, date, time, staff initials, weather conditions, and air sampler flow rate should be documented on the study's COC form. Air samples collected with sorbent tubes should be transported under dry ice with ascending time-temperature indicators present to the designated receiving warehouse and be logged in and kept frozen at -20°C (-4°F) until transfer to the laboratory for analysis. Confirmation (i.e., with staff name and signature) that confirms proper sample transport and storage was followed should be included in the sample COC form.

Samples received at the laboratory should be logged into a laboratory information database and assigned unique laboratory identification (IDs). The temperature and conditions of the sample at the time of receipt should be recorded. Sample processing procedures should be performed according to the appropriate laboratory procedural standard operating procedures (SOPs); the dates, times, and analyst(s') initials should be recorded.

At the analytical laboratory, all data should undergo a technical peer review by multiple analysts. A complete review of the full analytical data package should be performed by the laboratory supervisor before release of the summary data report to the air monitoring study leader. The air monitoring study leader should perform a third-level administrative review of the summary data report, which includes a check of sample dates (dates of submitted samples align with scheduled sampling days).

2.6.2 Electronic Record Keeping--Forms

Electronic data should be stored on the instrument data station at the analytical laboratory for a period of five years, after which time it may be purged. Results from the study must be entered into an electronic spreadsheet by the study leader and stored both on their computer's physical hard drive and on a backup method of data storage (e.g., external hard drive, optical disc, USB drive, cloud storage, etc.).

3 Data Generation and Acquisition

In this section, a detailed experimental design outline of the project including information on types of and number of ambient air samples required, sampling frequency, sampling period or duration, and how sampling locations will be selected. Specify how constraints such as weather, site access, or pesticide applications may affect scheduled activities and how those constraints will be dealt with. Be sure to include site and project safety plans. The citation of specific sections of SOPs which detail the sampling design may be used instead of extensive discussion.

3.1 Sampling Methods

3.1.1 Sample Collection

In this section, describe the type of sampling equipment that will be used as part of the ambient pesticide air sampling study including the sampler manufacturer and model number, sampling media utilized, type of tubing and other instrumentation instruments used as part of the sampling, target air flow values, sampling duration, sample set-up and removal procedures, and sample transport and storage.

3.2 Sample Handling and Custody Requirements

Samples must be collected in conjunction with a COC form. A COC form is an appropriate format to use to record important data associated with each individual sample. Normally, a COC form is used to record three types of information: field information, laboratory information, and information about the personnel who handle the sample.

3.2.1 Sample Custody, Sample Shipping, and Chain of Custody Procedures

Samples must be recovered by sampling personnel and delivered with a completed COC form to the sample receiving facility. Immediately after collection, samples must be stored on dry ice in an insulated container until they arrive at the receiving facility, where they must be stored in a freezer at -20°C (-4°F) until transferred to the analytical laboratory. Samples should not be stored for longer than the time period determined in the conducted storage stability study prior to shipment to the laboratory for analysis.

The person who prepared the sample container must sign the first “relinquished by” line. The “received by” line must be signed and dated by the person collecting the sample. That same person must then sign to relinquish the sample when it is delivered to the sample storage facility. The person who transports the sample to the laboratory must sign the COC form last. All signatures must be in ballpoint pen followed by a date and time that the COC form was signed. No erroneous information may be erased on the COC form. Errors must be lined out and initialed, and the correction written in.

3.2.1.1 Shipping Procedures

Samples should be placed in an insulated cooler immediately after sampling in the field and surrounded with sufficient dry ice to freeze the samples. COC forms must accompany samples at all times.

3.3 Analytical Methods

The following guidelines are meant to be a starting point; the procedures outlined here are the some of the quality control measures that should be reported in all ambient pesticide air monitoring studies. The method performance levels chosen should be consistent with the study objectives.

3.3.1 Method Detection Limit

List and describe the analytical methods and equipment needed for the analysis of each pesticide residue of interest. For any analytical method chosen, a Method Detection Limit (MDL) determination needs to be determined by following the U.S. EPA method (40 CFR, Part 136, Appendix B). Briefly, the MDL is determined by analyzing at least 7 low-level matrix spikes and performing the following calculation:

$$MDL = t \times S$$

where:

t = Student's t value for 99% confidence level (l-tailed) and n-l degrees of freedom
S = standard deviation

3.3.2 Method Reporting Limit

In addition to the MDL, a Method Reporting Limit (MRL) needs to be determined. The MRL is normally set at 1 - 5 times the MDL depending on the matrix and instrument.

3.3.3 Method Validation

A method validation that details the acceptable range of spike recoveries needs to be established. This range needs to be established by analyzing blank-matrix spike samples. Two to five replicate analyses at two to five different spike levels need to be used to determine the mean percent recovery and standard deviation. Number of replicates and spike levels need to be chosen and listed in the study QAPP. Additionally, warning limits need to be established at the mean percent recovery plus/minus 1 - 2 times the standard deviation. Control limits need to be established at the mean percent recovery plus/minus 2-3 times the standard deviation. Any subsequent spiked samples outside the control limits may require the set of samples associated with that spike to be reanalyzed.

3.3.4 Storage Stability

As mentioned earlier, storage stability is conducted to determine the stability of collected residues during sample storage prior to analysis. A storage stability study may validate the residue's rate of decomposition in a representative matrix. In general, the test should be run for the longest anticipated holding period, with at least four sampling intervals and two replicate samples at each sampling interval. Additional information is given in DPR (1995).

3.4 Quality Control

List the number and types of field and laboratory quality control samples that will be included in the proposed pesticide ambient air monitoring study.

3.5 Instrument/Equipment Testing, Inspection, and Maintenance

Describe the plans for routine inspection and preventative maintenance of field and laboratory equipment. Identify what equipment will be routinely inspected; include an equipment maintenance schedule, if appropriate.

Field equipment should be calibrated at the beginning of each sampling period with primary gas flow calibrators factory-certified with a National Institute of Standards and Technology (NIST)-traceable calibration by the manufacturer (ISO 17025-accredited facility). Flow readings must be recorded on COC forms for every sample. Initial sample flow should be ± 10 % of the desired flow rate. At the end of the sampling period, ending flow rates must be recorded on the COC form. If the ending flow rate is greater than established threshold level (± 10% recommended) of the starting flow rate, the sample should be

considered invalid and a make-up sample will be taken by sampling personnel.

3.6 Instrument/Equipment Calibration and Frequency

In this section, describe how sampling and analytical instruments will be calibrated. Be sure to include information on the frequency instruments will be calculated and the types of standards or certified equipment that will be used to calibrate sampling instruments. Indicate how you will maintain calibration records and ensure that records can be traced to each instrument. Sampling pumps should be calibrated at the beginning of each sampling period with primary gas flow calibrators. The flow calibrators are to be factory recertified annually with an NIST-traceable calibration.

All analytical laboratory equipment owned and operated by the analytical laboratory should have calibration records.

An audit from an outside organization, like DPR or Air Resources Board (ARB), is highly encouraged, as it would add support to the validity of the collected air monitoring data.

3.7 Electronic Record Keeping

Data will be first generated in the field during sampling set up. Specifically, record the date/time/location, sample identification, initial flow rates, etc. on the sample COC form. Once results are obtained by the analytical laboratory, the mass of pesticide residue per sample needs to be recorded on the appropriate COC form. Discuss the checks for accuracy and completeness of COC forms and laboratory forms. Also, note how errors will be minimized and otherwise corrected in calculations, data entry into databases, and reporting of results in the final report. Identify the computer hardware and software that will be utilized to manage and store data.

4 Assessment and Oversight

Indicate how field, laboratory, and data management activities, organizations/contractors, and individual personnel will be evaluated. This may include individual evaluations of personnel performance or systems audits of equipment and analytical procedures.

4.1 Assessment and Response Actions

The first assessments should begin in the field by personnel assigned to collect air samples as scheduled. This may include checking and calibrating equipment to ensure samples will be collected according to specified study criteria (e.g., flow rate and duration of collection). These self-assessments should include all personnel assigned to sample collection and the results of such assessments will be reported to the study leader.

The study leader should provide oversight as needed. Oversight is to include reviews of sampling procedures and techniques, reviews of field data and observations, and assistance to sampling personnel as requested. Field audits by an independent third party (DPR or ARB) is highly recommended to ensure integrity of the field samples collected and the resultant data generated.

The information expected from monitoring should be recorded on the COC form (date, time, flow rates, etc.) including the results from the analytical laboratory

4.2 Study Report

A report to DPR or other regulatory authorities regarding the study's results must be made at the conclusion of the study, or annually if the study is to be conducted for more than one year. The report must describe the study's results and any assessments of data quality and recommended solutions. All study raw data should be included either in the main body of the report or as an appendix.

5 Data Validation

Outline how data will be reviewed and how decisions will be made regarding the acceptance, or rejection, of data. How will data be validated and by whom?

5.1 Data Review, Validation, and Verification

Data obtained from the analysis of field samples needs to be first reviewed and validated by analytical laboratory personnel. For pesticide quantification, upper and lower warning and control limits should be set at ±2 and ±3 standard deviations derived from the average percent recovery. These limits should remain static for the duration of the study, but may be updated if significant changes are observed based on the on-going accuracy and precision data derived from the field and laboratory quality control samples. The upper control limit (3x standard deviation) and the lower control limit (3x standard deviation) must be determined by the analytical laboratory.

5.2 Verification and Validation of Methods

Describe the procedures used to validate and verify data. This may include comparing database entries of COC forms, reviewing for gaps in data, double-checking data fields on the COC forms and recorded sample or site information, reviewing equipment calibrations, checking of raw data for outliers, and having calculations reviewed for accuracy. Provide a description of how errors will be corrected if detected and how results will be reported to users of the study's data. Verification and validation of the methods used in the study must be published with the final report.

5.3 Reconciliation with User Requirements

Once the data and results are reported, what is the process to determine if they meet the study's objectives. This may include calculating and comparing data quality indicators (precision, accuracy, completeness, representativeness, and comparability) to those specified at the beginning of the study. If data quality indicators deviate from those specified earlier, what will be done? This may include discarding data, stating the limitations of the reported data or revising the study's data quality objectives.

6 References

DPR (1995). Standard Operating Procedure: Chemistry Laboratory Quality Control. SOP Number: QAQC001.OO. California Department of Pesticide Regulation, California Environmental Protection Agency.

DPR (2003). Standard Operating Procedure: Conducting a Trapping Efficiency Study for Air Monitoring using Standard in Solvent. SOP Number: FSAI003.OO. California Department of Pesticide Regulation, California Environmental Protection Agency.

U.S. EPA (1999). "Air Method, Toxic Organics-15 (TO-15): Compendium of Methods for the