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MEMORANDUM

TO: John Sanders, Chief
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Management Branch
Department of Pesticide Regulation

FROM:  Jeffrey P. Cook, Chief
Quality Management Branch
Monitoring and Laboratory Division

DATE: June 6, 2002

SUBJECT: FINAL PROTOCOL FOR THE 2002 CHLOROTHALONIL APPLICATION
AND AMBIENT AIR MONITORING

Attached is the final "Protocol for Application and Ambient Air Monitoring for Chlorothalonil in Fresno County During Summer, 2002". We received and appreciated your comments (May 16, 2002, memo, Sanders to Cook) on the draft protocol.

If you or your staff have questions or need further information, please contact me at 322-3726 or Kevin Mongar at 322-2249.

Attachment

cc: Randy Segawa, DPR (w/Attachment)
Shifang Fan, DPR (w/Attachment)
Jerry Prieto, Fresno County Agricultural Commissioner (w/Attachment)
David L. Crow, San Joaquin Valley Unified APCD (w/Attachment)
Kevin Mongar

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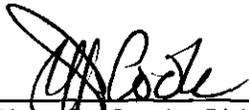
**Protocol for the Application and Ambient
Air Monitoring for Chlorothalonil
In Fresno County During Summer, 2002**

Quality Management Branch
Monitoring and Laboratory Division

Project No.
P-02-002

Date: June 4, 2002

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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- Attachment II - Standard Operating Procedures for the Analysis of Chlorothalonil in Ambient Air
- Attachment III - Pesticide Adsorbent Tube Sampling Procedures For Ambient Studies
- Attachment IV - Pesticide Adsorbent Tube Sampling Procedures For Application Studies

Protocol for the Application and Ambient
Air Monitoring for Chlorothalonil
In Fresno County During Summer, 2002

I. Introduction

At the request (January 2, 2002, Memorandum, Helliker to Lloyd) of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide chlorothalonil in Fresno County over a six-week ambient monitoring program and over a three-day application monitoring program. This monitoring will be done to fulfill the requirements of Assembly Bill (AB) 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), which requires the ARB "to document the level of airborne emissions ...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The ambient monitoring will be conducted for six consecutive weeks between May 26 and July 6, 2002, to coincide with the use of chlorothalonil as a fungicide. California growers primarily use chlorothalonil on tomatoes, potatoes, onion, celery, carrots, and garlic.

The sampling and analysis for chlorothalonil will follow the procedures and quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version)(Attachment I) as well as the procedures described in the "Standard Operating Procedure for the Analysis of 2,4,5,6-tetrachloro-1,3-benzenecarbonitrile (Chlorothalonil) in Ambient Air" (Attachment II) and the pesticide adsorbent tube sampling procedures outlined in Attachments III and IV.

II. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-2 resin. The sampling manifold is shown in Figure 1. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (on dry ice) or in a freezer until desorbed with organic solvent. The tubes are 8 mm x 110 mm with 400 mg XAD-2 in the primary section and 200 mg in the secondary section. The flow rate of 3.0 standard liters per minute (slpm) will be accurately measured and the sampling system operated continuously for 24 hours (ambient) with the exact operating interval recorded in the log book. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods and 1.5 meters above roof tops for the ambient monitoring. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter (or needle valve), train support, and either a 12 volt DC or a 115 volt AC vacuum pump. Tubes are prepared for use by breaking off the sealed glass ends and immediately inserting the tube into the Teflon fitting. The tubes are oriented in the sample train according to a small arrow printed on the side indicating the direction of flow. A needle valve with a range of 0-5 slpm is used to control sample flow rate. The flow rates will be set using a calibrated digital mass flow meter (MFM), scaled from 0-5 slpm, before the start of each sampling period. The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Samplers will be leak checked prior to each sampling period, with the sampling tubes installed. Any change in flow rates will be recorded on the field log sheet. The pesticide sampling procedures for adsorbent tubes are included as Attachment III (ambient) and IV (application).

Ambient Monitoring

The DPR recommendations for chlorothalonil request that ambient monitoring occur in Fresno County for 6 consecutive weeks between May 26 and July 6, 2002. Five sampling sites will be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). At each site, 24 discrete 24-hour samples will be collected, Monday through Friday (4 samples/week), during the 6-week sampling period. Background samples will be collected at the ARB air monitoring site in Fresno. Collocated (replicate) samples will be collected for 6 dates (each Wednesday) at each sampling location.

The sites will be selected by ARB personnel from areas of historic use of chlorothalonil in Fresno County. Sites will be selected for their proximity to the historic use areas with considerations for both accessibility and security of the sampling equipment. ARB understands that DPR staff will verify and quantify the actual use of chlorothalonil that takes place during the study when the information becomes available.

Application Monitoring

The use pattern for chlorothalonil suggests that application-site monitoring should be conducted in Fresno County sometime during the ambient study, and that the monitoring be associated with an application of chlorothalonil at the highest use rate of approximately 5.0 pounds active ingredient per acre. The exact application monitoring schedule will vary based on the type and length of application but will follow the schedule guidelines outlined below in Table 1. Ideally, the monitoring study will include samples taken before, during, and for approximately 72 hours following application.

TABLE 1. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	Sample duration time
Background (pre-application)	24 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset) ¹
1 hour post-application	2 hours (or up to 1 hour before sunset) ¹
3 hour post-application	3 hours (or up to 1 hour before sunset) ¹
6 hour post-application	6 hours (or up to 1 hour before sunset) ¹
1 hour before sunset	Overnight ² (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

¹ These sample duration times will be adjusted depending on length of application and time of sunset.

² All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "one hour before sunset", then the overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur over the course of two or more days. In these instances, samples are collected during the first daily application, followed by a sample from the end of application to one hour before sunset (if applicable), followed by an overnight sample, ending at either the start of application or one hour after sunrise the next morning, whichever is first (same for third or more application days). If the day two application does not start at or before 'one hour after sunrise', and the expected time between 'one hour after sunrise' and the start of application is more than two hours, then an additional sample will be collected during this period. Following the end of the final application, samples are collected according to the above schedule, starting with the one-hour sample. As stated above, if the application extends beyond "one hour before sunset", then the overnight sample will be started at the end of application (i.e., no one-, two-, or three-hour samples will be collected post application in this case).

A minimum of 8 samplers will be positioned, one on each side of the field and one in each corner. A ninth sampler will be collocated at one position (downwind). Background (before application) samples should be collected for 24 hours. Ideally, samplers should be placed at 20 meters from the field.

The exact location of the application monitoring study has not yet been determined. ARB staff will contact the County Agricultural Commissioner's offices in the Fresno County area to coordinate the selection of a study site and the test dates. The County Agricultural Commissioner's staff will make initial contact with, or will at least provide a list of local contacts for growers, applicators, and/or pesticide control advisers that may be willing to cooperate in conducting the study. Monitoring sites are arranged with the voluntary cooperation of growers and applicators. ARB staff will investigate contacts until a cooperative grower is found and an

appropriate site is selected. Permission to conduct the study will be obtained from the application plot land-owner and owners of adjacent land where samplers will be positioned.

Candidate fields for application monitoring will be 10 acres or larger. The crop type or specific application method for the application study were not specified by the DPR. However, the DPR recommended that, "monitoring should occur at a site using the highest allowed use rates (i.e., 5 pounds AI per acre for chlorothalonil)".

ARB will provide the following information in the monitoring report:

- 1) An accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field;
- 2) An accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, etc.;
- 3) Meteorological data collected at a minimum of 15-minute intervals, including wind speed and direction, humidity, and comments regarding degree of cloud cover;
- 4) The elevation of each sampling station with respect to the field;
- 5) The orientation of the field with respect to North (identified as either true or magnetic north); and
- 6) The start and end time of the application each day.

III. Analysis

The sampling and analytical methods used for this study are based on methods used to conduct similar monitoring (for DPR) in 1992. The "Standard Operating Procedure for the Analysis of 2,4,5,6-tetrachloro-1,3-benzenecarbonitrile (Chlorothalonil) in Ambient Air" (May 17, 2002 draft version) is included as Attachment II. The procedure consists of extraction of the exposed XAD-2 resin with an organic solvent followed by GC/MS analysis. DPR requested a target 24-hour estimated quantitation limit (EQL) of 1.0 nanograms per cubic meter (ng/m^3). The EQL actually achieved by the method was $2.3 \text{ ng}/\text{m}^3$.

IV. Quality Assurance

Field Quality Control for the ambient monitoring will include:

- 1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air at the background monitoring site (ARB Fresno site) for 24-hour periods at 3.0 slpm (i.e., collocated with a background sample). One field spike each will be collected during weeks 1, 3, 4, and 6.
- 2) Four trip spikes prepared at the same level as the field spikes.

- 3) Four lab spikes prepared at the same level as the field and trip spikes.
- 4) Collocated (replicate) samples will be taken for six dates (each Wednesday) at each sampling location.
- 5) A trip blank will be obtained each week of sampling.

Field Quality Control for the application monitoring will include:

- 1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air during background monitoring at the application site for the same duration as the background samples at 3.0 slpm (i.e., collocated with background samples).
- 2) Four trip spikes prepared at the same level as the field spikes.
- 3) Four lab spikes prepared at the same level as the field and trip spikes.
- 4) Collocated (replicate) samples will be taken for all samples at one of the sampling locations (downwind).
- 5) One trip blank will be obtained during the study.

A chain of custody sheet will accompany all samples. Mass flow meters will be calibrated by the ARB Standards Laboratory. The flow rate of each sampler will be audited by the ARB Quality Assurance Section prior to the monitoring studies.

V. Sample Labeling

Samples for the application study will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:

Location is designated as north 1, 2, or 3 (N1, N2, N3), west (W), south 1, 2, or 3 (S1, S2, S3), and east (E). These designations can be revised as necessary depending on the configuration of the field.

Chlorothalonil is designated as C.

Sampling period is designated as B (for background) or 1 through 9 (# of periods can vary).

The type of sample is designated as S (sample), CO (collocated), TB (trip blank),

TS (trip spike), and FS (field spike).

Examples: S2-C-B-S (South2, Chlorothalonil, background, sample)
S2-C-B-FS (South2, Chlorothalonil, background, field spike)
S2-C-1-S (South2, Chlorothalonil, sampling period 1, sample)
S2-C-1-CO (South2, Chlorothalonil, sampling period 1, collocated)

Samples for the ambient study will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:

Location is designated by 3-letters. The designations will be defined after the sites have been chosen.

Chlorothalonil is designated as C.

Sampling period is designated as 1 through 24 (e.g., 24 periods in 6 weeks).

The type of sample is designated as S (sample), CO (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Example: ARB-C-1-S (ARB Fresno site, Chlorothalonil, period 1, sample)
ARB-C-1-CO (ARB Fresno site, Chlorothalonil, period 1, collocated)

VI. Personnel

ARB personnel involved with coordinating and conducting the field activities will consist of staff of the Air Quality Surveillance Branch.

VII. Safety Recommendations

The DPR's 'Monitoring Recommendations' include the following safety recommendations:

"The chlorothalonil product labels alert that chlorothalonil is hazardous to humans and domestic animals. Chlorothalonil is corrosive, causes irreversible eye damage, and may cause allergic reactions in some individuals with prolonged or repeated skin contact. Inhalation may be fatal. Chlorothalonil products may be harmful if swallowed or absorbed through the skin."

"The label advises that applicators, mixers, loaders, and other handlers must wear long sleeve shirt and long pants, chemical resistant gloves, shoes and socks, protective eyewear, and a dust/mist filtering mask. The restricted-entry interval varies by product from 12 to 48 hours. Monitoring personnel should refer to the label of the product used and should use proper protective equipment to prevent exposure to the dust or spray mist."

MANIFOLD SAMPLER

01/29/02

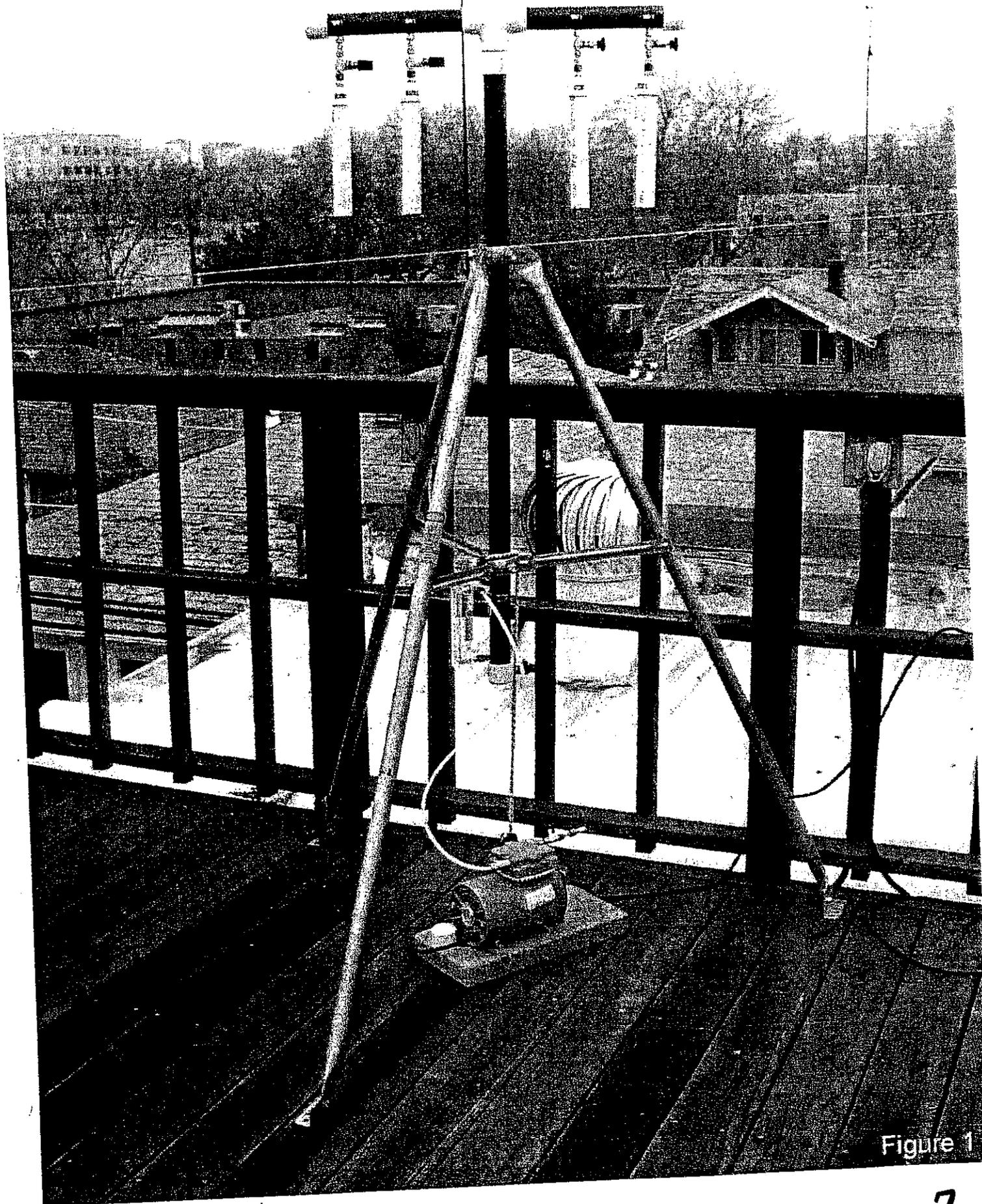


Figure 1

Attachment I

Quality Assurance Plan for Pesticide Air Monitoring

State of California
California Environmental Protection Agency
Air Resources Board

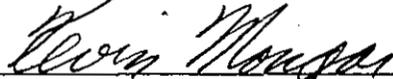
QUALITY ASSURANCE PLAN
FOR PESTICIDE AIR MONITORING

Prepared by the

Monitoring and Laboratory Division
Engineering and Laboratory Branch

Revised: May 11, 1999

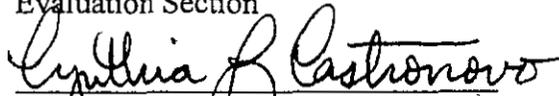
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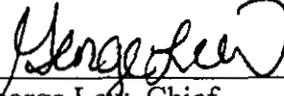
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This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff determines the airborne concentrations of specified pesticides following monitoring recommendations established by the DPR. This air monitoring is conducted to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB “to document the level of airborne emissions of pesticides which may be determined to pose a present or potential hazard...” when requested by the DPR. The documentation of airborne concentrations is usually accomplished through two types of monitoring. The first consists of five to eight weeks of **ambient** monitoring in the general area of, and during the season of, peak use of the specified pesticide. The second is monitoring around the perimeter of a field during and for 72 hours after an **application** has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with accurate, relevant and timely air monitoring measurements of airborne pesticide concentrations. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are as follows.

- (1) to establish the necessary quality control activities relating to site selection, method validation, analytical standard operating procedures (SOP), sample collection, sampling and analysis protocol, data reduction and final reports, and;
- (2) to assess data quality in terms of precision, accuracy and completeness, and;
- (3) to design air monitoring strategies to meet the pesticide target (estimated) quantitation levels as provided by the DPR.

II. Air Monitoring

All sampling will be coordinated through communication with the County Agricultural Commissioner’s Office. The local Air Quality Management District (AQMD) or Air Pollution Control District (APCD) will be notified prior to any monitoring. Sample collection will be conducted by staff of the Testing Section or staff of the Air Quality Surveillance Branch of the ARB, or an approved ARB contractor.

A. Siting

The location and time-frame for **ambient** and **application** monitoring are based on direction provided by the DPR in their "Use Information and Air Monitoring Recommendation for Pesticide Active Ingredient" documents. These recommendations are based on historical trends (normally 2 to 3 years prior) and are submitted to the ARB by the DPR approximately 1 year in advance of intended monitoring. The recommendations direct ARB to monitor for a pesticide in specific counties during specific use periods. Pesticide use maps (historical) and histograms are used along with close coordination with staff of the County Agricultural Commissioner's Office to predict areas (and times) of use for the pesticide for the upcoming use year. Approximately one month prior to the scheduled monitoring DPR will reevaluate the historical use trends using the most recent pesticide use data available.

For selection of **ambient** monitoring sites, ARB staff work through authorized representatives of school districts, private companies or city, county or state government agencies. The probe (sampler) siting criteria for **ambient** pesticide monitoring were obtained from the U.S. EPA "Ambient Air Quality Surveillance" criteria (40 CFR, Part 58) and are listed in TABLE 1. As per the DPR monitoring recommendations, three to five sites are chosen. The monitoring objective in choosing these sites is to estimate population exposure in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). Sampling sites should be located near (in regions of) specific agricultural crops as recommended by the DPR. One additional site is chosen and designated to be an urban area "background" site which is located away from any expected applications. Information will be collected for each site and reported to DPR regarding; 1) the proximity of the each sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground. Normally the **ambient** samplers will be located on the roof of a one-story building (e.g., at schools) with the sample cartridge located about 1.5 meters above the roof.

Probe siting criteria for placement of samplers around a pesticide **application** are the same as for **ambient** monitoring tests (TABLE I). A minimum of four samplers are positioned, one on each side of the field. A fifth sampler is collocated at one position, normally the downwind side (based on prevailing breezes). Once monitoring has begun, the sampling stations are not moved, even if the wind direction has changed. Ideally, samplers should be placed at a minimum distance of 20 meters from the perimeter of the field and should be equidistant from the field. *These requirements are nearly impossible to meet because of the physical limitations of most application sites. Twenty meters from a potential application field invariably places the sampler on another landowner's property, in another field where tractors and other equipment must operate, or into another orchard where the siting criteria cannot be met. Fences, canals, roads, ditches, railroad tracks, brush, trees, houses, barns, livestock, parked equipment, uncooperative neighbors, etc. are common obstacles. Monitors are placed as far as possible, up to 20 meters, from the field. Attempts are always made to center the samplers on the face of a side of the field. The sampler is placed to maximize the distance from the field and to avoid obstructions bordering the field. Conditions at the site will dictate the actual placement of monitoring stations.* Information is collected and reported to DPR regarding; 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that

the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees buildings and other obstacles; 3) the elevation of each sampling station with respect to the field and the orientation of the field with respect to North (identified as true or magnetic North). Determination of an appropriate site for an **application** test is based on the “recommendations” provided by the DPR. Parameters used to choose the site are:

1. crop type,
2. minimum field area of 10 acres,
3. minimum application rate (as directed by the DPR),
4. type of application (normally no preference by the DPR),
5. availability of sites on all four sides of the field which meet the criteria in Table 1 and can be sited 20 meters from the perimeter of the field (quite often this is not possible, i.e., normally 4 sites are chosen but they may not all meet the criteria), and
6. accessibility and security of the sampling sites/equipment.

Monitoring sites (fields) are arranged through communication with, and the voluntary cooperation of, applicators, growers or owners for **application** monitoring. Normally, representatives of the County Agricultural Commissioner’s Office will make initial contact with the applicators/growers or will at least provide a list of possible candidates.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

Height Above Ground (Meters)		2-15
Minimum Distance from Supporting Structure (Meters)	Vertical	1
	Horizontal	1
Other Spacing Criteria		<ol style="list-style-type: none"> 1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

B. Schedule

Samples for **ambient** pesticide monitoring will generally be collected over 24-hour periods on a schedule of 4 samples per week (Monday through Friday) for 5 to 7 weeks. Occasionally the normal schedule will be interrupted due to holidays and make-up samples may be collected over weekends.

Individual **application** monitoring schedules will vary based on the type and length of application but will follow the schedule guidelines outlined below in TABLE 2. Ideally, the

monitoring study will include samples taken before, during and for approximately 72 hours following application.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	Sample duration time
Background (pre-application)	Minimum of 12 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset) ¹
1 hour post-application	2 hours (or up to 1 hour before sunset) ¹
3 hour post-application	3 hours (or up to 1 hour before sunset) ¹
6 hour post-application	6 hours (or up to 1 hour before sunset) ¹
1 hour before sunset	Overnight ² (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

1 These sample duration times will be adjusted depending on length of application and time of sunset.

2 All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur all day long and over the course of two or more days. In these instances samples are collected during the first daily application, followed by a sample from end of application to 1 hour before sunset, followed by an overnight sample ending at either the start of application or 1 hour after sunrise the next morning (same for second or more application days). Following the end of the application, samples are collected according to the above schedule, starting with the 1-hour sample.

C. Meteorological Monitoring

Data on wind speed and direction, barometric pressure, relative humidity and air temperature will be collected during **application** monitoring by use of an on-site meteorological station. The meteorological data will be acquired using a data logger at a minimum of 15 minute intervals (averages). Meteorological systems will be calibrated as specified in the ARB manual, "Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring." Meteorological data are not collected for the **ambient** monitoring programs.

III. Method Validation

A. Method Detection Limit

The method detection limit (MDL) is defined as the lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and matrix.

MDL is defined as $3.14 \times s$; where s is equal to the standard deviation of seven replicate spiked samples (e.g., XAD sample cartridges). The spiked samples are prepared and analyzed in the same way as actual samples. The spikes should be prepared at a concentration that is between one to five times the estimated MDL.

B. Estimated Quantitation Limit

The estimated quantitation limit (EQL) is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix. This EQL is defined as $5 \times \text{MDL}$.

C. Reproducibility

The reproducibility of the method should be determined by performing five replicates at three different concentrations. The lowest level should be at or near the EQL. The average and standard deviation of each set of replicates should be determined and reported.

D. Extraction Efficiency

Extraction efficiency is defined as the amount of pesticide recovered from a spiked sample. Three replicates at two levels and blank should be extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added multiplied by 100 will give the percent recovery. Recommended recoveries should be between 70-130%.

E. Sampling Efficiency

Sampling efficiency is determined by spiking a sample with a known amount of pesticide. The spiked sample is placed in a sampler and set to the same flow rate and time that samples are collected. At a minimum three replicate spiked samples at a concentration two times the EQL of the method and a collocated background are collected. The samples are extracted and average recovery and standard deviation of the spike samples are determined.

F. Breakthrough

Breakthrough is determined by using a two stage sampling media (usually a filter or resin). The front stage is spiked with a known quantity of the pesticide. The breakthrough study samples are normally spiked at a relatively high level, e.g., at a level that might be observed

during an application study. If time and resources permit, both low and high level spike studies are run. The backup will be the same filter or resin type and placed in series with the front filter or resin. Air is passed through the sampler at the same flow rate and sample time as a real sample (minimum sample time of 24 hours). The front and backstage are recovered and extracted separately. If breakthrough is observed then the sampling strategy must be reviewed, modified and retested before the start of a sampling project.

G. Freezer Storage Stability

Spiked samples should be stored under the same conditions as the samples and for the anticipated time that the samples are stored. Recoveries are determined. A high (either at a level expected during the application study or at the high end of the calibration curve) and a low (1 to 2 times the EQL) concentration set should be studied. A set consists of three replicate spikes each for 3 time intervals.

IV. Field Sampling Quality Control Procedures

Monitoring programs will include the following quality control procedures:

A. Sample Labels

Sample labels will be affixed either directly to the sampling cartridge or will be placed in the individual sample container (e.g., culture tube or zip-lock bag). The sample labels will include at least the following information.

1. Pesticide name and the ARB project number.
2. Log number
3. Sample I.D.
4. Monitoring Location
5. Sampling end date
6. General comments

B. Log Sheets

Field data log sheets will be used to record the sampling log number, sample I.D., start and stop dates, start and stop times, start and end flow rate, initials of individuals conducting sampling, malfunctions, leak checks (at the beginning and end of each sampling period, see Appendix I), weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Refer to Appendix I for a recommended log sheet format.

C. Chain of Custody Forms

Attached as Appendix II is a recommended format for chain of custody (COC) sheets. A COC sheet must accompany any/all samples during transport, transfer or storage. All exchanges of sample possession must be recorded. The laboratory will keep copies of the COCs and

forward the originals to the project engineer. The original COC sheets must be retained in the pesticide project file.

D. Flow Controller Calibration and Audit

Field flow controllers (rotameter, electronic flow controller or critical orifice) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard (e.g., digital bubble flowmeter or electronic digital mass flowmeter) must be verified, certified or calibrated with respect to a primary standard at least once per year by the Quality Management and Operations Support Branch (QMOSB) of ARB. Appendix V shows an example of a form to document the flow controller calibration results.

A flow audit of the field air samplers will be conducted by the QMOSB before each pesticide monitoring project. If results of this audit indicate a difference from the calibrated values of more than 10%, then the field flow controllers should be rechecked until they meet this objective. A written report of the QMOSB audit results will be included as an appendix in the final monitoring report.

Sampling flow rates should be checked in the field and noted before and after each sampling period. A separate, certified flow meter (i.e., not the one used in the sample train to control flow) will be used to check the flow. The flow rates should be checked after the initial sampling system leak check and before the "end" sampling system leak check.

E. Background Sampling

A background sample will be taken at all sites (4 sides) prior to an **application** test. The duration of the background sample should be sufficient to achieve the pesticide target 24-hour EQL, as directed by the DPR prior to the test, and must be a minimum of twelve hours and up to 24 hours if scheduling permits. This sample will establish if any of the pesticide being monitored is present in the air prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for **ambient** monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site. Detectable levels of some pesticides may be found at an urban area background site if they are marketed for residential as well as commercial/agricultural use. An example of an urban area background site is the ARB air monitoring station in downtown Fresno.

F. Collocated Samples

For both ambient and application monitoring, the method precision will be demonstrated in part by collecting samples from collocated samplers (replicate analysis of samples also relates to method precision). An additional **ambient** sampler will be collocated at each of the sampling

sites. Normally, collocated samples will be collected at each **ambient** site every Wednesday for each week of sampling. The samplers should be located at least two meters apart if they are high volume samplers (>20 Lpm) in order to preclude airflow interference. This consideration is not necessary for low flow samplers. The collocated sampler for **application** monitoring should be positioned at the downwind sampling site where the highest concentrations are expected. The collocated site is not changed after the study starts.

G. Trip Blanks

A trip blank should be included with each batch of samples submitted for analysis. This will usually require one trip blank for an **application** monitoring study and one trip blank per week for an **ambient** monitoring program. Trip blanks are prepared by opening a sampling cartridge (e.g., breaking the ends of an XAD glass tube) in the field followed by normal labeling and sample transport (i.e., along with the samples).

H. Laboratory, Trip and Field Spikes

The *laboratory, trip and field* spikes are prepared, extracted and analyzed at the same time and they are generally all spiked at the same level. The *laboratory* spikes are immediately placed in the laboratory refrigerator (or freezer) and kept there until extraction and analysis. The *trip* spikes are kept in the freezer until transported to the field. The trip spike samples are kept on dry ice in an ice chest (the same one used for the samples) during transport to and from the field and at all times while in the field except for trip spike sample log-in and labeling. The *field* spikes are stored and transported in the same way as the trip spikes. However, field spikes are obtained by sampling ambient air through the spiked cartridge at the same environmental and experimental conditions as those occurring at the time of the study.

Ambient field spikes are collocated (same location, flow rate and sampling period) with a sample collected at the urban background sampling site (to minimize background concentrations). **Ambient** field spikes are normally prepared at a level of approximately 2 times the EQL, or at a level representative of ambient concentrations.

Application study field spikes are collocated with the background samples collected at the four sides of the application site (i.e., one background and one field spike per side). **Application** field spikes are normally prepared at a level close to expected air concentrations. Field spike results are corrected by subtracting the amount of pesticide residue found in the collocated, unspiked sample before calculation of residue recoveries.

I. Transportation of Samples

All samples will be capped, placed in a sample container (e.g., culture tube or zip-lock bag) and placed in an ice chest on dry ice immediately following sample collection and labeling. The samples will remain on dry ice until transferred to the laboratory and will then be stored in the lab refrigerator or freezer. Any special handling procedures will be identified during the method validation and will be outlined in the SOP.

J. Meteorological Station Calibration

Meteorological station calibration procedures will be performed as specified by the ARB manual, "Air Monitoring Quality Assurance, Volume II, Standard Operating Procedures for Air Quality Monitoring."

K. Preventive Measures

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

V. Analysis

Method development and analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, a systems audit may be performed, upon request, by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis per a pesticide project. After a history of competence is demonstrated, an audit prior to each pesticide project is not necessary. However, during each pesticide project, the spiked samples discussed above should be provided to the laboratory to demonstrate accuracy and precision. These spiked samples will be prepared by qualified ARB laboratory staff.

If using GC/MS, isotope dilution is the recommended method for quantitation. Isotope dilution is where the isotope analog of the target compound is spiked to the sample prior to sample preparation. The internal standard goes through the same sample and analytical steps that the target analyte does thus compensating for losses during sample preparation and instrument variability during analysis. When no isotope is available an internal standard is recommended. An internal standard is spiked to the sample just prior to analysis. The internal standard compensates for instrument variability. If no suitable internal standard is found then an external standard method may be used.

VI. Analytical Quality Control Procedures

A. Mass Spectrometer Tuning (if MS is used)

A daily tune shall be performed using perfluorotributyl amine (PFTBA). The MS should be calibrated to optimize the MS for the mode of operation and type of pesticide analyzed. Documentation and performance criteria shall be specified in the standard operating procedure. A record of the tune for each batch should be kept on file. A daily tune must be performed prior to the analysis of an analysis sequence and every 24 hours during an analysis sequence. If longer intervals between tunes are used, then the stability of the MS must be demonstrated during the method development phase and approved prior to the sample analysis.

B. Calibration

Initial Calibration

At the beginning of method development an initial multi-point calibration curve is performed to demonstrate the calibration range of the pesticide analyzed. A typical multi-point calibration consists of 5 different concentrations with a single replicate at each concentration. The calibration range usually should not exceed 40:1 with the lowest level standard at the EQL unless there is no need to measure values as low as the EQL. Depending on the linear range of the analyte, multi-points with other than 5 levels may be used although a multi-point with less than 3 levels is not permitted. Typically a linear calibration is preferred although a dynamic range using a quadratic is acceptable. For quadratic calibration curves quantitation can only be performed within the calibration range. Sample above the calibration curve must be diluted into the calibration range and reanalyzed.

Daily Calibration

Prior to the analysis of a set of samples a calibration must be performed. This calibration is called the daily calibration. The daily calibration is either a multi-point calibration or a mid-point calibration. The mid-point calibration consists of a single calibration at the mid-point of the initial multi-point calibration curve. If the mid-point is within a prescribed range (i.e., within +/- 20% of the original calibration) as determined from the initial calibration then the original initial calibration is still considered valid and the response is replaced. If the mid-point calibration is outside that range then another multi-point calibration must be performed. A calibration check at the same level is also run. If the mid-point calibration and the midpoint calibration check are within a prescribed range (i.e., +/-20%) of each other then analysis can begin. If the calibration check is outside the specified range then the problem must be rectified before analysis can begin.

C. Reagent Blanks.

A reagent (solvent) blank is performed at least for every batch of reagent used. The reagent blank uses the same solvent that was used for the sample preparation. The blank should be free of interferences. If low level contamination of the pesticide residue is found in the reagent blank (as may happen when using isotope dilution), then a reagent blank will be performed before analysis of each batch of samples. A reagent blank must be analyzed after any sample which results in possible carry-over contamination.

D. Laboratory Control Blank.

A laboratory blank is run with each batch of samples. A laboratory control blank (blank sampling media, e.g., resin cartridge or filter) is prepared and analyzed by the same procedures as used for field samples. Laboratory blank results must be no higher than 20% of the lowest value reported.

E. Laboratory Control Spike.

A laboratory control spike (LCS) is a resin cartridge spiked (at the level of the midpoint of the daily calibration runs) with a known amount of standard. The LCS is prepared and analyzed the same way as the samples. Two LCS are performed for each batch of samples. Laboratory control spikes need to be within 40% ($100 \times \text{difference/average}$) of each other and have recoveries that are $\pm 30\%$ of the theoretical spiked value. If in the method development stage it is found that the differences or recoveries are larger, then they must be approved by ARB before the analysis can begin.

F. Calibration Check Samples.

A calibration check sample (CCS) is a mid-point standard run after every tenth sample in an analysis set. The purpose of the CCS is to ensure sample drift is within specified values. The CCS sample must be within $\pm 25\%$ of its theoretical value. If the standard is outside this range, then the samples associated with that calibration check sample must be reanalyzed. If in the method development stage it is found that the CCS variation is greater than 25%, then the percent variation limit used for the method must be approved by the ELB Branch Chief before the analysis can begin.

G. Duplicate Analysis.

A duplicate analysis is a sample analyzed in duplicate as a measure of analytical precision. Every tenth sample of an analysis set must be run in duplicate.

H. Standard Operating Procedures

Analytical methods must be documented in a Standard Operating Procedure (SOP) before monitoring begins. The recommended format for the SOP is provided in Appendix III. The SOP will include a discussion of all of the procedures outlined above in this section. The SOP will also include a summary of method development results as outlined in Section III above.

VII. Sampling and Analysis Protocol

Prior to conducting any pesticide monitoring, a sampling and analysis protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.
4. Description of the analytical method (SOP included if possible).
5. Tentative test schedule and expected test personnel.
6. Safety information specific to the pesticide monitored.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Procedures which apply to all sampling projects include: (1) sample log sheets (APPENDIX I), (2) chain of custody forms (APPENDIX II), (3) sunlight and rain shields for sample protection during monitoring, (4) sample storage in an ice chest on dry ice until delivery to the laboratory, (5) trip blanks and, (6) laboratory, trip and field spikes. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

VIII. Final Reports and Data Reduction

The mass of pesticide found in each sample should be reported along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as $\mu\text{g}/\text{m}^3$ (microgram per cubic meter) or ng/m^3 (nanogram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units at conditions of 1 atmosphere and 25 °C. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume.

The final report should indicate the dates of sampling as well as the dates of laboratory receipt, extraction and analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring studies are sent to the Department of Pesticide Regulation, the Office of Environmental Health Hazard Assessment, the Department of Health Services, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering and Laboratory Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building)

including the locations Range/Township/ Section. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described. Information will be collected for each site and reported to DPR regarding; 1) the proximity of the each sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average ("detected" results are factored in as $(MDL+EQL)/2$, <MDL results are factored in as $MDL/2$), total number of samples, number of samples above the estimated quantitation limit (EQL), number of samples "detected" and the number of samples below the MDL. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX IV). Meteorological data will be reported in 15 minute averages for the application site during the monitoring period. Meteorological and pesticide air concentration data will also be summarized as wind roses for each application sampling period. The raw meteorological data file will also be transferred to DPR on 1.44 mb floppy disk.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, collocated etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

APPENDIX I
SAMPLE FIELD LOG BOOK

APPENDIX II
CHAIN OF CUSTODY FORM

APPENDIX III

ANALYTICAL STANDARD OPERATING PROCEDURE FORMAT

ELEMENTS TO BE INCLUDED IN LABORATORY STANDARD OPERATING
PROCEDURES FOR PESTICIDE AIR ANALYSIS

Engineering and Laboratory Branch
Air Resources Board
April 1999

I. SCOPE

- A. Description of scope and detection limits of pesticide(s) to be analyzed.
- B. Documents and references upon which method is based.
- C. Definitions of any special terms must be given.

II. SUMMARY OF METHOD

- A. General description of sampling and analytical procedure. Enough information should be included for an experienced analyst to readily recognize the principles of operation.

III. INTERFERENCES AND LIMITATIONS

- A. Comments made here should cover both analytical and sampling problems, known and potential.

IV. EQUIPMENT AND CONDITIONS

- A. INSTRUMENTATION: As specific a description as possible. Any modifications or improvements of the basic system must have an accompanying schematic. For chromatographic analysis list columns, flow rates, temperatures, detectors, amplifier ranges and attenuations, sample volumes, etc.
- B. AUXILIARY APPARATUS: Provide a description of the function and operating conditions. Include a description of the sampling equipment if the equipment is specific to this method. For example, "Vacuum pump, ACME Model 62, capable of maintaining a 1 CFM Air Flow at 10" vacuum."

V. REAGENTS AND MATERIALS

- A. Provide a list of all reagents used and specify purity and/or grade.
- B. Describe preparation of any special reagents for analysis and sampling.
- C. Specify composition, preparation, and concentrations of stock, intermediate, and working standards.
- D. Describe in detail any necessary safety precautions for handling and disposition of chemicals.

VI. PROCEDURES

A. FIELD SAMPLING TECHNIQUES

1. Refer to appropriate Field Sampling S.O.P. for exact details of sampling, chain of custody and sample identification procedures.
2. Describe equipment used.
3. List sampling conditions: materials, flow rates, etc.
4. Describe any potential problems and limitations, with means of controlling such problems.
5. Describe any methods used to split samples for other types of analyses, if necessary.

B. LABORATORY SAMPLE PREPARATION/PRETREATMENT TECHNIQUES

1. Describe (or refer to an appropriate section of a Laboratory Quality Control Manual) a protocol for sample log-in procedures, including document control and sample examination for damage. Any possible hazards due to toxic or flammable chemicals must be clearly identified. Any sample storage requirements, such as immediate refrigeration or protection for light must be noted.
2. Describe any methods used for preconcentration, dilution clean-up filtration, extraction, concentration, etc., after the sample is received from the field.

C. ANALYSIS

1. Describe as clearly as possible the exact instrument configuration and set-up techniques
2. Describe analysis blank and calibration procedure with associated limits on precision and accuracy. Describe analysis of Control Samples and limits of the resulting data. Describe steps taken in an "out-of-control" situation. Specify the format and location of recorded calibration and Control Sample data.
3. Describe sample analysis. Description must include an example of expected data (for example, a sample chromatogram with all components of interest labeled).
4. Give calculation procedures for results. Describe data recording and data submittal.

VII. PERFORMANCE CRITERIA

- A. Describe frequency of duplicate analyses, spikes, field blanks, and acceptable limits of each.
- B. Describe frequency of multiple standard analyses to check method linearity and detection limit.
- C. If confirmatory method is used, refer to specific S.O.P.

VIII. METHOD VALIDATION

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, method detection limit and estimated quantitation limit. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain. The following data will be included in the SOP.

- A. A table describing linearity (correlation coefficients), accuracy (method bias), precision (standard deviations at all levels analyzed), and detection.
- B. Data on sampling efficiencies, stability, pertinent breakdown products, break through volumes and desorption efficiencies.
- C. Data on storage stability and conditions for samples and standards.
- D. References to quality assurance information derived from published and/or interlaboratory sources if available.

APPENDIX IV
APPLICATION CHECKLIST

APPLICATION CHECKLIST

1. Pesticide:
2. County:
3. Crop:
4. Field Address:
5. Field Location (R/T/S):
6. Field Size (acres):
7. Contact Person:
8. Background Monitoring Period:
9. Target EQL Met?:
10. Product Applied:
11. Application Rate:
12. Comments on Tank Mix:
13. Method of Application (ground, air, irrigation, injection, tarping etc.):
14. Start of Application:
15. End of Application:
16. Pattern of Application: (e.g., east to west):
17. Weather Conditions:
18. Met Station Location (and elevation):
19. Any Other Applications in Area:
20. Sampler Elevations:

- Camera pictures of each sampler from all 4 directions
- Camcorder video of each sampler in relation to field and surroundings
- Rotameter #s logged
- Check dimensions of field with known acreage (43560 ft²/acre) & compare sides
- Crops around field labeled on diagram

APPENDIX V

FLOW CONTROLLER CALIBRATION FORM

FLOW CONTROLLER; 1-POINT FLOW CALIBRATION SHEET

Project: _____ Pre: _____ Post: _____ Project #: _____ Date: _____

Desired Flow Rate: _____ Calib. by: _____
 _____ (name)

BUBBLEMETER READINGS

Controller ID: _____
 Controller Set: _____
 -Readings: _____
 -Readings: _____
 -Readings: _____
 Average: _____
 Deviation: _____

Controller ID: _____
 Controller Set: _____
 -Readings: _____
 -Readings: _____
 -Readings: _____
 Average: _____
 Deviation: _____

Average of Averages _____ :

PROCEDURE

1. Set-up sampler as if to collect sample, including filled sample cartridge.
2. Set flow controller to achieve desired flowrate and record controller setting.
3. Observe and record Bubblemeter flow (on form or direct to floppy - Change File name).
4. Reset to zero. Then repeat step 3 two more times.
5. Calculate the average of 3 readings.
6. Repeat steps 1 thru 5 for each Rotameter.
7. Average of Averages and Deviation automatically calculated. Replace any Rotameters that deviate by 10% or more from the Average of Averages.
8. QA Section will get a copy for comparison with their results for the same setups.

Attachment II

**Standard Operating Procedures for the
Analysis of Chlorothalonil in Ambient Air**

California Environmental Protection Agency



**Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division**

Draft

**Standard Operating Procedure
Sampling and Analysis of 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile
(Chlorothalonil) in Ambient Air**

May 17, 2002

Approved by:

**Russell Grace, Manager
Special Analysis Section**

1. SCOPE

This is a gas chromatography/mass selective detector (GC/MSD) method for determination of 2,4,5,6-tetrachloro-1,3-benzenecarbonitrile (chlorothalonil) from ambient air samples. The method was adapted from the California Air Resources Board Standard Operating Procedure for the Analysis of Chlorothalonil in Ambient Air dated January 1992.

2. SUMMARY OF METHOD

Ambient air is collected on XAD-2 cartridges. Sample cartridges are stored at 4 degrees centigrade (°C) prior to extraction. Samples cartridges are extracted using methylene chloride and an ultrasonic bath. Samples analysis is performed using a GC/MSD in the selected ion-monitoring mode (SIM). Sample analysis and quantitation uses the internal standard Aldrin ¹³C₄, which is added to each extract prior to GC/MSD analysis. Estimated quantitation levels for this method range from approximately 3 nanogram per cubic meter to 300 nanogram per cubic meter (ng/m³) prior to sample dilution.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 cartridges that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting pesticide components may cause significant contamination of the analytical equipment. Both a system blank and extraction blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Hewlett Packard 5890 Series II gas chromatograph:

Detector: 300° C

Injector: 250° C

Column: Restek Rtx-5MS, 30 meters, 0.32 mm i.d., 0.25 µm film thickness, or equivalent

Temperature Program:

Initial Temperature: 50° C for 1 minute

Ramp 1: 50 to 175° C at 50° C per minute hold for 1 minute

Ramp 2: 175 to 250° C at 25° C per minute hold for 0 minutes

Final Ramp: 250 to 300° C at 50° C per minute hold for 3 minutes

Splitter opens at 1.0 minute
Carrier gas: Helium at 1.5 ml/minutes constant flow mode

Hewlett Packard 5972 mass selective detector:

Acquisition Mode: SIM

Masses: 5 minutes to 7.45 minutes 264, 266, and 268 for chlorothalonil

Masses: 7.45 to 12 minutes 265, 267, 269 for Aldrin ¹³C₄

Tune File: PFTBA Autotune at maximum sensitivity

B. Auxiliary Apparatus

XAD-2 cartridges (SKC cat # 226-30-6) or equivalent

Glass amber vials, 2-ml capacity with septum caps.

Sonicator

C. Reagents

Hexane (B&J brand pesticide grade or equivalent)

Acetone (B&J brand reagent grade or equivalent)

Chlorothalonil 98.5% pure (Chem Service Inc. PS-1020)

Aldrin ¹³C₄ 99% pure, 100 µg/ml (Cambridge Isotopes Laboratories Inc. CLM-3347)

D. Gases

Compressed Helium Grade 5 or better

5. SAMPLE COLLECTION

- a) Samples are collected in the field with a maximum flow rate of three (3) liters per minute (lpm).
- b) After collection the samples are placed in a glass tube and stored in a cooler at 4° C or less until extracted.
- c) According to EPA method TO-10A the cartridges should be extracted within seven (7) days. An analyte specific holding time should be determined. See section 8F for storage stability summary.

6. SAMPLE EXTRACTON

- a) Prepare a method blank and laboratory control sample (LCS) cartridge with every batch of field samples not to exceed twenty (20) samples in an analytical batch.
- b) Spike the LCS with 20 ng of Chlorothalonil prior to extraction.

- c) Carefully score and break the XAD-2 cartridge just above the glass wool plug and spring on the primary section.
- d) Remove the glass wool plug using forceps.
- e) Pour the XAD-2 resin from the primary section into the glass vial.
- f) Carefully score and break the XAD-2 cartridge just above the glass wool plug on the secondary section.
- g) Carefully using 3.0 ml of methylene chloride rinse the inside of the primary section into the glass vial. Cap tightly.
- h) Retain the secondary section for later analysis to check for breakthrough.
- i) Place all the vials in an ultrasonic bath and sonicate for 30 to 45 minutes.
- j) Filter the extract through a 2.7-micron filter into a second vial and store at 4°C until ready for analysis.

7. ANALYSIS OF SAMPLES

- a) Transfer 1.0 ml of the sample extract to a 1.5-ml amber autosampler vial. Add 30 ng of internal standard (Aldrin $^{13}\text{C}_4$). Sample extract is now ready for analysis.
- b) Prior to sample analysis perform a PFTBA autotune using the maximum sensitivity tune option. Evaluate the tune using the criteria listed in Appendix 1. If the tune does not meet the criteria, retune. If the tune continues to be unsuccessful, perform corrective maintenance and then retune.
- c) Perform an initial calibration curve using concentrations at or near the EQL to approximately 30 times higher. At least 5 points must be analyzed to establish a calibration curve. Appendix 2 lists the concentrations used when the EQL is approximately 3 ng/m^3 .
- d) Prepare a sample sequence for the GC/MSD. The sequence should include a continuing calibration verification standard (CCV), and a system blank, for every 10 samples analyzed. If this batch of samples includes a method blank and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.
- e) Because of the nature of the XAD-2 cartridge, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every 5 to 10 sample or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.
- f) A 2- μl injection volume will be used for all analyses.
- g) Review and edit the quantitation reports as needed.
- h) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.

- i) The final results will be adjusted by an appropriate dilution factor and reported in ng/ml.
- j) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc (ng/m}^3\text{)} = \frac{\text{Extract Conc (ng/ml)} \times 3 \text{ ml}}{\text{Air Volume Sampled (m}^3\text{)}}$$

- k) Given instrument sensitivity and a maximum sample of 4.2 m³ the EQL for this method will be approximately 3 ng/m³.

8. QUALITY ASSURANCE

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. The low, mid and high concentrations were 7, 37 and 88 ng/ml, respectively.

B. Linearity

A 6-point calibration is performed. Calibration standards ranging from at or near the EQL to approximately 30 times higher are used for Chlorothalonil. The results are used to calculate calibration curves using linear or quadratic regression. An r² of 0.995 or higher is required for an initial calibration to be acceptable. See Appendix 2 for an example calibration curve. A CCV will be run at the start of each analytical batch, and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25% of the actual value.

C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicates of a low-level standard, the MDL and EQL for Chlorothalonil are calculated as follows:

$$\text{MDL} = 3.143 \cdot \text{STD}$$

$$\text{EQL} \approx 5 \cdot \text{MDL}$$

Where STD equals the standard deviation of the calculated results for the seven replicate spikes. The calculated MDL for Chlorothalonil is 0.6432 ng/ml. The EQL for Chlorothalonil using a three-ml extraction volume and a sample collection volume of

4.2 m³ is 2.30 ng/m³. Results above the EQL are reported to three significant figures. Results below the EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (non-detect).

D. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The LCS stock standard should come from different source or lot than the daily calibration standards. The analytical value of the LCS must be within three standard deviations of it's historical mean. If the LCS is outside of limits then the samples in the analytical batch must be reanalyzed.

E. Collection and Extraction Efficiency (Recovery)

The target compound at a low (20.2 ng/ml) and high (101 ng/ml) level are spiked on XAD-2 cartridges, three at each concentration. The spiked cartridges are placed on field samplers with airflows of 3 Lpm for 24 hours. The samples are extracted with methylene chloride and prepared as described in section 7. The average percent recovery should be $\pm 20\%$ of the expected value. The average recoveries were 88% and 89% for the low and high levels. No breakthrough occurred at the levels tested.

F. Storage Stability

Storage stability studies were done in triplicate for 50 ng Chlorothalonil spikes on XAD-2 cartridge primary sections over a period of 21 days.

G. Breakthrough

Three XAD-2 cartridges were spiked with 1 μg of Chlorothalonil to evaluate analyte breakthrough. Air was collected at approximately 3 Lpm for 24 hours. Chlorothalonil was not detected in the back section of the XAD-2 cartridges. Average recovery for Chlorothalonil from the front sections was 92%.

H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Appendix 1

Autotune Criteria

A maximum sensitivity autotune should be performed on the detector each day prior to sample analysis. The autotune report should be evaluated for the following:

1. Any unusual change in the EM voltage
2. Peak width for all tune masses should be between 0.4 amu and 0.6 amu.
3. The relative abundance of tune mass 219.0 should be greater than 25% of tune mass 69.0
4. Isotope abundance ratio for tune mass 70.0 should be between 0.54% and 1.6%; isotope abundance ratio for tune mass 220.0 should be between 3.2% and 5.4%.
5. Masses 28 and 18 should be evaluated to check for air leaks in the system.

If autotune criteria are not met the system should be evaluated for problems. After the system problems are corrected the detector should be autotuned prior to sample analysis. Autotune reports should be filed in the instrument autotune folder.

Appendix 2

Calibration Standard Preparation for Chlorothalonil

The certified neat standard used for calibration was purchased from Chem Service Inc., West Chester, Pennsylvania and has the following specification:

Lot No:	276-95A
Expiration date:	February 2007
Chlorothalonil	98.5% pure (solid)

A stock standard with a concentration of approximately 1-milligram (mg) per ml was prepared by weighing 25 mg of chlorothalonil into a 25 ml volumetric flask and bringing to volume with methylene chloride.

Using a serial dilution technique the following calibration standards were prepared in methylene chloride: 3.04, 6.07, 15.18, 25.30, 43.01, 60.72, 91.08, and 121.4 ng/ml.

A minimum of six standards was used to generate the calibration curve, with the standard at 3.04 ng/ml being the low point.

All standard and sample injection used a volume of 2 μ l.

Initial calibration curve acceptance requires an r^2 of at least 0.995.

Attachment III

Pesticide Sampling Procedures for Adsorbent Tubes
For Ambient Monitoring Studies

Pesticide Ambient Sampling Procedures For Adsorbent Tubes

Overview:

- Collect samples over the 6-week sampling period; 24-hour samples; 4 sampling periods per week per site; 5 sampling sites plus an urban background site (ARB Fresno station).
- Collect a collocated sample from each site each Wednesday,
- Submit 1 trip blank per week,
- With the trip blank there normally will be 31 samples collected per week,
- 4 field spikes will be run at the ARB site (time collocated exactly with the ambient sample. The field spikes will be distributed over the monitoring period (e.g., 1 per week on weeks 1, 3, 4, and 6). A trip spike will also accompany each field spike. These field and trip spikes will be logged in and shipped along with the regular samples. The field and trip spikes will be kept on dry ice during transport to and storage in the field.
- All samples are stored either in an ice-chest on dry ice or in a freezer,
- The field log sheet is filled out as the sampling is conducted. The originals stay in the field binder. Please include a copy with sample shipments. All QA samples must be logged onto the log sheet,
- The chain of custody (COC) forms are filled out prior to sample shipment; the originals are shipped with the samples; make and retain copies if desired (not necessary),
- (Disregard if samples are driven back to Sacramento) The samples are shipped by UPS, next day delivery, to 13th and T. This is normally done each Monday. The original chain of custody sheets must accompany the samples. The samples are shipped on 5 pounds of dry ice. Review the COCs and log sheet to insure that all documentation is correct and that the appropriate QA samples have been included.

Sampling Procedure:

Materials that will be needed on the roof to conduct the sampling include:

- Clip board with log sheets
- pencils/pens
- sample labels
- sample cartridges
- end caps
- plastic test tubes
- 0 to 5 sLpm mass flow meter (MFM) with battery

Figure out your route for sampling the six locations and try to keep this the same throughout

the study. In general, try to make each sampling period 24 hours; e.g., if start time is 11:10 then end time should be 11:10. (round off to the nearest 5 minutes.) The sample period may not always be exactly 24 hours, but that is the target time frame.

Preparation and Set-up

On the way to the first site, plug the MFMs into the batteries. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFMs plugged in until the last sample for the day is taken; then unplug for the night to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Upon arrival at the site, check in if needed. Fill out the sample labels for that site. I suggest a backpack and/or fannypacks to carry the stuff to the roof.

Securely attach one adsorbent sample cartridge to the sampling tree. **MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.**

Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the 5 slpm MFM, set the flow rate exactly to 3.0 slpm.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, any comments, and the weather conditions.

Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFMs; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each day (6) in a zip-lock bag and place on dry ice in a cooler or in a freezer. While driving the route the collected samples need to be kept on dry ice.

Collect the collocated (duplicate) samples from each site every Wednesday. These should be started and stopped at the same times as the regular samples.

Collect a trip blank (TB) once per week while at one of the field sites. It doesn't matter

which site (or which day), but note it in the comment section of the log sheet. The TB is collected by breaking the ends off of a tube, capping and labeling as usual, and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment IV

**Pesticide Sampling Procedures for Adsorbent Tubes
For Application Monitoring Studies**

Pesticide Adsorbent Tube Sampling Procedures For Application Studies

Overview:

- Collect samples according to the schedule in Table 1 of this protocol.
- Collect 4 background samples, one each from the mid-field sampling positions.
- Collocate 1 field spike with each of the 4 background samples.
- Collect a collocated sample from the downwind site for all sampling periods (except the background period).
- Submit 1 trip blank.
- The number of samples collected during the study will vary based on the time and duration of the application (refer to Table 1 of the protocol).
- All samples are stored after sampling either in an ice-chest on dry ice or in a freezer. The trip and field spikes are also kept on dry ice before use in the field.
- The field log sheet is filled out as the sampling is conducted. All QA samples must be logged onto the log sheet.
- The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples. Make and retain copies if desired (not necessary).

Sampling Procedure:

Materials that will be needed to conduct the sampling include:

- Clip board with log sheets
- pencils/pens
- sample labels
- sample cartridges
 - end caps
 - plastic test tubes
- zip-lock bags
- 0 to 5 sLpm mass flow meter (MFM) with batteries
- ice chest
- dry ice

Figure out the route for sampling the 8 locations, and keep this the same throughout the study.

Preparation and Set-up

On the way to study site, plug the MFM into the battery. It takes the MFMs about

10 minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge the batteries regularly.

Securely attach one adsorbent sample cartridge to the sampling tree. **MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.**

Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the appropriate MFM, set the flow rate exactly to 3.0 slpm.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including log #, start date, time, start counter reading, leak check OK, MFM Serial #, any comments, and the weather conditions.

Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each period in a zip-lock freezer storage bag and place on dry ice in a cooler.

Collect a trip blank (TB) by breaking the ends off of a tube, capping and labeling as usual, and storing along with the rest of the samples. Log the TB into the log sheet.

Make sure that the trip spikes are labeled and logged-in.