

# **APPENDIX A**

## **Sampling Protocol**



*California Environmental Protection Agency*

**AIR RESOURCES BOARD**

Monitoring and Laboratory Division  
Air Quality Surveillance Branch

**Sampling Protocol for Propanil Application Study**

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The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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## 1.0 Introduction

The California Department of Pesticide Regulation's (DPR) memorandum dated January 4, 2008, "Proposed Toxic Air Contaminant Monitoring For 2008", requests that the Air Resources Board (ARB) conduct a comprehensive air monitoring study for propanil during an aerial rice field application.

This study will consist of up to eight sampling periods; a background sample period, an application sampling period, a post application sampling period ending one (1) hour before sunset, three (3) overnight sampling periods and two (2) daytime sampling periods. The background sampling period will be performed for twelve to twenty-four hours prior to application of propanil onto a rice field. The application sampling period will begin thirty minutes prior to the application of propanil onto the rice field. There will be a total of 100 sample filters (6 backgrounds, 4 field spikes, 1 trip spike, 1 trip blank, 77 application and 11 spares) and 18 sample XAD-4 sorbent tubes (2 backgrounds, 1 trip blank, 14 application and 1 spare).

Background sampling will be started the day before the application and filters collected approximately one (1) hour prior to the start of the application. Four background samplers and four collocated field spikes on each side of the field will sample for twelve to twenty-four hours.

## 2.0 Project Goals and Objectives

The primary goal of this monitoring project is to measure the concentrations of propanil in the ambient air during and after application.

To achieve the project goal, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.
2. Appropriate application of sampling/monitoring equipment to determine propanil concentrations in the air adjacent to the application.
3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.
4. A final report containing all relevant information, data and results gathered in the course of MLD's activities during the planning and execution of this project.

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#### 4.0 Study Location

A propanil application is planned for the week of June 16 through 20, 2008 in the county of Colusa. There is no address for the field, but it lies between Dunnigan and Grimes just south of White Road.

#### 5.0 Study Design

The propanil sampling schedule is listed in Table 1 (Sampling Periods). For June 2008 the approximate sunrise time will be 0440 PST and the approximate sunset time will be 1940 PST.

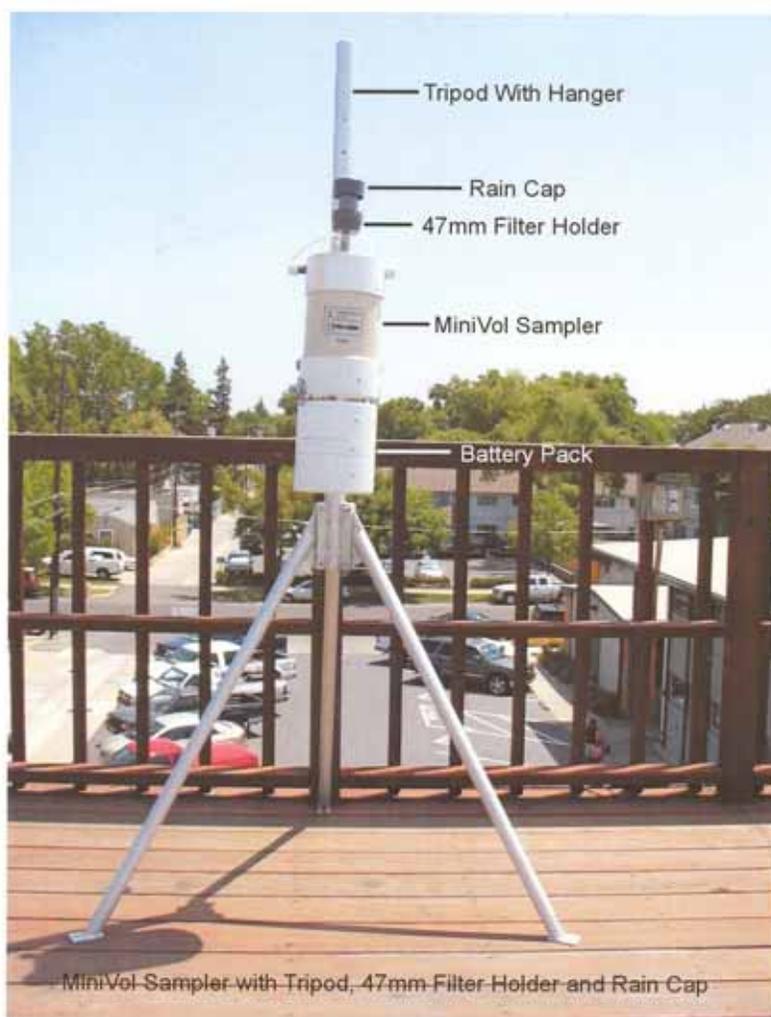
**TABLE 1: SAMPLING PERIODS**

<b>Sample Period Begins</b>	<b>Sample Duration/Time</b>
Background (pre-application)	Minimum 12-24 hours
Application	Start of application until 1 hour after end of application
End of Application (post application)	1 hour after end of application until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise (1 <sup>st</sup> overnight sample)
1 hour after sunrise	Daytime until one hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise (2 <sup>nd</sup> overnight sample)
1 hour after sunrise	Daytime until one hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise (3 <sup>rd</sup> overnight sample)

- a) Background sampling will start the day before the application for a minimum of twelve hours, but no more than twenty four hours. The background samples will be removed at least one (1) hour prior to the start of the application. The background samplers will be located close to midway on each of the four sides of the field with four (4) field spikes collocated next to each site. The field spike will be spiked with a concentration of 1.0 ug/m<sup>3</sup> of propanil. The total number of background and spiked sample filters will be eight (8).
- b) The propanil application sampling will consist of at least six sampling periods. The application sampling period will start approximately thirty minutes prior to the arrival of the plane or helicopter. It will continue until thirty minutes after the application is complete. A post application sampling period will immediately start and then end one (1) hour before sunset. The rest of the study will consist of three (3) overnight sampling periods and two (2) daytime sampling periods. Each overnight sampling period will start one (1) hour prior to sunset and end one (1) hour after sunrise. Each daytime sampling period will start one (1) hour after sunrise and end one (1) hour before sunset.
- c) There will be eight (8) sampling sites around the rice field. For a square field, four (4) sites will be located at each corner and four (4) sites will be located

midway on each side. The estimated downwind site will have a collocated sampler within one (1) meter of the regular sampler. All sampler intakes will be 1.7 meters (67 ±6 inches) above the ground. Samplers will be placed 20 ±10 meters (33 to 98 feet) from the edge of the field.

- d) Each air sampler will consist of an AirMetrics MiniVol Sampler, a filter holder with a 47mm quartz filter in its cassette and a rain cap. The MiniVol is powered by a 12 VDC gell cell battery pack. After each sampling period the used battery will be replaced with a newly charged battery. Flows will be set at 3.0 lpm and the average of the start and stop flows shall be 3.0 lpm ±20%. Figure 1 (MiniVol Sampler) demonstrates an assembled sampler.



**FIGURE 1: MINIVOL SAMPLER**

- e) In order to reduce direct exposure to ARB staff during the pesticide application period all samplers will begin a minimum of thirty minutes prior to the start of the application. At the end of each sampling period the following general procedure will occur at each site; Flows will be verified, documentation completed, all filter cassettes will be removed, the battery replaced, a new filter cassette installed

and flows adjusted if necessary. Field notes and observations will be recorded (such as propanil application flow rate and total amount of propanil applied).

- f) Meteorological data will be collected using a Met One Instruments' AutoMet Digital Meteorological Monitoring System located on a trailer with a crank up tower. The AutoMet will be located no closer than twenty meters from the edge of the field being monitored. The meteorological sensors will be installed between 5.9 and 6.9 meters above the ground. The AutoMet station will continuously measure and record 5 minute averages for wind speed, wind direction, ambient temperature and percent relative humidity throughout the background and application sampling periods.
- g) The MLD will provide DPR with a final report containing all relevant information, collected data and analytical results gathered during the course of the study.
- h) Some questions came up as to whether filters would collect all of the propanil available. It was decided to run two each collocated samplers at the NWC and the SEC sites with an XAD-4 sorbent tube following the quartz filter. As the Mini-Vols cannot maintain flow through this media MLD will be using battery powered pumps with a metering valve to control the flows. The XAD-4 sorbent tubes will have both ends capped, a label attached over the breakthrough section and stored on dry ice till delivered to the laboratory. Analysis will be performed by the California Department of Food and Agriculture laboratory.

## **6.0 Sampling and Analysis Procedures**

Special Purpose Monitoring Section (SPM) staff will hand-carry filters to and from MLD's laboratory in Sacramento, and to and from the sampling location. The filters will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample. At the end of the each sampling period, all filter cassettes will be removed from the sampler, placed in a cassette protective case, labeled, and secured in a dry ice cooler.

At each sampling site, the operator will replace the battery on each MiniVol sampler with a charged battery; install a new 52 mm filter cassette with filter installed and a rain cap on the tripod. The filter field log sheet shall be filled out along with the filter cassette case label. Prior to any sampling, flows will be set to  $3.0 \pm 0.1$  lpm. At the start of each sampling period, the MiniVols will be manually turned on and the start date, time, elapsed time meter reading and flow will be recorded. At the end of each sampling period, the flow will be measured, the MiniVol manually shut off and the following recorded on the filter field log sheet; end date, time, elapsed time meter reading and flow.

Sampling will occur as scheduled unless ambient conditions at the start include rain or instantaneous gusts of wind over 10 miles per hour. All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply SPM with one hundred (100) quartz fiber filters installed in a serialized Delron 52 mm cassette placed inside a protective case (6 backgrounds, 4 field spikes, 1 trip spike, 1 trip blank, 77 application and 11

spares) and 18 sample XAD-4 sorbent tubes (2 backgrounds, 1 trip blank, 14 application and 1 spare). A label will be affixed to the top of the filter cassette case, initiated by the lab, identifying the filter by the cassette SN. Spiked filters and other QC filters will be identified. The NLB will perform analyses for propanil on all collected samples and report results to SPM in electronic format (Excel) and hardcopy.

Laboratory analysis will be performed in accordance with the draft standard operating procedures, "Standard Operating Procedure for Analysis of 3,4-Dichloropropionanilide (Propanil) in Application and Ambient Air Using Gas Chromatography/Mass Selective Detector". This analytical method currently has a Method Detection Limit (MDL) of 0.0019 micrograms per milli-liter ( $\mu\text{g}/\text{mL}$ ). The laboratory's operating procedure is included in this Protocol as Appendix A.

The following filter validation and analytical quality control criteria will be followed during pesticide analysis.

1. **Sample Hold Time:** Sample hold time criteria will be consistent with the laboratory's operation procedure stated four (4) weeks.
2. **Duplicate Analysis:** Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.
3. **Method Detection Limit (MDL):** Sample analysis results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions.
4. **Analytical Linear Range:** Any analytical result greater than 10% of the highest calibration standard shall be diluted and reanalyzed within the calibrated linear range.

## 7.0 List of Field Equipment

<u>Quantity</u>	<u>Item Description</u>
(1)	Met-One Auto met portable meteorology system consisting of a data logger and calibrated sensors measuring 5 minute averages for wind speed, direction, ambient temperature, and relative humidity.
(1)	Measuring Wheel
(1)	200 ft measuring tape
(1)	Tripod and compass
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Aalborg mass flow meter 0-5 lpm
(82)	Quartz filters in cassettes and cases with labels (4 backgrounds, 4 field spikes, 1 trip spike, 1 trip blank, 63 application and 9 spares)
(10)	MiniVol sampler, each equipped with a filter holder and rain cap.
(24)	Battery for MiniVol with case and chargers.
(10)	Tripod, adjustable for mounting MiniVol samplers.

## 8.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST) traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the MiniVol's flow controllers will be measured using certified mass flow meters with a range of 0-5 liters per minute.

The metrological sensors will be calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link.

<http://arb.ca.gov/airwebmanual/amwmn.php?c=5&t=sop>

Each filter sample cassette will be assigned a serial number for sample tracking. The filter's cassette case will have a label where the following data will be recorded; SN of cassette, sample name, start and stop date and time and the operator's initials.

Collocated (side-by-side) air samplers will operate at one site during the study period. This collocated site will be located at the estimated downwind site.

**Field Spike (FS):** Four (4) field spikes will be prepared by the laboratory by injecting filters with a known volume and concentration of propanil. The field spike filters will be coupled with a MiniVol sampler and will be collocated next to the background samplers at the field's sides. The field spikes will sample for a minimum of twelve hours to a maximum of twenty four hours. The background is scheduled for the day before the scheduled propanil application.

**Trip Spike (TS):** A trip spike will be prepared by the laboratory by injecting a filter with a known volume and concentration of propanil and should be the same level as the field spikes. The trip spike filter accompanies the sample filters from the lab to the field but is not sampled.

**Trip Blank (TB):** A trip blank will be prepared by the laboratory. The trip blank filter accompanies the sample filters from the lab to the field and returns but is not sampled.

**Collocated (C):** Collocated samples will be collected at the designated down wind sampling site during all sampling periods starting with the application period.

Valid samples are those that have a final corrected average flow within  $\pm 20\%$  of 3.0 lpm.

The propanil sampling sites will be named accordingly for the background, application, and post application as follows:

**Background Site Naming:**

- Site: NS-P-B & NS-P-FS
- Site: ES-P-B & ES-P-FS
- Site: SS-P-B & SS-P-FS
- Site: WS-P-B & WS-P-FS

**Application and Subsequent Sampling Periods Site Naming:**

- Site: NS-P#                      Site: SWC-P#
  - Site: NEC-P#                    Site: WS-P#
  - Site: ES-P#                      Site: NWC-P#
  - Site: SEC-P#                    Downwind Site: SEC-P#-C
  - Site: SS-P#                      Collocated with XAD tubes: SEC-P#-X and NWC-P#-X
- # = the run number. #1 will be the application, #2 will be the next sampling period and so forth.

**Letter Abbreviations as follows:**

- The first letter or two designates the cardinal direction from the center of the field in relation to true north such as: W = West and SW = Southwest  
The second or third letter designates whether the site is located at a side (S) or corner (C).
- B = Background Sample
  - FS = Field Spike
  - C = Collocated Sample
  - TS = Trip Spike
  - TB = Trip Blank

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will insure accurate field and laboratory results.

**9.0 Deliverables**

**9.1 Northern Laboratory Branch (NLB) Deliverables**

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

- 1) Table(s) of sample to include:
  - a. Sample identification (name).
  - b. Date sample received from field.
  - c. Date sample analyzed.
  - d. Dilution ratio.
  - e. Analytical results.
- 2) All equations used in calculating analytical results.
- 3) Table of duplicate results including calculated relative percent difference (RPD).
- 4) Table of collocated results.

- 5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries.
- 6) Table of analytical results from all trip blanks.
- 7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.
- 8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
- 9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

## **9.2 Air Quality Surveillance Branch Deliverables**

Within 60 days from receipt of the final results report from the NLB, AQSB will provide DPR with a report containing the following topics:

- 1) Sampling Protocol.
- 2) Personnel Contact List.
- 3) Site Maps.
- 4) Site Photographs.
- 5) Site Descriptions and Measurements (site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments, propanil application rate, and total pounds or gallons of propanil applied).
- 6) Sample Summary Table.
- 7) Field Log Sheets.
- 8) Laboratory Analysis Reports with calculations in electronic format.
- 9) Met Station and Sampler Calibration Reports.
- 10) Transfer Standards' Certification Reports.
- 11) Disk containing electronic files of 5-minute averaged Meteorological Data.
- 12) Disk containing electronic files of Report.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.



**APPENDIX A: STANDARD OPERATING PROCEDURE FOR ANALYSIS OF 3,4-DICHLOROPROPIONANILIDE (PROPANIL) IN APPLICATION AND AMBIENT AIR USING GAS CHROMATOGRAPHY/MASS SELECTIVE DETECTOR**

The Special Analysis Section of MLD's Northern Laboratory Branch will perform the analyses for propanil collected by the filter method. This analytical procedure is entitled, "Standard Operating Procedure for Analysis of 3,4-Dichloropropionanilide (Propanil) in Application and Ambient Air Using Gas Chromatography/Mass Selective Detector" and can be located starting on the next page.