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MEMORANDUM

TO: John Sanders, Ph.D., Chief
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Department of Pesticide Regulation

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

DATE: November 4, 2003

SUBJECT: FINAL PROTOCOL FOR THE 2003 CHLOROPICRIN APPLICATION
AIR MONITORING

Attached is the final "Protocol for Air Monitoring Around a Bed Fumigation Application of Chloropicrin, Fall, 2003". Thank you for your quick review of the draft protocol and the October 14, 2003 comments. We have made the changes you suggested.

If you or your staff have questions or need further information, please contact me at 322-3726 or via email at jcook@arb.ca.gov or Kevin Mongar at 322-2449 or via email at kmongar@arb.ca.gov.

Attachment

cc: see next page

*The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption.
For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <http://www.arb.ca.gov>.*

California Environmental Protection Agency

John Sanders, Ph.D., Chief
November 4, 2003
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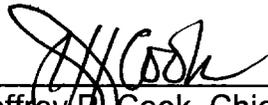
State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

**Protocol for Air Monitoring
Around a Bed Fumigation Application
of Chloropicrin
Fall 2003**

Prepared by
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Quality Management Branch
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Date: November 3, 2003

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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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**Protocol for Air Monitoring
Around a Bed Fumigation Application
of Chloropicrin
Fall 2003**

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (October 18, 2002 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide chloropicrin around a bed fumigation application, tentatively scheduled to be conducted in Fall 2003. This monitoring will be done 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 DPR has requested that a chloropicrin application where methyl bromide is also being used be selected for the monitoring study. The DPR will collect samples for methyl bromide, which will be analyzed by the California Department of Food and Agriculture's pesticide laboratory. This protocol will only address the sampling for chloropicrin (i.e., will not address the DPR sampling/analysis for methyl bromide).

The sampling and analysis will follow the quality assurance guidelines described in Attachment I, "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version).

The sampling and analysis will follow the procedures outlined in this protocol as well as the procedures described in Attachment II, "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector".

II. Sampling

Chloropicrin samples will be collected on XAD-4 resin sampling cartridges. For chloropicrin, the tubes are 8 mm x 140 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). Sample collection is at a flow rate of 100 standard cubic centimeters per minute (sccpm). Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples are transported (driven) to the ARB laboratory in Sacramento. DPR recommends a target 24-hour estimated quantitation limit (EQL) for chloropicrin of 0.1 ug/m³.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter or needle valve, train support, and a 12 volt DC vacuum pump (see Figure 1). Each tube is prepared in the field by breaking off each sealed glass end and then immediately inserting the tube into the fitting. The tubes are oriented in the sample train with a small arrow printed on the side of each tube indicating the direction of flow. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFM used for the chloropicrin samplers has a range of 0-200 sccpm. The mass flow meter has been calibrated to standard conditions (1 atm and 25 °C). The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Any change in flow rates will be recorded in the field logbook (see Attachment IV). The pesticide sampling procedures for adsorbent tubes are included as Attachment III. The sampling schedule consists of samples collected during daylight and overnight periods as shown below in Table 1.

Table 1
Application Sampling Schedule

<u>Sample period begins</u>	<u>Sample duration</u>
Background (pre-application)	Two sequential 12-hour samples
During application and post –application	Start of application until 1 hour before sunset (or until end of application if after sunset)
1 hour before sunset	Overnight (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	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)

The application monitoring study will be conducted at the location and under the conditions described in Table 2.

Table 2
Application Information

Location:	To be Determined
Field Size:	Largest field that can be fumigated in 1 day
Product Applied:	50 to 60% methyl bromide, 40 to 50% chloropicrin (by weight)
Type of Application:	Bed tarpaulin fumigation
Commodity:	To be Determined
Application Rate:	Maximum label rate
Grower/Applicator:	To be Determined

DPR staff will coordinate the selection of the study site and the test dates with representatives of the Chloropicrin Manufacturers Task Force (CMTF) and will obtain permission from the grower (and any other land owners where samplers may be located). Chloropicrin/methyl bromide bed-tarpaulin applications typically proceed at a pace of about one acre per hour or about 10 acres per day per application rig.

A minimum of 8 samplers will be positioned, one on each side of the field and one at each corner. A 9th replicate sampler will be collocated at one position (downwind site). Samplers should be positioned at the required inner buffer distance. Site conditions will dictate the exact placement of samplers but no sampler will be positioned closer than the inner buffer distance. Sampler positions for this study differ from earlier bed fumigation application monitoring studies for reasons noted in the memorandum (Sanders to Cook, October 31, 2003) included as Attachment VI.

In regard to field data, the monitoring report will include: 1) a record of the positions of the monitoring equipment with respect to the field, 2) the application start location, 3) the direction of crop rows 4) how the field was divided to treat if over several days, 4) a drawing of the monitoring sites showing the precise location of the meteorological equipment, trees, buildings and other obstacles, 5) meteorological data collected at a minimum of 15-minute intervals including wind speed and direction, humidity, and air temperature and comments regarding degree of cloud cover, 6) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North), and 7) the start and end time of the application. In addition, the materials and procedures used to tarp the field will be documented.

III. Analysis

The sampling and analysis method and validation results for the sampling and analysis of chloropicrin are included as Attachment II. The chloropicrin method will consist of sampling with XAD-4 resin cartridges along with GC analysis with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin are 3.96 ng/sample and 19.8 ng/sample, respectively. For a 24-hour

sample at 100 sccpm, the MDL and EQL would be 27.5 ng/m³ and 137 ng/m³, respectively. The DPR target EQL was 100 ng/m³. The analyses will be performed by the ARB laboratory in Sacramento.

IV. Field Quality Assurance

Field Quality Control for the application monitoring will include the following:

- 1) Four field spikes will be obtained by sampling ambient air at the application monitoring site for 24 hours. The field spikes will be obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions). The spike levels for chloropicrin in the adsorbent tube samples have not yet been determined.
- 2) Four trip spikes will be prepared at the same level as the field spikes. The trip spikes will be labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.
- 3) Four lab spikes will be prepared at the same level as the field and trip spikes. The lab spikes will remain in the laboratory freezer and will be extracted and analyzed along with the field and trip spikes.
- 4) Collocated (replicate) samples will be taken for all sampling periods (except the background period) at one sampling location (downwind).
- 5) A trip blank will be obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

V. Sample Labeling

Samples will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where (as an example):

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.

Chemical is designated as C for chloropicrin.

Sampling period is designated as B (for background) or 1 through 6.

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

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

VI. Personnel

ARB sampling personnel will consist of staff from the Air Quality Surveillance Branch.

VII. Safety Recommendations

Refer to Attachment V for general information on and toxicology of chloropicrin and methyl bromide gas fumigants. The DPR's Monitoring Recommendations include the following safety recommendations for chloropicrin.

"The chloropicrin product labels warn that chloropicrin is a poisonous liquid and vapor and is readily identifiable by smell. Inhalation of vapors may be fatal and exposures to low concentrations of vapor will cause irritation of the eyes, nose, and throat. Exposure to high concentrations or for a prolonged period of time may cause painful irritation to the eyes or temporary blindness. Contact with the liquid will cause chemical burns to the skin or eyes and is harmful or fatal if swallowed.

The acceptable air concentration for persons exposed to chloropicrin is 0.1 ppm. If air concentrations exceed 0.1 ppm, an air purifying respirator must be worn. The highest concentrations of chloropicrin at 20 m from the field should not exceed 0.05 to 0.08 ppm. The label states that the applicator and other handlers must wear: loose fitting, long -sleeve shirt and long pants, shoes and socks, and full-face shield or safety glasses with brow and temple shields. Monitoring personnel should refer to the label of the product used and should use proper protective equipment to prevent exposure to the dust, vapors, or spray mist."

The DPR's Monitoring Recommendations include the following safety recommendations for methyl bromide.

"According to the product labels for methyl bromide, it is an extremely hazardous liquid and vapor under pressure. Inhalation may be fatal or cause serious acute illness or delayed lung or nervous system injury. Liquid or vapor may cause skin or eye injury. Methyl bromide vapor is odorless and non-irritating to skin and eyes during exposure and toxic levels may occur without warning or detection.

The acceptable air concentration for persons exposed to methyl bromide is 5

ppm, except for those in residential or commercial structures. A respirator is required if air concentrations exceed 5 ppm at any time. According to the label, proper protective equipment for applicators include loose fitting or well-ventilated long-sleeved shirts and long pants, shoes and socks, full-face shield or safety glasses with brow and temple shields. Monitoring personnel should refer to the label of the actual product used for further precautions. Methyl bromide concentrations at the buffer zone distance should not exceed 1 ppm at any time.”

MANIFOLD SAMPLER

01/29/02

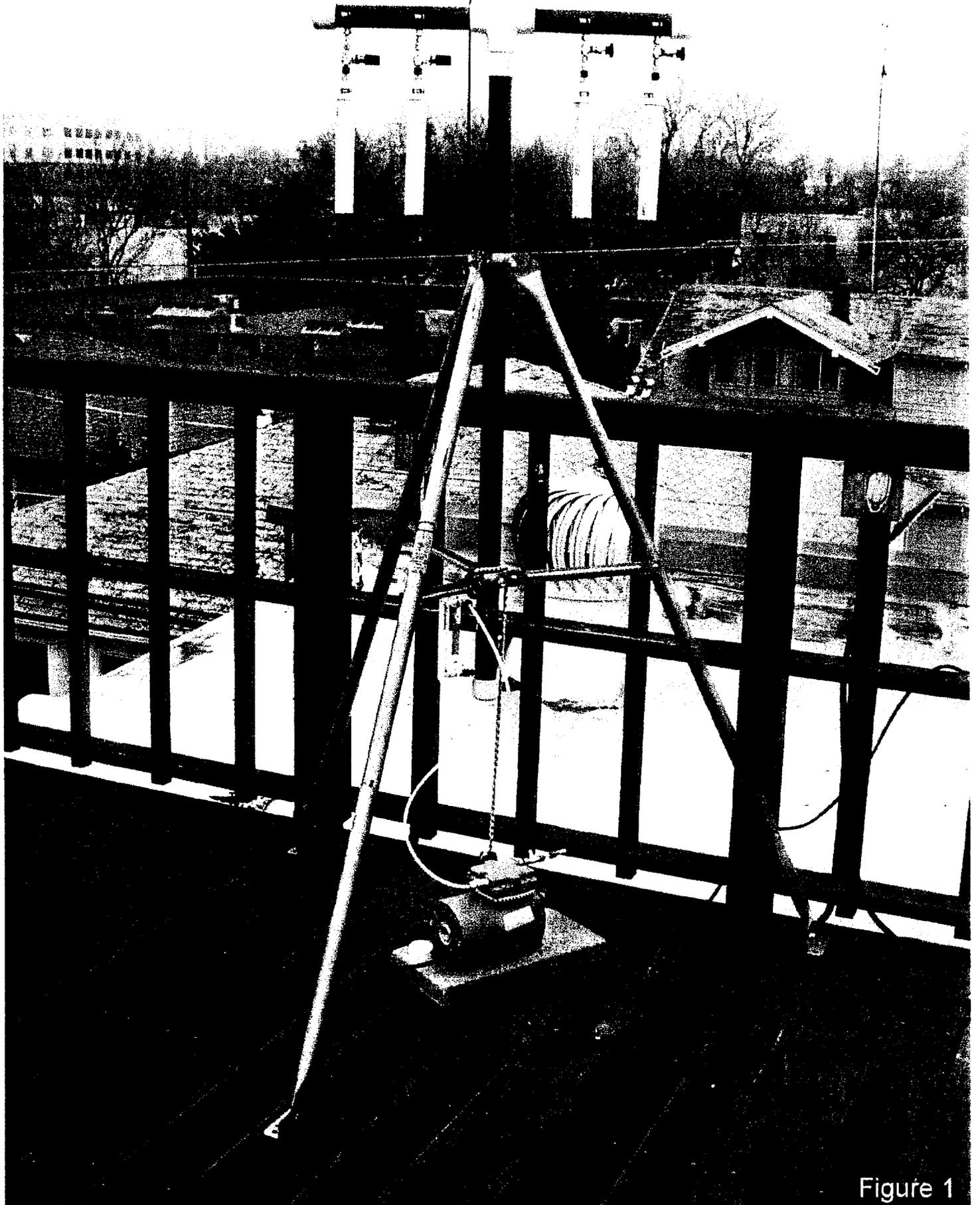


Figure 1

Attachment I

Quality Assurance Plan for Pesticide Air Monitoring

State of California
California Environmental Protection Agency
Air Resources Board

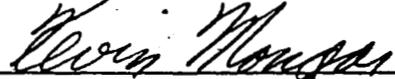
QUALITY ASSURANCE PLAN
FOR PESTICIDE AIR MONITORING

Prepared by the

Monitoring and Laboratory Division
Engineering and Laboratory Branch

Revised: May 11, 1999

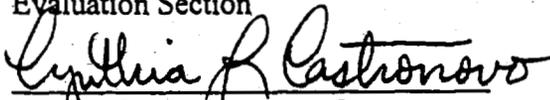
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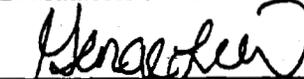
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This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does 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		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*difference/average) of each other and have recoveries that are +/-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 +/- 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

Attachment II

**Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane
(Chloropicrin) in Application and Ambient Air
using Gas Chromatography/Mass Selective Detector**

**Standard Operating Procedure for
Sampling and Analysis of Trichloronitromethane
(Chloropicrin) in Application and Ambient Air using Gas
Chromatography/Mass Selective Detector**

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

**Revision 1
10/29/02**

Approved by:

**Russell Grace, Manager
Special Analysis Section**

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1. SCOPE

The current method is for the analysis of trichloronitromethane (TCNM) using a gas chromatograph/mass selective detector. The procedure is for the analysis of application and ambient air monitoring of TCNM using XAD-4 resin tubes. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for TCNM during agricultural/structural application with a requested quantitation limit of $1.0 \mu\text{g}/\text{m}^3$ and ambient monitoring with a quantitation limit of $0.1 \mu\text{g}/\text{m}^3$.

2. SUMMARY OF METHOD

Resin tubes, XAD-4, are placed on the sampler for 24 hours at a flowrate of 0.1 liters per minute (LPM or 100 mLPM). The samples are stored in an ice chest or refrigerator until extracted with 3.0 ml of dichloromethane (DCM). A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

3. INTERFERENCES/LIMITATIONS

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank, including both solvent and resin, must be analyzed with each batch of samples to detect any possible interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Hewlett-Packard 6890 Series gas chromatograph
Hewlett-Packard 5973 Network mass selective detector
Hewlett-Packard 6890 Enhanced Parameters ALS

MS Transfer line: 280°C

Injector: 210°C, Splitless, Liner 4 mm straight liner with glass wool

Column: Restek Rtx-200, 60 meter, 320 μm i.d., 1.5 μm film thickness, or equivalent

GC Temperature Program: Oven initial 40°C, hold 4 min. Ramp to 220°C @ 12°C/min., hold 1 min., ramp to 240°C @ 20°C/min., hold 2.0 min.

Retention time: TCNM 11.93 min.

Splitter open @ 1.0 min.

Flows: Column: He, 1.6 ml/min, 9.1 psi. (velocity: 32cm/sec)

Splitter: 50 ml/min.

Mass Spectrometer: Electron Ionization

Selective Ion Monitoring: trichloronitromethane: 117 (quant. ion 100%), 119 (qual. ion 98%); Tuning: PFTBA on masses 69, 219, 502

B. Auxiliary Apparatus

1. Precleaned vials, 8 ml capacity with teflon caps
2. Whatman filters, 0.45 μm
3. Disposable syringes, 3 ml
4. Sonicator
5. GC vials with septum caps

C. Reagents

1. Dichloromethane, Pesticide grade or better
2. Trichloronitromethane, Chem Service PS-4, 98.8%
3. XAD-4 resin sorbent tubes, 400/200mg, SKC, Fullerton, CA

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at $\frac{1}{2}$ the peak height, 0.60 ± 0.05 , and the criteria for relative abundance: 69:100%, 219:90-120%, and 502: 5-12%.
2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample that may result in possible carry-over contamination.
3. A five-point calibration curve shall be analyzed with each batch of samples. For the ambient studies the calibration will be 5.0-50.0 ng/mL and for the application studies 50.0-500 ng/mL.
4. A calibration check sample (7.5 ng/ml for ambient, and 75 ng/ml for application) is run after the calibration, after every ten samples and at the end of the sample batch. The value of the calibration check must be within $\pm 3\sigma$ (the standard deviation) or $\pm 10\%$ of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after the last calibration check that was within limits need to be reanalyzed.
5. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 extracted and analyzed the same way as the samples. A laboratory control spike is XAD-4 spiked with a known amount of standard. The laboratory control

sample is extracted and analyzed the same way as the samples. Laboratory control samples should have recoveries that are greater than or equal to 70% of the theoretical spiked value.

6. Score and snap the sample resin tube, transfer the front bed of the resin tube into an 8-ml vial. (Save the back-up bed for future analysis if necessary.) Rinse the tube with 3.0 ml of DCM into the extraction vial. Cap and place the vial in the sonicator for one hour.
7. Filter the samples using 0.45 μm filter attached to a 3-ml syringe directly into a GC vial and cap securely.
8. The atmospheric concentration is calculated according to:

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

6. QUALITY ASSURANCE

A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0 μl injections of trichloronitromethane standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 5, 20 and 50 ng/ml, respectively.

B. Calibration

A five-point calibration curve is made ranging from 5.0 ng/ml to 50.0 ng/ml for ambient monitoring and 50 ng/ml to 500 ng/ml for application monitoring.

C. Calibration Check

A calibration check sample is run after the calibration, after every ten samples and at the end of the sample batch to verify the system is in calibration. The value of the check must be within $\pm 3\sigma$ (the standard deviation) or $\pm 10\%$ of the expected value whichever is greater. If the calibration check is outside the limit, then those samples in the batch after the last calibration check that was within the limit need to be reanalyzed.

D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for trichloronitromethane is calculated

by: $MDL = 3.14 * (\text{std dev values})$, where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For TCNM the MDL is 3.96 ng/sample (1.32 ng/mL). EQL, defined as $5 * MDL$, is 19.8 ng/sample (6.60 ng/mL) based on a 3.0 ml extraction volume. Results are reported to three significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect) or <MDL.

E. Collection and Extraction Efficiency (Recovery)

Trichloronitromethane at a low and high level are spiked on XAD-4 tubes (three at each concentration). The spiked tubes are placed on field samplers with airflows of 100 mLpm for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6-7. The average percent recovery of trichloronitromethane should be $\pm 20\%$ of the expected value. The recoveries both for the low and high levels are greater than 80.0%.

F. Storage Stability

Storage stability was set up for a four-week study. Three (3) XAD-4 tubes each were spiked at the low and high-end concentrations. The tubes were stored in the freezer until analyzed. At the low-end concentrations (5 ng/ml), the recovery for the three spikes averaged 106.8 percent, ranging from 103.68 to 113.68 percent. The average percent recovery peaked after fourteen days and was at the lowest after 28 days. At the high end (50 ng/ml), the recovery for the three spikes averaged 90.24 percent, ranging from 88.90 to 92.00 percent. The average percent recovery peaked at fourteen days and was at the lowest at twenty days.

G. Breakthrough

The most recent study for ambient monitoring for 24 hours required a low sample flow rate to meet the requested EQL. A new breakthrough analysis study was conducted. The flow rates tested were 1.0, 0.5, 0.2 and 0.1 Lpm. To meet the EQL and minimize breakthrough possibility, the flow rate for the field sampling was set at 100 mLpm.

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.

Attachment III

**Application Sampling Procedures
For Adsorbent Tubes**

Application Sampling Procedures For Adsorbent Tubes

Overview:

- Collect samples, according to the schedule in Table 1 of this protocol.
- Collect 4 background samples, from each corner sampling position.
- 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.
- With the trip blank there should be a total of 59 samples collected during the study, plus 4 trip and 4 field spikes.
- 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. 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 2 00 sccpm mass flow meter (MFM) with battery
- ice chest
- dry ice

Figure out the route for sampling the 8 locations and try to 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 once per week to be on the safe side.

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

Using the 0-200sccpm MFM set the flow rate exactly to 100 sccpm. Use the MFM calibration linear regression equation to set the flow rate.

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; 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 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.

Attachment IV
Field Log Sheet

Attachment V

**Chloropicrin and Methyl Bromide
"Information Profiles"**

EXTOXNET

Extension Toxicology Network

Pesticide Information Profiles

A Pesticide Information Project of Cooperative Extension Offices of Cornell University, Oregon State University, the University of Idaho, and the University of California at Davis and the Institute for Environmental Toxicology, Michigan State University. Major support and funding was provided by the USDA/Extension Service/National Agricultural Pesticide Impact Assessment Program.

EXTOXNET primary files maintained and archived at Oregon State University

CHLOROPICRIN

TRADE OR OTHER NAMES: Some trade names for products containing chloropicrin include "Chlor-O-Pic," "Metapicrin" "Timberfume" and "Tri-Clor." A partial list of trade names for chloropicrin mixtures with methyl bromide includes "Tri-Con," "Terr-O-Gas," "Preplant Soil Fumigant" and "Pic-Brom." Chloropicrin mixtures with 1,3-Dichloropropene include "Telone C-17," "Tri-Form" and "Pic-Clor."

REGULATORY STATUS: Chloropicrin is currently undergoing USEPA FIFRA reregistration. It is a Class I toxicity, Restricted Use Pesticide (RUP), labeled with the signal word "Danger" (231). The U.S. Department of Transportation (DOT) proper shipping name is "Chloropicrin, 6.1, UN 1580, PGI, Poison Inhalation Hazard, Hazard Zone B." The Emergency Response Guide (ERG) number is 56. NFPA designations are 4-Health, 0-Fire, 3-Reactivity. Chloropicrin is not listed under the EPA Clean Air Act, EPA Clean Water Act or the EPA Marine Pollutant List (258). A tolerance is not required for preplant soil fumigation uses of chloropicrin.

INTRODUCTION: Chloropicrin is a clear, colorless, oily liquid with a strong, sharp, highly irritating odor. It is a strong lachrymator (231). Chloropicrin has been used as an insecticide since 1917 and as a soil fumigant since 1920 (259). The primary use today is for preplant soil fumigation to control soil borne fungi, diseases and nematodes (231). It also is used to treat wood poles and timbers for internal decay by fungi and insects; as a warning/clearing agent for sulfuryl fluoride (structural fumigant) and methyl bromide (soil and structural fumigant); and is also used in organic synthesis. For soil fumigation and wood treatment, chloropicrin is packaged in DOT 4BW240 steel cylinders and bulk tanks which may be pressurized. When used as a warning agent for methyl bromide, chloropicrin is packaged along with the methyl bromide in steel cylinders. When used as a structural fumigation warning agent for sulfuryl fluoride, chloropicrin is packaged in small plastic bottles in DOT approved overpacks. Chloropicrin has a moderate vapor pressure (18.3 mmHg at 20 degrees C) and exists as a liquid at room temperature. Chloropicrin/methyl bromide mixtures will volatilize readily upon opening of the cylinder valve. Materials incompatible with chloropicrin are PVC, fiberglass, aluminum and magnesium and their alloys (231,260).

TOXICOLOGICAL EFFECTS

- **Acute Toxicity:** Undiluted chloropicrin is highly toxic by ingestion or direct contact with the skin or eyes. According to the American Conference of Governmental Industrial Hygienists (261), airborne

exposure to 0.3-0.37 ppm (2-2.5 mg/meters cubed) for 3-30 seconds results in eye irritation. This response is reported to be highly variable among individuals and tearing (lachrymation) may occur at airborne exposures of 0.15-0.3 ppm (1-2 mg/meters cubed) (261). Inhalation exposure to 4 ppm (26 mg/meters cubed) for a few seconds may cause some degree of incapacitation (261) and an exposure of a few seconds to 15 ppm (100 mg/meters cubed) can cause injury to the respiratory track. Exposure to concentrations above 15 ppm can result in lacrimation, vomiting, and if allowed to continue for a minute or longer, can cause pulmonary edema and possibly death (261). The American Industrial Hygiene Association Emergency Response Planning Guideline for one hour exposure to chloropicrin is 3 ppm (20 mg/meters cubed)(262). Animal studies established that the 4-hour inhalation LC50 for chloropicrin vapor in rats is 11.9 ppm (79.7 mg/meters cubed)(293) and the respiratory irritation potential threshold (RD50) in mice is 7.98 ppm (53.5 mg/meters cubed)(293). The FIFRA Toxicity Classification for chloropicrin acute effects is Category I and the signal word for that classification is "Danger."

- **Signs and Symptoms of Poisoning:** Undiluted chloropicrin is severely and immediately irritating to the upper respiratory tract, eyes and skin upon direct contact. Exposure to airborne concentrations of chloropicrin exceeding 0.15 ppm (1 mg/meters cubed) can cause tearing and eye irritation which is reversible upon termination of exposure. Prolonged inhalation exposures at airborne concentrations above 1 ppm may cause symptoms of respiratory system damage including irritation of the airways, shortness of breath and/or tightness in chest and difficulty in breathing. Inhalation exposure to very high levels, even if brief, can lead to pulmonary edema, unconsciousness and even death.
- **Chronic Toxicity/Subchronic Effects:** Studies with male and female CD rats and CD-1 mice exposed to chloropicrin vapor in whole body inhalation chambers at concentrations of 0.3, 1.0, or 3.0 ppm for six hours per day, five days per week for thirteen weeks (263) and male Fisher 344 rats exposed to chloropicrin (264) indicated that respiratory tissue is the target for chloropicrin inhalation toxicity. Portal-of-entry effects occurred in the upper respiratory tissue of animals inhaling chloropicrin vapor for 90 days at concentrations at or above 0.1 ppm (0.67 mg/meters cubed).
- **Reproductive Effects:** A study utilizing chloropicrin vapor administered by whole body inhalation for six hours per day, seven days per week to male and female CD rats at concentrations of 0.5, 1.0, or 1.5 ppm through two generations of animals indicated that reproduction fitness is not adversely affected by chloropicrin inhalation even at systemically toxic levels (265). The No Observable Adverse Effect Level (NOAEL) was 1.0 ppm for systemic toxicity and greater than 1.5 ppm for developmental toxicity and reproductive parameters.
- **Teratogenic Effects:** In a study with sexually mature virgin female Sprague-Dawley rats exposed by whole body inhalation to chloropicrin vapor for six hours per day for days 6-15 of gestation, there were no treatment-related fetal malformations (266). The incidence of developmental variations in the mid- and high-dose groups increased over the control group and was statistically significant in the high-dose group. The NOAEL for maternal toxicity was 0.4 ppm and the NOAEL for fetal toxicity was 1.2 ppm indicating that the developing fetus is not a target tissue for chloropicrin. The developmental toxicity of chloro-picrin in sexually mature virgin female New Zealand White SPF rabbits was evaluated by whole body exposure/inhalation to chloropicrin vapor for six hours per day for days 7-20 of gestation (267). There were no treatment related fetal malformations reported, the incidence of developmental variations in the mid- and high-dose groups was increased over the control group and was considered to be treatment related but was not dose related nor was it statistically significant. The NOAEL for maternal toxicity was 0.4 ppm and the NOAEL for fetal toxicity was 1.2 ppm indicating that the developing fetus is not a target tissue.
- **Mutagenic Effects:** Chloropicrin has been evaluated in several in vitro genetic toxicity test systems (268, 271). Bacterial cell testing for gene mutation produced some evidence of genetic toxicity in one of five tester strains in the presence of an exogenous metabolic activation system but testing in higher order cells (mammalian cells) did not confirm the potential for chloropicrin to produce gene mutation. Chloropicrin did not cause damage to mammalian cell DNA. In vitro testing of

mammalian cell chromosomes for damage (breaks, exchange figures, fragments, etc.) produced evidence suggestive of a clastogenic effect but the data were equivocal.

- **Carcinogenic Effects:** Six long-term bioassays have been performed to evaluate the potential of chloropicrin to cause chronic and/or carcinogenic effects by inhalation, oral, and gavage dosing (272, 276). Chronic toxicity was limited to inflammatory and other degenerative changes associated with chronic wound healing at the portal-of-entry and at associated tissues (i.e. rodent forestomach following life-long oral dosing). No neoplastic or tumorigenic response was produced by chloropicrin in any species tested by the three routes of exposure.
- **Organ Toxicity:** Target organs for chloropicrin toxicity include eyes, skin, respiratory tract and tissue associated with portal-of-entry into the body.
- **Fate in Mammals:** The octanol/water partition coefficient (Log₁₀ K_{ow}) is 2.50 at 25 degrees C indicating that chloropicrin would not be expected to bioaccumulate in mammalian cells (277).

ECOLOGICAL EFFECTS

- **Effects on Birds:** Little information is available about the effects of chloropicrin on bird life. A feeding study in chickens (278) demonstrated no adverse effects at doses as high as 100 ppm for 120 days. This was the highest dose tested.
- **Effects on Aquatic Organisms:** Chloropicrin is toxic to fish. For trout and bluegill the 96-hour LC₅₀ was 0.0165 mg/L and 0.105 mg/L respectively (278).
- **Effects on Other Animals (Nontarget species):** When used according to label, exposure to nontarget species is unlikely. However, because of its toxicity to mammals and invertebrates, it can be assumed that chloropicrin may be harmful to many nontarget organisms.

ENVIRONMENTAL FATE

- **Breakdown of Chemical in Soil and Groundwater:** The half-life of chloropicrin in sandy loam soil was 8-24 hours (279) and 4.5 days (280) with carbon dioxide being the terminal breakdown product (280). Chloropicrin moves rapidly in soils within twelve inches of injection but may diffuse to a maximum depth of four feet in sandy soil (281). Since it is only slightly soluble in water, it will not move rapidly in aquatic environments. In an anaerobic aquatic/soil system, chloropicrin was converted to nitromethane with a half-life of 1.3 hours (282). In the absence of sunlight or microorganisms, chloropicrin does not undergo hydrolysis (283, 284). The calculated Henry's Law Constant is 2.51×10^{-3} atm meters cubed mole⁻¹ (285). The K_{oc} for silt loam and agricultural sand soils was 5.29 and 93.59 respectively (289). Chloropicrin can be produced during chlorination of drinking water if nitrated organic contaminants are present (286, 287). In a sampling of 1,386 wells in California between 1984 and 1989, no chloropicrin was detected (288). In a sampling of 15,175 wells in Florida, chloropicrin was found in three wells at 0.035-0.068 Hg/L (288).
- **Breakdown of Chemical in Surface Water:** Since chloropicrin has a higher density than water (1.65 g/ml) and is only slightly soluble, it will sink to the bottom of surface water. The half-life of chloropicrin in water exposed to light was 31.1 hours with carbon dioxide, bicarbonate, chloride, nitrate and nitrite being the breakdown products (284).
- **Breakdown of Chemical in Plants:** No chloropicrin or nitromethane was detected in crops grown in soil treated with radiolabelled chloropicrin (290). Carbon dioxide, as the terminal breakdown product, was metabolized by plants and incorporated into natural plant biochemical compounds via the single carbon pool (291).
- **Breakdown of Chemical in Air:** Chloropicrin is efficiently photolyzed in the atmosphere. The half-life of chloropicrin in air exposed to simulated sunlight was 20 days (292). The photoproducts were phosgene (which will hydrolyze to carbon dioxide and hydrogen chloride), nitric oxide,

chlorine, nitrogen dioxide and dinitrogen tetroxide.

- **Analytical Methods:** The concentration of chloropicrin in air may be measured using Kitagawa direct reading gas detector tube#172 (Matheson-Kitagawa, East Rutherford, NJ). Gas chromatography methods are available to measure chloropicrin in air (283) and may utilize XAD-4 solid sorbent tubes (SKC Inc., Eighty Four, PA).

PHYSICAL PROPERTIES AND GUIDELINES

Physical Properties:

- **Appearance:** Heavy, colorless, liquid with a sharp odor
- **Chemical Names:** Trichloronitromethane; Methane, trichloronitro; Nitrotrichloro-methane, Nitrochloroform
- **CAS Number:** 76-06-2
- **Molecular Weight:** 164.38
- **Water Solubility:** 1.6 g/L @ 25 degrees C
- **Solubility in Other Solvents:** Miscible in most organic solvents
- **Melting Point:** -64 degrees C
- **Vapor Pressure:** 18.3 mmHg @ 20 degrees C, 24 mmHg @ 25 degrees C
- **Partition Coefficient:** Not Available
- **Adsorption Coefficient:** Not Available

Exposure Guidelines:

- **ADI:** Not Available
- **MCL:** Not Available
- **RfD:** Not Available
- **PEL:** 0.1 ppm
- **HA:** Not Available
- **TLV:** 0.1 ppm TWA

BASIC MANUFACTURERS

Niklor Chemical Corp.
2060 E. 220th Street
Long Beach, CA 90810

REFERENCES:

References for the information in this PIP can be found in Reference List Number 10

DISCLAIMER: The information in this profile does not in any way replace or supersede the information on the pesticide product label/ing or other regulatory requirements. Please refer to the pesticide product label/ing.

EXTOXNET

Extension Toxicology Network

Pesticide Information Profiles

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EXTOXNET primary files maintained and archived at Oregon State University

Revised June 1996

Methyl bromide; Bromomethane

Tradenames: Trade or common names of methyl bromide containing products include: Brom-o-Gas, Bromomethane, Celfume, Embafume, Haltox, MB, MeBr, Methogas, Profume, Terr-o-Gas, and Zytex.

Regulatory Status: Methyl bromide is a highly toxic compound in EPA Toxicity Class I. Labels for products containing it must bear the Signal Word DANGER. Methyl bromide is a Restricted Use Pesticide (RUP). RUPs may be purchased and used only by certified applicators.

EPA has expressed concerns and proposed restrictions on methyl bromide due to concerns over its potential to destroy ozone. Ozone-depleting chemicals fall within the scope of the Clean Air Act. Unlike FIFRA, the Clean Air Act does not contain a risk/benefit balancing process that would allow retention of essential or high benefit uses, nor does the listing and phase-out of ozone depleters depend on the availability of alternative products.

Chemical Class: Not Available

Introduction: Methyl bromide is chiefly used as a gas soil fumigant against insects, termites, rodents, weeds, nematodes, and soil-borne diseases. It has been used to fumigate agricultural commodities, grain elevators, mills, ships, clothes, furniture, and greenhouses. About 70% of methyl bromide produced in the U.S. goes into pesticidal formulations.

Formulation: Methyl bromide is chiefly used as a gas soil fumigant against insects, termites, rodents, weeds, nematodes, and soil-borne diseases.

Toxicological Effects:

- **Acute toxicity:** Since bromomethane is a gas at ambient temperatures, the most significant route of

exposure is inhalation [188]. The reported 1-hour inhalation LC50 in rats is 4.5 mg/L, and the 11-hour LC50 in rabbits is 8 mg/L [8]. Inhalation of 6 mg/L for 10 to 20 hours, or 30 mg/L for 1.5 hours is lethal to humans [8]. The compound is readily absorbed through the lung alveoli (gas exchange regions). Methyl bromide can be highly irritating to the mucous membranes of the eyes, airways, and skin with contact [17]. About 1000 human poisoning incidents caused by methyl bromide exposure have been documented, with effects ranging from skin and eye irritation to death [17]. Most fatalities and injuries occurred when methyl bromide was used as a fumigant. The lowest inhalation level found to cause toxicity in humans is 0.14 mg/L in air [17]. A typical delay in onset of symptoms following exposure combined with an odor threshold (level at which most people can smell it) well-above the level at which toxic effects occur, means that the victim may not realize a harmful exposure is occurring until it is too late [17]. Initial acute effects may include headache, dizziness, nausea or vomiting, chest and abdominal pain, and irritated eyes, nose, and throat [188]. With sufficient exposure, symptoms of slurred speech, blurred vision, temporary blindness, mental confusion, and sweating may occur [188]. More severe symptoms at even higher doses may include lung swelling; congestion; hemorrhaging of the brain, heart, and spleen; severe kidney damage; and numbness, tremors, and convulsions [188]. The nervous effects observed in lab animals included degeneration of key nerve cells in various portions of the brain and peripheral nervous system [188]. Death may occur from respiratory failure [188]. The rat oral LD50 (bromomethane administered as a liquid, or in solution) is 214 mg/kg [1], also indicating moderate to high toxicity.

- **Chronic toxicity:** Chronic exposure to methyl bromide can cause extensive damage to neurons (nerve cells) involved in cognitive processes and physical coordination or muscular control [188]. These effects were seen in rats exposed to 0.51 to 1.3 mg/L 6 hours per day for 5 days [188]. Rats exposed to 65 ppm over 4 weeks for an average of 7 hours per day for 4 to 5 days did not show neurological effects, but this level of exposure did result in severe, in some cases irreversible, neurological effects in rabbits over a similar time period [188]. Exposure levels of 0.1 mg/L over 8 months (7.5 hours per day, 4 days/week) did not produce observable neurotoxicity [188]. The symptoms of chronic exposure may include dizziness, vision and hearing disturbances, depression, confusion, hallucinations, euphoria, personality changes, and irritability [8]. A chronic pneumonia-like syndrome may become apparent after repeated exposure to sufficient levels [8]. Other targets of the fumigant identified through long-term animal studies are the heart, adrenal gland, and the testis [189].
- **Reproductive effects:** No reproductive effects were seen in rats exposed to up to 0.3 mg/L for 7 hours/day, 5 days a week, for 3 weeks prior to mating and during gestation [188]. This suggests that methyl bromide does not cause reproductive effects.
- **Teratogenic effects:** No teratogenic effects were seen in rats exposed to up to 0.3 mg/L for 7 hours/day, 5 days a week, for 3 weeks prior to mating and during gestation [188]. This evidence indicates that bromomethane is unlikely to cause teratogenic effects.
- **Mutagenic effects:** Mutagenic effects were seen in mouse cell cultures, mutagenicity assays with bacteria, and in human white blood cells [190]. Rat liver cells did not display increased rates of mutation after exposure to methyl bromide [190]. Methyl bromide is considered to be weakly mutagenic [188].
- **Carcinogenic effects:** In one study of industrial workers exposed to various brominated compounds, exposure to methyl bromide was suggested as the possible common factor in two fatal cases of testicular cancer, but other exposures could not be ruled out [189]. In a rat study, methyl bromide given at 50 mg/kg/day by stomach tube for 90 days (gavage) induced stomach tumor increases [188,190]. It appeared that the cancerous growth was due to severe localized cellular injury, with subsequent increased cell reproduction to repair tissue damage amplifying the natural incidence of mutant or abnormal cells [188]. This is not likely to occur at low doses. Thus, the data are inconclusive.
- **Organ toxicity:** Acute exposure primarily damages the lung and results in nervous system effects;

chronic exposure may cause damage to the central nervous system, kidneys, and lungs. Other targets of the fumigant are the heart, nasal cavities, adrenal gland, and the testis.

- **Fate in humans and animals:** The major route of absorption of methyl bromide vapors is through the lungs [188]. Some of the compound is excreted through the lungs as unchanged methyl bromide, but a significant amount also undergoes metabolic decomposition [32]. The primary breakdown products are the bromide ion and methanol, which are detectable in the blood and tissues and are excreted in the urine [32]. Organic bromides (formed by reaction of bromide ion with molecular carbon centers in biomolecules) also appear in stomach fluids and mucus. In humans, methyl bromide's half-life in blood is about 12 days [32]. As a result, the toxic effects of methyl bromide can be delayed or prolonged [32]. Additionally, once in a cell, this chemical inactivates many enzyme systems, so prolonged small doses can cause severe toxicity [32].

Ecological Effects:

- **Effects on birds:** Bromomethane is most likely to be in vapor form, and unless birds are in the fumigation area, during the fumigation, they are unlikely to be exposed .
- **Effects on aquatic organisms:** Methyl bromide is moderately toxic to aquatic organisms. Acute toxicity in freshwater fish (bluegill sunfish) occurs at concentrations of 11 mg/L and in saltwater fish (tidewater silversides) at about 12 mg/L [8].
- **Effects on other organisms:** It is not toxic to bees [1].

Environmental Fate:

- **Breakdown in soil and groundwater:** Methyl bromide quickly evaporates at temperatures ordinarily encountered in fumigating, but some may be entrapped in soil micropores following application [11]. Methyl bromide is moderately persistent in the soil environment, with a field half-life of between 30 and 60 days; a representative half-life is estimated to be about 55 days [11]. Transformation of methyl bromide into bromide increases as the amount of organic matter in the soil increases. It is soluble in water and very poorly sorbed by soils. Some leaching may occur if bromomethane is entrapped in soil micropores following fumigation; the rate of degradation for retained bromomethane in fumigated soil is 6 to 14% per day at 20 C [11].
- **Breakdown in water:** Methyl bromide quickly evaporates at temperatures ordinarily encountered in fumigating; therefore run-off from fields into surface waters is very rare. If it does contact surface waters, the average half-life for methyl bromide under field conditions has been calculated to be 6.6 hours at 11 C [8]. Another study showed the half-life in water to be 20 days at 25 C in a neutral solution [8].
- **Breakdown in vegetation:** The amount of bromide ion (the metabolite of methyl bromide) taken up from the soil, is proportional to the protein content of the crop. Higher levels of the bromide ion will most likely be found in high-protein plants [8].

Physical Properties:

- **Appearance:** Methyl bromide is a colorless gas or volatile liquid which is usually odorless, but has a sweet, chloroform-like odor at high concentrations [1].
- **Chemical Name:** bromomethane [1]
- **CAS Number:** 74-83-9
- **Molecular Weight:** 94.94
- **Water Solubility:** 13,400 mg/L at 25 C [1]

- **Solubility in Other Solvents:** easily miscible with ethanol, ether, aromatic carbon disulfide, and ketones [1]
- **Melting Point:** -93.6 C [1]
- **Vapor Pressure:** 227,000,000 mPa @ 25 C [1]
- **Partition Coefficient:** Not Available
- **Adsorption Coefficient:** 22 [11]

Exposure Guidelines:

- **ADI:** 1.0 mg/kg/day (as bromide ion) [12]
- **MCL:** Not Available
- **RfD:** 0.0014 mg/kg/day [13]
- **PEL:** 80 mg/m³ (ceiling) [14]
- **HA:** Not Available
- **TLV:** Not Available

Basic Manufacturer:

Great Lakes Chemical Corporation
One Great Lakes Blvd.
P.O. Box 2200
West Lafayette, IN 47906

- **Phone:** 317-497-6204
- **Emergency:** 501-862-5141

References:

References for the information in this PIP can be found in Reference List Number 10

DISCLAIMER: The information in this profile does not in any way replace or supersede the information on the pesticide product labeling or other regulatory requirements. Please refer to the pesticide product labeling.

Attachment VI

Memorandum

"Protocol Changes for Chloropicrin Application-site Monitoring"



Department of Pesticide Regulation



Gray Davis
Governor

Winston H. Hickox
Secretary, California
Environmental
Protection Agency

Paul Helliker
Director

MEMORANDUM

TO: Jeffrey P. Cook, Chief
Quality Management Branch
Air Resources Board
P.O. Box 2815
Sacramento, California 95812

FROM: John S. Sanders, Ph.D., Chief *John S. Sanders*
Environmental Monitoring Branch
(916) 324-4100

DATE: October 31, 2003

SUBJECT: PROTOCOL CHANGES FOR CHLOROPICRIN APPLICATION-SITE
MONITORING

The Department of Pesticide Regulation (DPR) recommends changing the Draft Protocol for the upcoming Chloropicrin Study concerning the location of samplers and the sampling duration for the background-sample period. DPR believes these changes will better meet the data collection requirements of the Protocol, and still provide adequate safety for sampling staff.

Previous application-site monitoring for chloropicrin did not achieve the study objective because the samplers were located too far from the treated field. The study objective is to determine the maximum acute chloropicrin exposure to people working or living near an application of methyl bromide and chloropicrin. To achieve this objective, samplers should be placed as close as the general public would have access to a large application. During the previous application-site monitoring, samplers were placed at a distance assuming the entire field would be treated in a single day. Instead, the field was treated over a 3-day period and samplers were located further than people might work or live. Chloropicrin air concentrations detected at the sampled distances were unlikely to meet the criteria for listing as a toxic air contaminant.

DPR recommends that the samplers be placed at the inner buffer zone. Samplers placed at the inner buffer zone distance will more likely give useful results even if a smaller area is treated than originally planned. In addition, the field chosen for monitoring is being treated in sections over several weeks. Samplers will be near or in sections treated several days earlier. Background concentrations from the previously treated areas may confound the results. Placing samplers closer to the monitored section will decrease the effect of the background concentrations.

Entry into the buffer zones is governed by pesticide regulations. Exposure to sampling personnel at the inner buffer zone will still be less than allowed for the general public. At the outer buffer zone distance there are no restrictions and it provides maximum protection. The general public is allowed at the outer buffer zone distance for 24 hours/day. Activity at the inner buffer zone distance is limited to 12 hours/day and requires prior approval by the county agricultural commissioner. With the county agricultural commissioner's approval, the general public may

Jeffrey P. Cook
October 31, 2003
Page 2

occupy the inner buffer zone distance for 12 hours/day per all applicable regulations. Sampling personnel are likely to spend no more than two to three hours per day at the inner buffer zone distance changing sample tubes, less than the 12 hours allowed.

DPR agreed to placing the samplers at the outer buffer zone distance for the previous study assuming that the study objectives could still be achieved and provide maximum protection to field staff. Results of the previous application and circumstances of the current application make it unlikely that the study objectives can be achieved if the samplers are placed at the outer buffer zone. The changes DPR proposes greatly increases the chances for a successful study and still provides adequate protection for field staff.

A related issue is the background samples. The registrants have great concerns about monitoring this application due to the possibility of background concentrations overestimating exposures. They suggest, and DPR agrees, that the 24-hour background samples should be collected in two, 12-hour sampling intervals.

Thank you for considering this request. If you have any questions, please contact me or Randy Segawa, of my staff, at (916) 324-4137 or <rsegawa@cdpr.ca.gov>.

cc: Randy Segawa
Ken Stroud, Air Resources Board
Dennis Goodenow, Air Resources Board
Webster Tasat, Air Resources Board
Lynn Baker, Air Resources Board