

APPENDIX I  
DPR MONITORING RECOMMENDATION

# Memorandum

To : Genevieve A. Shiroma, Chief  
Toxic Air Contaminant  
Identification Branch  
Air Resources Board  
1102 Q Street, P.O. Box 2815  
Sacramento, California 95814

Date : February 1, 1991

Place :

From : Department of Food and Agriculture 1220 N Street, P.O. Box 942871  
Sacramento, California 94271-0001

Subject: ARB Monitoring for Oxydemeton-methyl

In order to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), the California Department of Food and Agriculture requests that the Air Resources Board document the airborne levels of oxydemeton-methyl (S-[2-(ethylsulfinyl)ethyl] O,O-dimethyl phosphorothioate, also called demeton-S-methyl sulfoxide) and the breakdown product demeton-S-methyl sulfone. This memorandum provides background and recent use information on oxydemeton-methyl products and identifies how they are used.

Technical oxydemeton-methyl is a clear amber liquid which has a molecular weight of 246.29 g/mole and a vapor pressure of  $3.83 \times 10^{-5}$  mm Hg at 25 C. Oxydemeton-methyl is soluble in water to approximately  $1.0 \times 10^{+5}$  ppm and has a specific gravity of 1.289 at 20 C. The acute oral and dermal LD<sub>50</sub> (rat) for oxydemeton-methyl is 60 mg/kg and 112 mg/kg respectively. Female rat and mouse LC<sub>50</sub> inhalation values are 1.5 and 0.51 mg/L, respectively.

The EPA has classified oxydemeton-methyl in Toxicity Category I for dermal exposure and Category II for both oral and dermal exposures. Oxydemeton-methyl has entered the risk assessment process at the California Department of Food and Agriculture under SB 950 (Birth Defect Prevention Act of 1984) because of reproductive effects. In addition, concern over the potential adverse effects of oxydemeton-methyl on cholinesterase inhibition was a consideration for its selection as a candidate toxic air contaminant for 1807/3219 review.

Oxydemeton-methyl is a systemic organophosphorus insecticide and acaricide which is an active ingredient in 3 currently registered products. Oxydemeton-methyl-containing products are formulated as liquids (1 product) and emulsifiable concentrates (2). Oxydemeton-methyl-containing products control a variety of pests and are registered for use on fruit, field and vegetable crops.

Oxydemeton-methyl is listed as a restricted use material under Title 3, California Code of Regulations, Section 6400, a permit is

required to purchase oxydemeton-methyl-containing products and users must file a Pesticide Use Report after using this material. Therefore, Pesticide Use Report data provides information on the use pattern of this material and identifies the county, month and commodity of greatest use.

The following table summarizes 1987 and 1988 Pesticide Use Report data for oxydemeton-methyl:

Oxydemeton-methyl Use by Crop (pounds of active ingredient)

<u>Crop</u>	<u>1987</u>	<u>1988</u>
Broccoli	41,493	39,318
Cauliflower	28,704	27,550
Sugarbeet	11,415	11,281
Cabbage	8,118	9,709
Melons	12,297	7,897
TOTAL REPORTED USE	153,091	127,083

Pesticide Use Report data summarized in this table show the largest reported use of oxydemeton-methyl-containing products occurs on broccoli and cauliflower. Additionally, 1988 data indicates that, when ranked in descending order, counties with highest use were Monterey (44,059 pounds of active ingredient), Santa Barbara (21,104), San Luis Obispo (7,269), Kern (7,038), and Ventura (5,830).

Oxydemeton-methyl is used on broccoli and cauliflower to control aphids and other insect pests. Oxydemeton-methyl can be applied with either tractor-driven application equipment, such as hydraulic boom-sprayers, aircraft or irrigation systems. Typically, oxydemeton-methyl applications to broccoli and cauliflower use between three-eighths and one-half pound of active ingredient per acre. Air applications are made using 3 to 5 gallons of water per acre and ground applications use 10 to 15 gallons of water per acre.

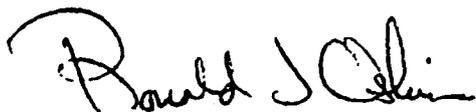
Recommendation

The use pattern for oxydemeton-methyl suggests that monitoring should take place in Monterey County during a 30-day sampling period during August. In Monterey County, oxydemeton-methyl applications to broccoli and cauliflower peak in late summer, during August. Three sampling sites should be selected in relatively high-population areas or areas frequented by people. Sampling sites should be in broccoli and cauliflower growing areas, but not

Genevieve A. Shiroma  
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immediately adjacent to fields. At each site, nineteen discrete 24-hour samples should be taken during the 30-day sampling period. The specific dates for 24-hour sampling should be chosen at random, during the 30 day sampling period.

Replicate (co-located) samples are needed for three dates at each site. Two co-located air samplers (in addition to the primary sampler) should be run on those days. The date chosen for collecting the replicate samples should be distributed over the 30 day period. They may, but need not be, the same dates at every site.



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APPENDIX II  
SAMPLING PROTOCOL

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

Protocol for the Application and Ambient Monitoring  
of Oxymeton Methyl in Monterey County During Summer, 1995

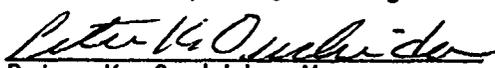
Engineering and Laboratory Branch  
Monitoring and Laboratory Division

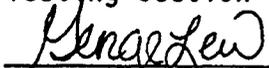
Project No. C91-092 (Ambient)  
C91-092A (Application)

Date: August 7, 1995

APPROVED:

  
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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.

Protocol for the Application and Ambient Monitoring  
of Oxydemeton Methyl in Monterey County During Summer, 1995

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine levels of oxydemeton methyl (Metasystox R, MSR) and its primary breakdown product, dioxydemeton methyl during a 3-day ambient air monitoring at an application site and a 4-week ambient monitoring program in populated areas. The monitoring will be done in Monterey County and is in support of the DPR toxic air contaminant program. Section 14022(c) of the Food and Agriculture Code 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. This monitoring follows a similar study conducted in the summer of 1992 (Airborne Concentrations of Oxydemeton-Methyl and Dioxydemeton-Methyl in Salinas Valley from Sampling Conducted August 31 to October 9, 1992). This monitoring is repeated because the DPR believes that the detection limits of the earlier study were too high to assess the possible affects to public health.

II. Sampling

A sketch of the sampling apparatus is shown in ATTACHMENT I. Calibrated rotometers will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling media, approximately 30 cc of XAD-4 resin contained in a Teflon Holder, installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data, including field size, application rate, formulation, method and length of application.

A. Application Monitoring

Prior to application, background samples will be taken to establish if any oxydemeton methyl or its breakdown product are detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with XAD resin using battery powered pumps capable of flows of approximately 15 liters per minute. Five samplers will be used; one on each side (assuming a rectangular field) of the field at a distance of approximately 15 yards. The fifth sampler will be collocated at one of the sites in order to collect duplicate samples. These distances are approximate and dependent on the physical obstacles surrounding the field. As closely as feasible, the sampling media will be changed according to the schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" (ATTACHMENT II).

## B. Ambient Monitoring

Three to five samplers will be set up at various locations throughout the county. Sampling sites will be selected based upon the criteria outlined in the "Quality Assurance Plan for Pesticide Monitoring". The sites are expected to be in population centers near expected application sites. The samplers will be powered by 115VAC vacuum pumps.

Twenty-four hour samples will be taken Monday through Friday at a flow rate of approximately 15 liters per minute. Sampling will continue for 4 weeks.

## III. Analysis

The analysis will be conducted under contract by staff at the Trace Analysis Laboratory, Department of Environmental Toxicology, UC Davis. All samples will be stored in an ice chest containing dry ice or a freezer until analysis. Samples will be extracted with 75 ml of ethyl acetate and analyzed directly for dioxymeton methyl using a gas chromatograph with a nitrogen/phosphorus detector. A portion of the extract will be oxidized then analyzed in order to determine the amount of oxydemeton methyl present. The (S.O.P.) for the analysis of oxydemeton methyl and deoxydemeton methyl will be included in the final report.

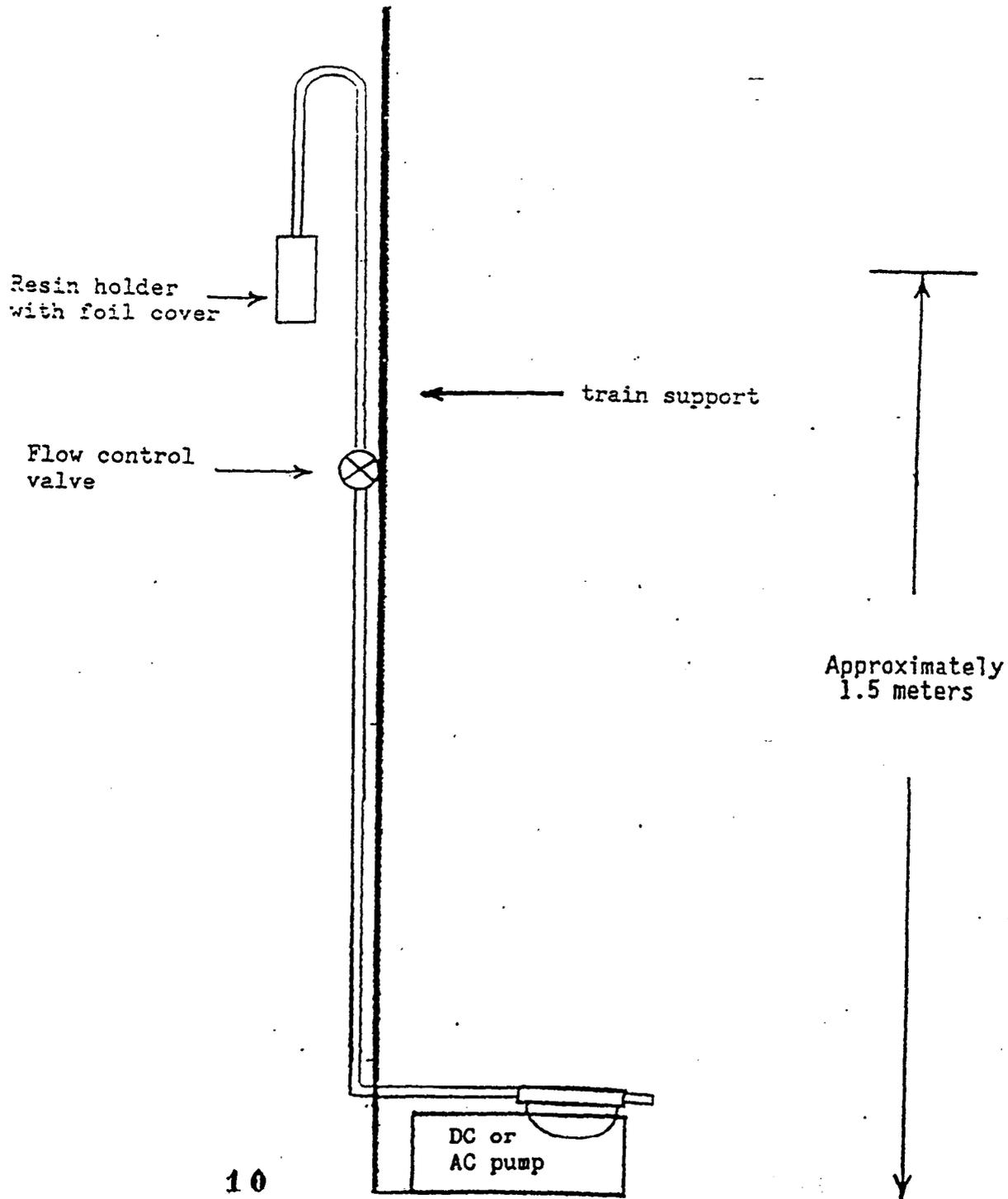
## IV. Quality Assurance

Procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring." The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Sample flow rates will be calibrated prior to and after sampling in the field.

## V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and an Instrument Technician.

ATTACHMENT I  
PESTICIDE MONITORING APPARATUS



ATTACHMENT II  
QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

State of California  
California Environmental Protection Agency  
Air Resources Board

QUALITY ASSURANCE PLAN  
FOR PESTICIDE MONITORING

Prepared by the

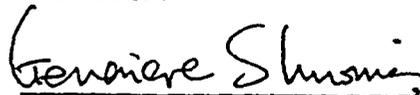
Monitoring and Laboratory Division

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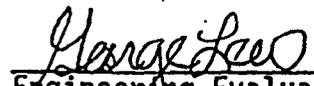
Stationary Source Division

Revised: February 4, 1994

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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) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) 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 as reliable and accurate data as possible. 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: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

### II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

### III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

#### A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present 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.

#### B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

#### C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

#### D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

#### E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

#### F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

#### G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

#### H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

#### I. Preventative Maintenance

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.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

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

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

#### IV. Protocol

Prior to conducting any pesticide monitoring, a 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.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. 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.

#### V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

##### A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

#### 1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

#### 2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

#### 3. Calibration Procedures

The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

#### 4. Quality Control

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). 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.

## VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used 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). 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. 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; however, the minimum and maximum concentrations possible for that sample should also be presented.

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

Final reports of all monitoring are sent to the Department of Pesticide Regulation, 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 Evaluation 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). 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.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. 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 II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

### C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, 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.

CALIFORNIA AIR RESOURCES BOARD  
 MONITORING & LABORATORY DIVISION  
 P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: \_\_\_\_\_ Date: \_\_\_\_/\_\_\_\_/\_\_\_\_  
 Sample/Run #: \_\_\_\_\_ Time: \_\_\_\_\_  
 Job name: \_\_\_\_\_  
 Sample Location: \_\_\_\_\_  
 Type of Sample: \_\_\_\_\_  
 Log #'s: \_\_\_\_\_

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
			GIVEN BY	TAKEN BY	
Sample Collected					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: \_\_\_\_\_

## APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX III  
TAL LABORATORY REPORT

**Method Development, Ambient Site and Application Site Monitoring for  
Oxydemeton-methyl in Air Samples Using XAD-4® Resin as a Trapping  
Medium**

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Gregory L. Hall

Takayuki Shibamoto

January 3, 1996

**Trace Analytical Laboratory,  
Department of Environmental Toxicology,  
University of California, Davis**

Covered Period: July 12, 1995 to December 31, 1995

Prepared for California Air Resources Board and the California Environmental Protection  
Agency

## Disclaimer

The statements and conclusions in the report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

## ABSTRACT

An analytical method utilizing gas chromatography was developed for the detection of oxydemeton-methyl and a potential transformation product, dioxydemeton-methyl, in air samples using XAD-4® resin as a trapping medium. Method recoveries for oxydemeton-methyl was  $102\% \pm 11.6\%$  and dioxydemeton-methyl  $112\% \pm 8.25\%$ . For the parent compound, trapping efficiency studies were in the range 27-45%, while the total mass recoveries were 60-80% and none was found in the backup resin trap. Trapping efficiencies for both compounds demonstrated that a limit of quantitation of  $12 \text{ ng/m}^3$  for both oxydemeton-methyl and dioxydemeton-methyl is possible when using flow rates of 15 liters per minute, and sampling periods of 24 hours. A 29-day freezer storage stability study was conducted indicating that oxydemeton-methyl and dioxydemeton-methyl fortified XAD-4® resin samples were stable with negligible loss of parent or a transformation product during storage at  $-20 \text{ }^\circ\text{C}$ . This method and procedures, which are outlined herein, were applied both to ambient and application site studies.

Ambient air sampling for oxydemeton-methyl was conducted from 8/14/95 to 9/6/95 at four ambient locations in Monterey County. An urban (background) site was established in the city of Salinas. None of the sites had positive responses above the limit of quantitation for either oxydemeton-methyl or dioxydemeton-methyl. An application site was also established in Monterey County where air samples of various periods were collected during and after an application of oxydemeton-methyl. None of the application site samples had residues above the limit of quantitation for either the parent or the transformation product.

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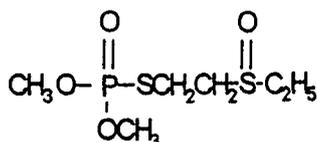
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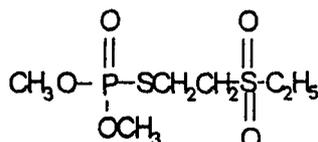
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## I. INTRODUCTION

Oxydemeton-methyl, S-[2-(ethylsulfinyl)ethyl] O,O-dimethyl phosphorothioate, Figure 1., is a systemic contact insecticide with approximately 120,000 pounds applied in the State of California during 1993 (References 1,2). Approximately one half of the total was applied to the broccoli crop group, and 20 percent was applied to cauliflower during the year.



Oxydemeton-methyl



Dioxydemeton-methyl

Figure 1. Structures for Oxydemeton-methyl and Dioxydemeton-methyl

Dioxydemeton-methyl, S-[2-(ethylsulfonyl)ethyl] O,O-dimethyl phosphorothioate, is a potential transformation product in air samples. Oxydemeton-methyl is most notably sold under the trade name of Metasystox R<sup>®</sup>. Other names include Bay 21097 and R 2170. The physicochemical properties of oxydemeton-methyl are listed in Table 1. It would be speculated that oxydemeton-methyl would be detected in air samples near application sites (point sources) but not in long-range transport (ambient) from application sites, because of the relatively low vapor pressure and high water solubility.

Table 1. Physicochemical Properties of Oxydemeton-methyl<sup>1</sup>

Chemical	Molecular Weight (g/mole)	Solubility (Water)	Vapor Pressure (kPa)	Log K <sub>(ow)</sub>	Log K <sub>(oc)</sub>
Oxydemeton	246.3	All Proportions	3.80 E-6	-1.97	1.49

<sup>1</sup> Values from reference 3

There have been numerous materials that have been employed as trapping media for the detection of pesticides in air, most significantly: polyurethane foam (PUF), ethylene glycol-impingers, charcoal, glass fiber filters (GFF), and resins. Of the resin mediums that have been used, the XAD<sup>®</sup> series of resins have proved to be the most beneficial for air sampling for pesticides, with diverse ranges of physicochemical properties, and sampling durations. XAD<sup>®</sup>-2, 4, and 7 have been preferred for use for air sampling. Of these resins, XAD-4<sup>®</sup>, a 20/50 mesh macroporous resin, whose structure is a styrene-divinylbenzene copolymer, was

## QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

### I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) 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 as reliable and accurate data as possible. 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: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

### II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

### III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

#### A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present 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.

#### B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

#### C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

#### D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

#### E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

#### F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

#### G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

#### H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

#### I. Preventative Maintenance

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.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

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

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

#### IV. Protocol

Prior to conducting any pesticide monitoring, a 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.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. 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.

#### V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

##### A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

### 1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

### 2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

### 3. Calibration Procedures

The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

### 4. Quality Control

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). 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.

## VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used 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). 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. 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; however, the minimum and maximum concentrations possible for that sample should also be presented.

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

Final reports of all monitoring are sent to the Department of Pesticide Regulation, 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 Evaluation 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). 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.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. 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 II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

### C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, 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.

CALIFORNIA AIR RESOURCES BOARD  
 MONITORING & LABORATORY DIVISION  
 P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: \_\_\_\_\_ Date: \_\_\_\_/\_\_\_\_/\_\_\_\_  
 Sample/Run #: \_\_\_\_\_ Time: \_\_\_\_\_  
 Job name: \_\_\_\_\_  
 Sample Location: \_\_\_\_\_  
 Type of Sample: \_\_\_\_\_  
 Log #'s: \_\_\_\_\_

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
			GIVEN BY	TAKEN BY	
Sample Collected					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: \_\_\_\_\_

## APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX III  
TAL LABORATORY REPORT

**Method Development, Ambient Site and Application Site Monitoring for  
Oxydemeton-methyl in Air Samples Using XAD-4<sup>®</sup> Resin as a Trapping  
Medium**

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Gregory L. Hall

Takayuki Shibamoto

January 3, 1996

**Trace Analytical Laboratory,  
Department of Environmental Toxicology,  
University of California, Davis**

Covered Period: July 12, 1995 to December 31, 1995

Prepared for California Air Resources Board and the California Environmental Protection  
Agency

## Disclaimer

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## ABSTRACT

An analytical method utilizing gas chromatography was developed for the detection of oxydemeton-methyl and a potential transformation product, dioxydemeton-methyl, in air samples using XAD-4<sup>®</sup> resin as a trapping medium. Method recoveries for oxydemeton-methyl was 102% ± 11.6% and dioxydemeton-methyl 112% ± 8.25%. For the parent compound, trapping efficiency studies were in the range 27-45%, while the total mass recoveries were 60-80% and none was found in the backup resin trap. Trapping efficiencies for both compounds demonstrated that a limit of quantitation of 12 ng/m<sup>3</sup> for both oxydemeton-methyl and dioxydemeton-methyl is possible when using flow rates of 15 liters per minute, and sampling periods of 24 hours. A 29-day freezer storage stability study was conducted indicating that oxydemeton-methyl and dioxydemeton-methyl fortified XAD-4<sup>®</sup> resin samples were stable with negligible loss of parent or a transformation product during storage at -20 °C. This method and procedures, which are outlined herein, were applied both to ambient and application site studies.

Ambient air sampling for oxydemeton-methyl was conducted from 8/14/95 to 9/6/95 at four ambient locations in Monterey County. An urban (background) site was established in the city of Salinas. None of the sites had positive responses above the limit of quantitation for either oxydemeton-methyl or dioxydemeton-methyl. An application site was also established in Monterey County where air samples of various periods were collected during and after an application of oxydemeton-methyl. None of the application site samples had residues above the limit of quantitation for either the parent or the transformation product.

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## I. INTRODUCTION

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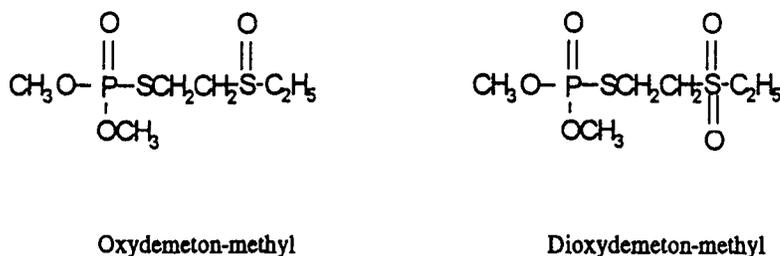


Figure 1. Structures for Oxydemeton-methyl and Dioxydemeton-methyl

Dioxydemeton-methyl, S-[2-(ethylsulfonyl)ethyl] O,O-dimethyl phosphorothioate, is a potential transformation product in air samples. Oxydemeton-methyl is most notably sold under the trade name of Metasystox R<sup>®</sup>. Other names include Bay 21097 and R 2170. The physicochemical properties of oxydemeton-methyl are listed in Table 1. It would be speculated that oxydemeton-methyl would be detected in air samples near application sites (point sources) but not in long-range transport (ambient) from application sites, because of the relatively low vapor pressure and high water solubility.

Table 1. Physicochemical Properties of Oxydemeton-methyl<sup>1</sup>

Chemical	Molecular Weight (g/mole)	Solubility (Water)	Vapor Pressure (kPa)	Log K <sub>(ow)</sub>	Log K <sub>(oc)</sub>
Oxydemeton	246.3	All Proportions	3.80 E-6	-1.97	1.49

<sup>1</sup> Values from reference 3

There have been numerous materials that have been employed as trapping media for the detection of pesticides in air, most significantly: polyurethane foam (PUF), ethylene glycol-impingers, charcoal, glass fiber filters (GFF), and resins. Of the resin mediums that have been used, the XAD<sup>®</sup> series of resins have proved to be the most beneficial for air sampling for pesticides, with diverse ranges of physicochemical properties, and sampling durations. XAD<sup>®</sup>-2, 4, and 7 have been preferred for use for air sampling. Of these resins, XAD-4<sup>®</sup>, a 20/50 mesh macroporous resin, whose structure is a styrene-divinylbenzene copolymer, was

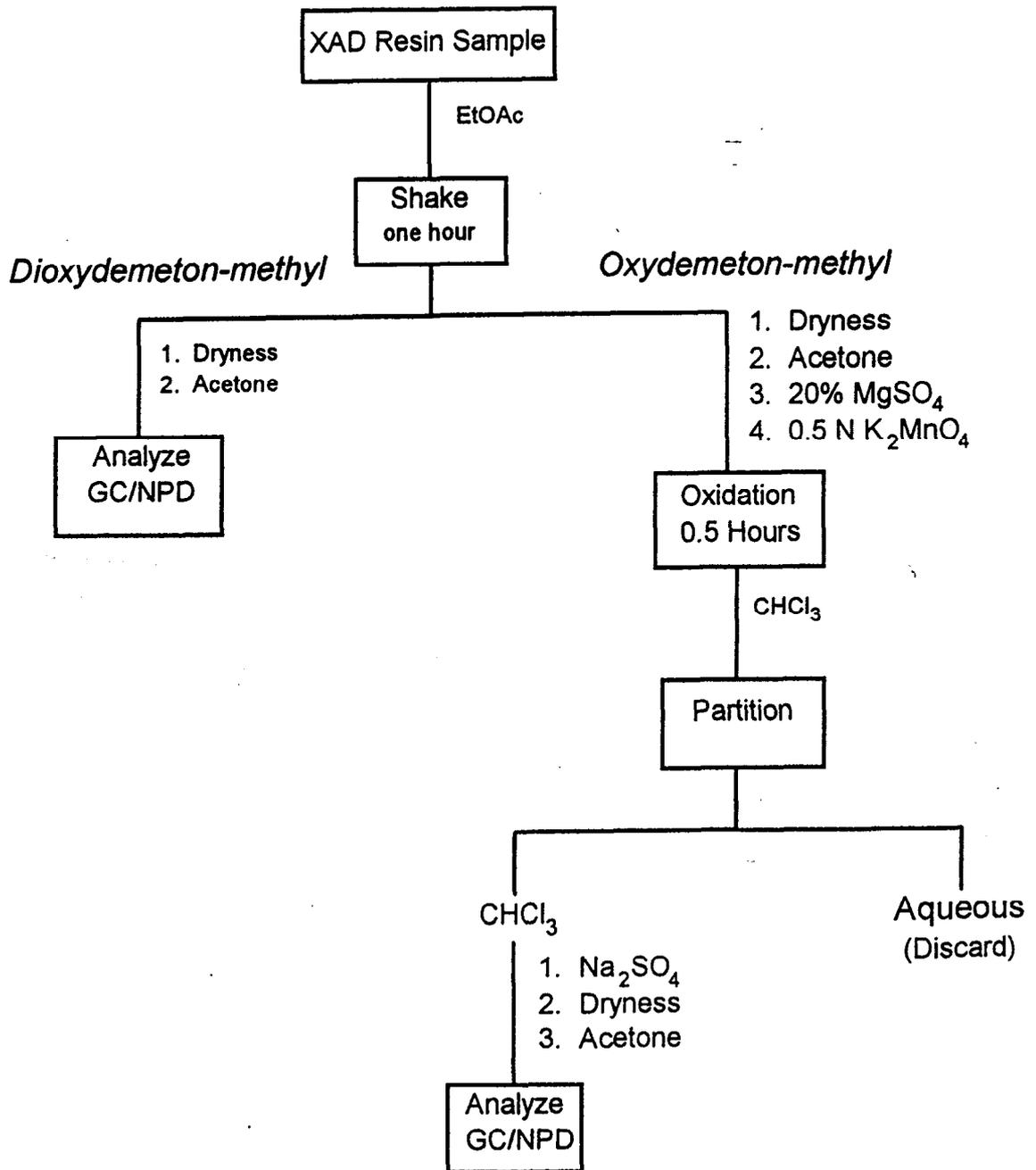
selected because of its high surface area, bulk price and ability for trapping chemicals for long periods of sampling.

An analytical method for oxydemeton-methyl was adapted from a procedure used for agricultural crop residue analysis (Reference 4). The amount of metabolite was determined by using a gas chromatograph with a nitrogen/phosphorus detector. The sample was converted by oxidization, and the total amount of combined metabolite was determined as before. The amount of parent was calculated as the difference between the oxidized and unoxidized sample. A schematic of the analytical scheme for the analysis of oxydemeton-methyl and dioxydemeton-methyl is given in Figure 2.

The objective of the current study is to provide the California Air Resources Board with an easy, rapid, sensitive and effective analytical method for the detection of oxydemeton-methyl and its transformation product, dioxydemeton-methyl, in air samples from communities that are located near agricultural areas, for sampling periods of up to 24 hours and analysis of ambient and application site samples.

This report addresses five key areas of the oxydemeton-methyl project: 1) Development of an analytical method, 2) trapping efficiencies of air samples using XAD-4 as a trapping medium, 3) ambient site sampling for oxydemeton and its transformation product, 4) analysis of samples from an application site, and 5) quality assurance samples from the Air Resources Board Quality Assurance unit.

**Figure 2. Method Schematic of Analysis for Oxydemeton-methyl**



## II. ANALYTICAL METHOD

### Literature Review

A computer-aided literature search for air sampling and analytical methodology was done for oxydemeton-methyl and dioxydemeton-methyl. The resulting references generated by the computer search of Chemical Abstracts were assessed for any applicable methodology that may pertain to oxydemeton-methyl and dioxydemeton-methyl analysis. Files maintained in the laboratory were reviewed for pertinent methodological information. Notebooks and files on previous projects referenced by pesticide in the Trace Analytical Laboratory (TAL) were assessed, as well as those files maintained by the Environmental Toxicology Documentation Center, and were evaluated for relevant information and articles.

A list of materials used in the analytical methodology is given in Appendix A.

### Method Principle

Oxydemeton-methyl, like most agrochemicals that have sulfoxide functional groups, is thermally labile to most gas chromatographic conditions. Therefore, the common procedure is to convert sulfoxides to the corresponding sulfones, which are stable to analytical conditions, and the compound of interest is analyzed as the sulfone. The method employed here involves a two-step process of first analyzing an aliquot directly as dioxydemeton-methyl (sulfone of the parent), which may be present as a transformation product of oxydemeton-methyl, and then oxidizing a second aliquot of the air sample that may contain oxydemeton-methyl, with potassium permanganate, to dioxydemeton-methyl. The amount of oxydemeton-methyl present in samples may be determined by subtracting the amount of dioxydemeton-methyl in the non oxidized sample from the total amount found in the oxidized sample. A correction for the difference in molecular weight between oxydemeton-methyl and dioxydemeton-methyl must be made.

### Analytical Standards

Analytical standards of oxydemeton-methyl, (Chem Services reference number: 136-151A, 95.0% pure) and dioxydemeton-methyl (Chem Services reference number: 151-146B, 99% pure) for use in analysis were obtained from Chem Service (one gram each). Shipment of the standards was via Federal Express overnight service to minimize potential breakdown of standards. Standards were received in July 1995 and were logged into TAL's analytical standard repository. Neat standards were kept at -20 °C until the time of use. Stock solutions, 100 mL each, 1.0 mg/mL concentrations, were prepared using pesticide grade ethyl acetate and kept at 4 °C until the time of use. Dilute spiking and analysis standards were prepared from these stock solutions using pesticide grade acetone.

## Trapping Medium

XAD-4® resin (Rohm and Haas, through Supelco), a macro reticular resin, was employed as the trapping medium for oxydemeton-methyl and its transformation product. XAD-4® along with XAD-2® has been used extensively for air sampling of pesticides for sampling periods as great as 24 hours (References 5, 6). XAD-4® resin was prepared prior to use as described in Appendix B.

## Analytical Method

### Laboratory Fortifications

With each set of samples, laboratory spikes were done in triplicate as outlined below.

### Extraction

In separate experiments, 5.0 µg of oxydemeton-methyl or dioxydemeton-methyl, in triplicate, was added to 30 mL of resin with a 25 µL syringe and the solvent was allowed to evaporate. 75 mL of pesticide grade ethyl acetate (ca 1.5 bed volumes) was added to resin sample jars and the jars were swirled for one hour at moderate speed, using a rotary platform shaker.

### Evaporation

One fourth of the extract was quantitatively transferred to an appropriate size round bottom flask (50 or 100 mL) and concentrated just to dryness via rotor-evaporator with a water bath at approximately 40 °C. Two to four mL of acetone was added, to alleviate any residual ethyl acetate, and the sample was again evaporated to dryness. The sample volume was adjusted with acetone, and the dioxydemeton-methyl was analyzed.

### Oxidation

A second aliquot, one fourth of the sample, was evaporated to dryness and 2 mL of acetone was added to each flask and swirled. Samples were oxidized to dioxydemeton-methyl by first adding 5 mL of 20% magnesium sulfate followed by 20 mL of 0.5 N potassium permanganate. Samples were periodically swirled for 30 minutes. The oxidized samples were transferred to 125 mL separatory funnels and partitioned three times with pesticide grade chloroform. The organic layer (bottom layer) was dried with anhydrous sodium sulfate and drained into 50 or 100 mL round bottom flasks. The sodium sulfate was rinsed with an additional 5 mL of chloroform. Samples were taken to dryness, rinsed with acetone, taken to dryness and brought up in 2.0 mL acetone.

### Method Notes:

- 1) It is important that potassium permanganate persist for the duration of the 30 minute oxidation period.
- 2) The concentration of manganese dioxide, in some samples, will be sufficient enough to make it difficult to see the phase separation and caution will need to be taken when draining the organic layer from the separatory funnel so as to not introduce the aqueous layer into the round bottom flask.
- 3) In some cases, the addition of 10-15 mL of chloroform will be needed to make the aqueous and organic phases separate.
- 4) All traces of the chloroform solvent used in the partition step must be removed during evaporation or else the effect on the N/P detector will be detrimental causing an erratic baseline and poor quantitation.

### Analysis

A Hewlett Packard (HP) model 5890A gas chromatograph equipped with a nitrogen-phosphorus (N/P) detector and a HP-GC System Injector-autosampler were used to quantitate dioxymeton-methyl. The detector was modified with a ceramic bead rather than the standard rubidium sulfate bead found in nitrogen/phosphorous detectors, to increase stability and sensitivity. The column used was a 0.53 mm (i.d.) X 30 m XTI-5 wide bore capillary column (1.5 micron film) (Restek Scientific). The voltage for the bead was adjusted to provide a minimum quantified amount of 0.094 ng of standard. Data acquisition was accomplished via a TurboChrom® (version 4.1) data station (Perkin Elmer) and data reductions of the results were performed using an EXCEL® (Version 5, Microsoft) spreadsheet program and macro. Note that there can be small discrepancies (< 1%) between averages calculated manually from the tabulated data due to rounding errors. Parameters for the analytical instrumentation are listed in Table 2.

Table 2. Gas Chromatograph Instrument Parameters

Injector Temp	Detector Temp	Column Temperature (°C)			Flow Rates (ml/min)			
		Initial	Rate	Final	Carrier	Make up Air	Hydrogen	
250 °C	280 °C	200	0	200	20	10	110	3.5

Analysis of samples was quantified by using a 4-point external linear regression standard curve for dioxymeton-methyl. Each sample was injected twice and standard(s) were interdispersed between samples during each analysis (set). The average of both analyses was reported.

## Recoveries

Preliminary recovery data was generated by fortifying three replicates each of the XAD-4 resin with oxydemeton-methyl or dioxydemeton-methyl. All replicates were fortified with 5.0  $\mu\text{g}$  of either compound. Samples were extracted and one-fourth of each sample was analyzed without oxidation while a second quarter of the sample underwent oxidation with potassium permanganate. The oxidized samples were analyzed as dioxydemeton-methyl. Method recoveries for both oxydemeton-methyl and dioxydemeton-methyl are given in Table 3. The average recovery for dioxydemeton-methyl was 108 percent while the average recoveries for oxidized oxydemeton-methyl and dioxydemeton-methyl were 102 and 112 percent, respectively.

**Table 3. Recovery Data for non-Oxidized and Oxidized Oxydemeton-Methyl**

	Replicate (Percent Recovery)			Average	Std. Dev.
	1	2	3		
Non-Oxidized DODM <sup>1</sup>	108	105	112	108	3.6
Oxidized ODM <sup>2</sup>	91	100	114	102	11.6
Oxidized DODM	120	104	112	112	8.25

1: DODM = dioxydemeton-methyl. 2: ODM = oxydemeton-methyl.

## Storage Stability

A 29-day storage stability study was initiated for both oxydemeton-methyl and dioxydemeton-methyl on July 19, 1995. A total of 24 samples (30 mL resin each) were prepared: 12 fortified with 50  $\mu\text{g}$  of oxydemeton-methyl and 12 fortified with 50  $\mu\text{g}$  of dioxydemeton-methyl. All samples were stored at -20 °C for 29 days. Eight of the replicates, four oxydemeton-methyl and four dioxydemeton-methyl samples, were extracted and analyzed on August 17, 1995. The average recovery for oxydemeton-methyl was 93 percent and dioxydemeton-methyl was 102 percent. The results for all replicates, averages and standard deviations are listed in Table 4 (See note page 6).

**Table 4. Storage Stability Results for Oxydemeton-methyl and Dioxydemeton-methyl**

	Replicate (Percent Recovery)				Average	Std. Dev.
	1	2	3	4		
Oxydemeton-methyl	88	95	97	92	93	3.9
Dioxydemeton-methyl	100	106	101	102	102	2.5

## Quality Assurance

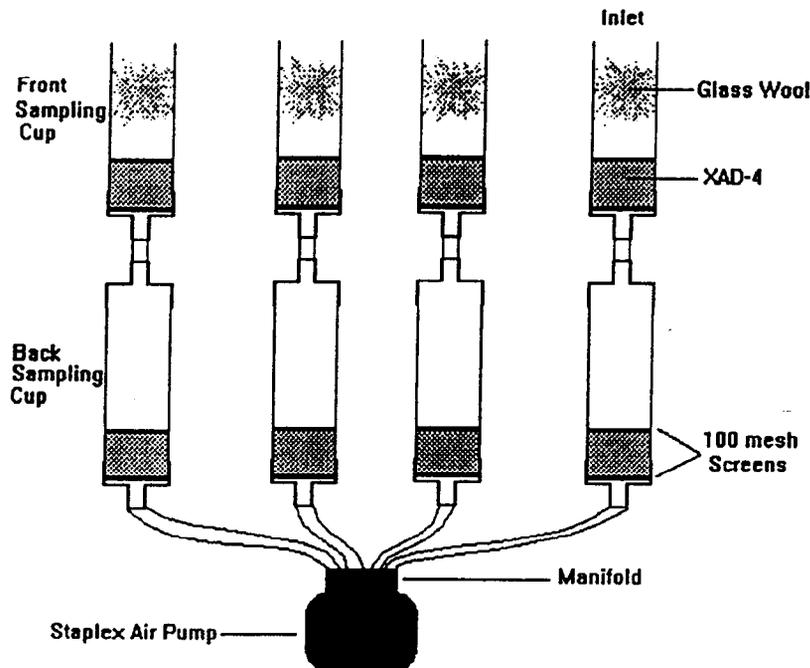
While it was not a requirement to follow strict Good Laboratory Practices (GLP) guidelines, quality assurance was kept at a maximum to keep the integrity of the project. Controls (checks, blanks) and fortifications of controls were run with every set. Documentation for the project was at a maximum, including the use of notebooks, instrument logbook and/or computer spreadsheets. All of the necessary components were in place to assure that the study would be reconstructible, a prime requisite for a GLP study.

### III. TRAPPING EFFICIENCIES

#### Apparatus

The apparatus used for trapping efficiencies consisted of two 12 cm x 4 cm (i.d.) Teflon® cartridges (cups), (Savillex Corp). The resin was held in place by installing 100-mesh stainless steel screens on each side of the resin inside each cup. The cups were connected in series via a Teflon® tube (Figure 3) with the top cup the primary trap and the bottom the backup. Traps were attached to a six m x 1.2 cm diameter lab rack that made the height of the sampling cups approximately 1.7 m above the sampling surface. The traps were adapted with Tygon® tubing (1 cm i.d. x 1 mm wall x 1.25 cm o.d.) and connected the apparatus to a Staplex high volume air sampler fitted with a 5-port manifold. With this configuration, the flow rate for two traps in tandem will be between 25-35 lpm. If there is only a primary trap, the air flow range through the samplers would be 50 to 100 liters per minute (lpm). The exact flow rate will depend on how many ports are being used in the manifold, the volume of resin used and the length of the Tygon® tubing.

Figure 3. Trapping Efficiency Apparatus



## Procedure

Each cartridge was charged with 30 mL of XAD-4 resin, a top Teflon® retainer was added to form a sandwich and keep the resin from "vortexing" and thus causing a build up of resin on the sides and a thin bed in the center ("dishing" effect). The backup trap was then attached to the primary trap. The backup trap also contained a 30-mL resin sandwich. Acetone washed glass wool was placed above the resin-sandwich in the primary cup and the wool was spiked with either 50 µL of oxydemeton-methyl or dioxydemeton-methyl using a 1.00 µg/µL solution. The solvent was allowed to evaporate for five minutes before turning on the air pumps, so that only the compound of interest remained. Flow rates were measured at the beginning and end of each sampling period.

For oxydemeton-methyl, two concurrent trapping experiments were run on the roof of the Environmental Toxicology building during July. The experiments consisted of the following: experiment a: three air samplers fortified with 50 µg each of oxydemeton-methyl and experiment b: three air samplers with 50 µg each of dioxydemeton-methyl. Each experiment had its own blank (control) sampler consisting of glass wool, primary and backup traps with XAD resin but no compound. Each experiment was run for a 12 hour period. Near the end of the sampling period, one of the replicates was heated for 30 minutes with a heat gun with estimated temperatures of 250 °F for 15 minutes then 160 °F for 15 minutes. The resin samples were extracted and analyzed as previously described. The glass wool was extracted by swirling with ethyl acetate. A second set of trapping experiments were initiated on July 28th. These were also twelve hour runs with the same mass applied to the glass wool. While no meteorological parameters were recorded during these experiments, the local afternoon temperature was above 37 °C during the second set of experiments. This would imply that the roof temperature would be above 40 °C and would provide the optimal conditions for the volatilization of oxydemeton-methyl and dioxydemeton-methyl from the glass wool. The trapping efficiency can be calculated using the following equation:

$$\text{trapping efficiency} = \frac{\text{Amount trapped} \times 100}{(\text{amt. spiked} - \text{amt. recovered on glass wool}) \times \text{Lab Recovery}}$$

where the amount that actually volatilized is the original amount spiked on the glass wool minus the amount found on the glass wool after the experiment is completed. Note that in this study, an adjustment for "Lab Recovery" was not necessary, since the laboratory recoveries were greater than 95%.

## Results

The results of each of the replicates for the first trapping is given in Table 5 and the individual results for the second experiment is given in Table 6. Upon visual inspection of these results it can be seen that: 1) oxydemeton-methyl is relatively non-volatile, even under the most adverse conditions of an estimated maximum roof temperature of 40 °C and 2) only approximately 45 percent of the amount that is volatilized is actually trapped on the primary resin. There was no breakthrough in any of the replicates to the backup trap.

Seiber *et al* in 1989, encountered similar problems with methyl parathion when using the same trapping procedures (Reference 6). Methyl parathion trapping efficiencies were approximately 50% during this study. Trapping efficiencies were done on a daily basis, on a roof top, during the 1987 rice application season. These results were similar to those found for both oxydemeton-methyl and dioxydemeton-methyl. It should also be pointed out that, for compounds with low vapor pressure and high water solubility, there is a large degree of error when only a small amount of material volatilizes from the glass wool (Reference 7).

Furthermore, during a prior ARB air sampling study for the cotton defoliant DEF, The trapping efficiency determined was 60% (Reference 8). DEF, a non-polar organophosphate, would be expected to give a higher trapping efficiency due to its higher vapor pressure.

However, an detailed explanation describing possible routes of the loss of material is beyond the scope of this project contract.

**Table 5. Trapping Efficiencies Results, Experiment 1<sup>A</sup>**

Sample (50µg)	Glass Wool (µg)	Primary (µg)	Backup (µg)	Trapping Efficiency (%)	Total Mass Recovery <sup>B</sup> (%)
Oxydemeton-methyl Rep 1	35.6	4.43	< 0.50	31	80
Oxydemeton- methyl Rep 2	42.5	1.70	< 0.50	23	88
Oxydemeton-methyl Rep 3	30.1	5.63	< 0.50	28	71
Dioxydemeton-methyl Rep 1	33.6	1.90	< 0.50	12	71
Dioxydemeton-methyl Rep 2	39.7	2.05	< 0.50	20	83
Dioxydemeton-methyl Rep 3	51.8	3.83	< 0.50	0	111

A: Roof temperature projected to be ca 32 °C maximum; Sampling period: 12 hours.

B: Total mass recovery = [(Glass wool + Primary + Backup)\*100]/50

**Table 6. Trapping Efficiencies Results, Experiment 2<sup>A</sup>**

Sample (50µg)	Glass Wool (µg)	Primary (µg)	Backup (µg)	Trapping Efficiency (%)	Total Mass Recovery <sup>B</sup> (%)
Oxydemeton-methyl Rep 1	15.6	15.0	< 0.50	44	61
Oxydemeton- methyl Rep 2	15.1	13.7	< 0.50	39	58
Oxydemeton-methyl Rep 3	19.3	14.9	< 0.50	49	69
Oxydemeton-methyl Rep 4 (heat)	3.43	22.4	< 0.50	48	52
Dioxydemeton-methyl Rep 1	41.9	11.7	< 0.50	140	107
Dioxydemeton-methyl Rep 2	42.3	11.5	< 0.50	150	108
Dioxydemeton-methyl Rep 3	43.4	15.5	< 0.50	230	118

A: Roof temperature projected to be ca 40 °C maximum; Sampling period: 12 hours.

B: Total mass recovery = [(Glass wool + Primary + Backup)\*100]/50

## IV. AMBIENT AIR SAMPLING

### Sampling Sites and Apparatus

Five ambient air sampling sites were established in Monterey County, on the central coast of California, by ARB personnel. The locations of all of the sites were along the Highway 101 corridor (Figure 4). Sites consisted of four ambient sampling sites and an urban background site. Locations established included: Prunedale, at the Prunedale school maintenance yard; Salinas, at the La Joya School; Chualar, at the Chualar School; Soledad, at the California Department of Forestry Fire Station and Greenfield, at the Greenfield School district Maintenance yard. Each site established was chosen due to the proximity of agricultural use and potential oxydemeton-methyl (Metasystox R<sup>®</sup>) use, as well as criteria established for collection of air samples.

The sampling apparatus consisted of a motorized pump, and tubing connected to Teflon cups that were charged with 30 mL of XAD-4 resin. All sites were installed with primary samplers only and samplers had average flow rates approximately 15 lpm, while sampling durations were on the order of 24 hours. For three of the four sites, one sample was taken at each site, for each period, for the duration of the project. The fourth site had a second replicate sampler. The replicate site was kept at one location for a week and then moved to another site during the project. ARB personnel were responsible for all air sampling including set up, sampling procedures and sample shipment to the laboratory.

Sampling commenced on 8/14/95 and concluded on 9/8/95. Each week, with the exception of the last week, had four 24-hour sampling periods. The final week had three days due to the Labor Day holiday. All samples were kept in the field until the time of delivery to TAL personnel. Samples, for the most part, were received on Friday afternoons and worked up that evening and analyzed within 24 hours of extraction.

### Sample Storage and Shipment

All samples were kept on dry ice until the time of transport to the laboratory. Samples were boxed and placed in ice chests packed with dry ice and transported directly to the laboratory at the end of the week (Friday) by ARB personnel. The exception was that the third week of samples, which were kept at the ARB facility until Saturday morning, where upon they were transported to the TAL Laboratory.

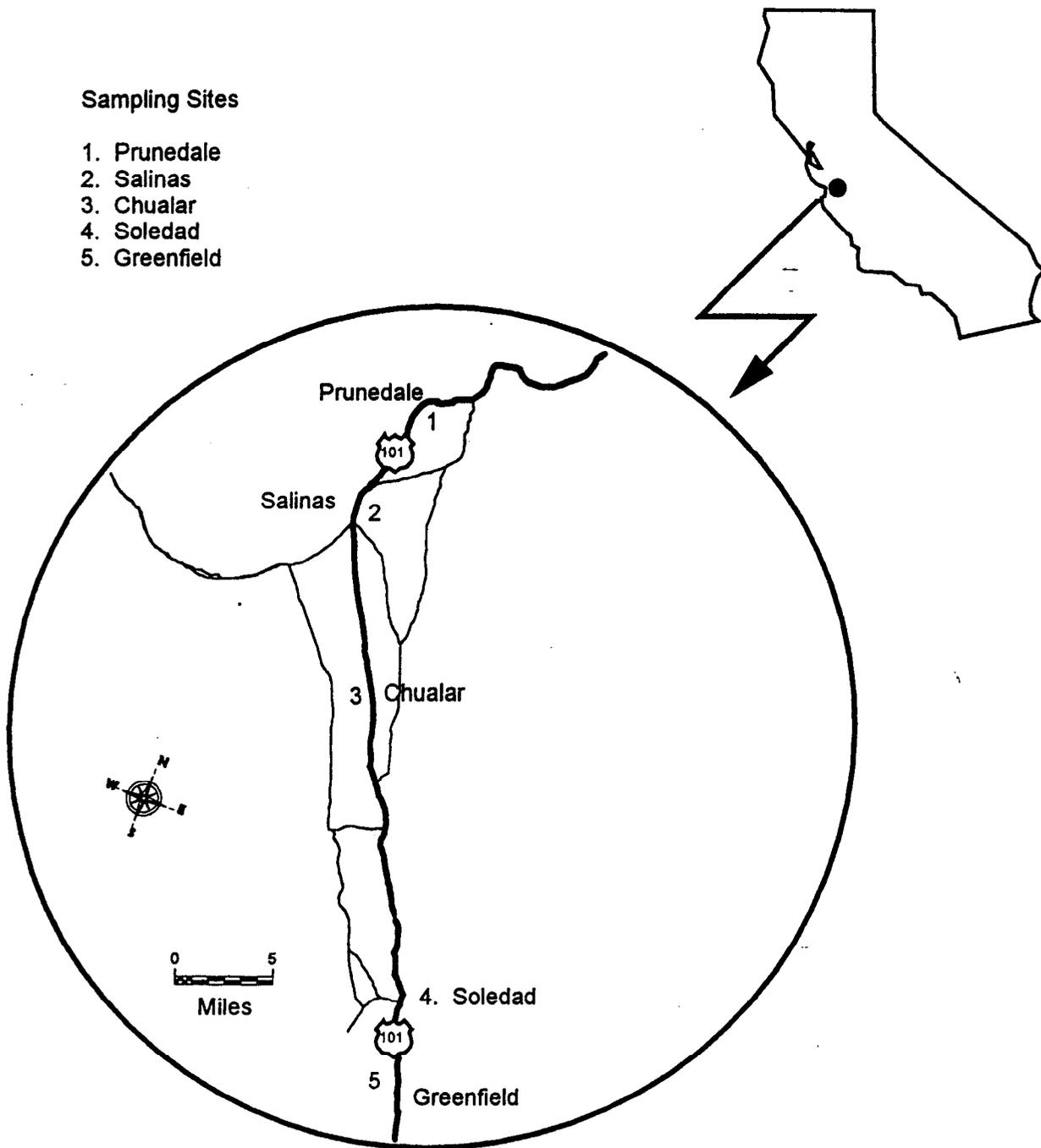
### Analysis

Upon receipt of the samples, samples were logged into an Excel spreadsheet and the sample jar labels were checked against the chain of custody. Laboratory fortification samples, in triplicate, were prepared by adding 30 mL of XAD-4 resin to the same type of jars that the ambient samples were in. Laboratory fortifications ranged from 1.0 to

**Figure 4. Location of Ambient Sites**

**Sampling Sites**

- 1. Prunedale
- 2. Salinas
- 3. Chualar
- 4. Soledad
- 5. Greenfield



2.5 µg/sample each for oxydemeton-methyl and dioxydemeton-methyl. All samples were extracted and worked up within 12 hours of receipt. The analysis for dioxydemeton-methyl was completed within 24 hours of sample receipt and the oxydemeton-methyl analysis was completed within 48 hours of sample receipt. Each sample set had one field blank and three laboratory resin fortifications.

## Results

For all sites, there were no detectable residues above the limit of quantitation (LOQ - 0.25 µg/sample) for either oxydemeton-methyl or dioxydemeton-methyl at any of the ambient sites during the study period. Table 7 has the results for the concurrent laboratory resin fortification samples run with each set of ambient samples.

## Quality Assurance

All fortified XAD-4 resin laboratory validation samples gave reasonable recoveries for both oxydemeton-methyl and dioxydemeton-methyl. The recovery for oxydemeton-methyl laboratory/ambient validation samples was from 66% to 116% with an average recovery of 99.8% and a standard deviation of 15.3% (n = 12). For dioxydemeton-methyl the laboratory/ambient recovery range was from 99% to 135% with an average recovery of 122% with a standard deviation of 10.0% with (n = 12). The results of all laboratory validation samples, listed by week, are given in Table 7 and in Appendix E.

**Table 7. Concurrent Fortification Results**

Week #	Fort. Level (µg)	Oxydemeton-methyl (Percent Recovery) (Replicate)					Dioxydemeton-methyl (Percent Recovery) (Replicate)				
		1	2	3	Avg	Std D.	1	2	3	Avg	Std D.
1	1.0	79	107	102	96	14.8	122	99	122	114	13.2
2	2.5	111	67	89	89	22.2	110	127	115	118	8.95
3	1.0	116	109	92	106	12.3	133	135	128	132	3.8
4	1.0	93	112	115	107	12.2	123	124	127	125	2.31

All of the recovery data were well within an acceptable range for this study. The dioxydemeton-methyl recovery values may be 5 to 10% higher than actual due to the presence of dioxydemeton-methyl in the oxydemeton-methyl fortification standard.

## V. APPLICATION SITE

### Location

An application site was selected for monitoring the following week after the completion of the ambient site study. The criterion used was the first available application that was compatible with ARB field personnel. The location of the site was northwest of the City of Salinas in Monterey County. Approximately 14 acres was applied with oxydemeton-methyl at a rate of 0.25 quart active ingredient/acre. The chemical was applied via a ground application on 9/12/95. The application took approximately one hour to complete.

### Field Spikes

Eight field spikes (trip spikes) were prepared by fortifying four 30-mL resin blank samples with 1.0  $\mu\text{g}$  of oxydemeton-methyl and four 30-mL resin blank samples with 1.0  $\mu\text{g}$  of dioxydemeton-methyl. Samples were placed on dry ice and picked up by ARB personnel on 9/8/95. Samples were kept on dry ice and transported to the application site area. The field spikes were sent back to the laboratory for analysis along with the first and second period application samples on 9/13/95.

### Application Site Procedures

The following sampling periods were set up by ARB personnel to monitor the application site. Each period had four sampling points placed around the field at the northwest, southwest, southeast and east compass points. There were a total of seven periods of sampling for various durations plus a background or control sampling prior to the application. Three of the four sites had a single non-replicated sampler while at the fourth site duplicate samplers were installed. Table 8 has a list of proposed sampling period and durations. A total of 41 application site samples were taken over the three day period.

### Results

#### Application Site Samples

None of the samples had masses (residues) for either oxydemeton-methyl or dioxydemeton-methyl above the limit of quantitation (LOQ - 0.25  $\mu\text{g}/\text{sample}$ ). There were only a few of the application site samples that had responses above the limit of detection (LOD - 0.05  $\mu\text{g}/\text{sample}$ ) but less than the LOQ. Oxydemeton-methyl had a maximum trace residue during the application sampling period (period 1) at the southwest site. The next highest residue was during the fifth period at the southeast site. In all, 14 of the 41 samples had oxydemeton-methyl residues at or above the limit of detection. There were no residues of dioxydemeton-methyl detected until the 24-hour

**Table 8. Sampling Periods for the Application Site.**

Period	Duration	Date	Sample Duration
0	12 hr max	9/12/95	Background Air Sampling Prior to Application
1	Application	9/12/95	During application and 1 hour after completion
2	2 hr	9/12/95	2 hr sample starting 1 hr after application completion
3	4 hr	9/12/95	4 hr sample starting 3 hr after application completion
4	ca 12 hr	9/12/95	sample for 12 hr. starting 7 hr after application completion
5	ca 12 hr	9/13/95	sample for 12 hr. Starting 19 hr after application completion
6	24 hr	9/14/95	sample for 24 hr approximately 1 day after application completed
7	24 hr	9/15/95	sample for 24 hr approximately 2 days after application completed

sampling periods. The highest residue found (trace) for dioxydemeton-methyl was during the second 24-hour period (period 7) at the southeast site. There were only four samples that gave residues above the detection limit for dioxydemeton-methyl. Samples that have values less than the limit of quantitation but greater than the limit of detection are only estimates of residues. Chromatograms from the application site may be found in Appendix F.

**Table 9. Laboratory Fortification Results for Application Site**

Sample ID	Spike Level	Oxydemeton-methyl ( $\mu\text{g}$ )	Dioxydemeton-methyl ( $\mu\text{g}$ )	Oxydemeton-methyl (Percent Recovery)	Dioxydemeton-methyl (Percent Recovery)
2.5R7	2.5 $\mu\text{g}$	2.17	2.76	87	110
2.5R8	2.5 $\mu\text{g}$	1.63	3.59	65	144
2.5R9	2.5 $\mu\text{g}$	1.87	3.36	75	134
0.25R1	0.25 $\mu\text{g}$	0.30	0.30	122	121
0.25R2	0.25 $\mu\text{g}$	0.22	0.36	86	144
0.25R3	0.25 $\mu\text{g}$	0.33	0.31	133	122

## Field Spike Results

The results for the eight individual field spikes (trip spikes) are given in Table 10. The percent average recovery for the four oxydemeton-methyl samples was 113% with a standard deviation of 5.5% while the percent recovery for dioxydemeton-methyl was 124% and a standard deviation of 8.7%.

**Table 10. Application Site Field Spike Results ( $\mu\text{g}/\text{sample}$ )**

Sample ID	Compound/ Spike Level	Oxydemeton- methyl	Dioxydemeton- methyl	Percent Recovery
1.0R7	Oxy-d/ 1.0 $\mu\text{g}$	1.09 $\mu\text{g}$	T <sup>1</sup>	109
1.0R8	Oxy-d/ 1.0 $\mu\text{g}$	1.10 $\mu\text{g}$	T	110
1.0R9	Oxy-d/ 1.0 $\mu\text{g}$	1.21 $\mu\text{g}$	T	121
1.0R10	Oxy-d/ 1.0 $\mu\text{g}$	1.12 $\mu\text{g}$	T	112
1.0R11	Dioxy-d/ 1.0 $\mu\text{g}$	n.d.	1.18 $\mu\text{g}$	120
1.0R12	Dioxy-d/ 1.0 $\mu\text{g}$	n.d.	1.18 $\mu\text{g}$	120
1.0R13	Dioxy-d/ 1.0 $\mu\text{g}$	n.d.	1.26 $\mu\text{g}$	130
1.0R14	Dioxy-d/ 1.0 $\mu\text{g}$	n.d.	1.36 $\mu\text{g}$	140

1: T = Trace amount detected.

## VI. ARB QUALITY ASSURANCE

### Procedures

The quality assurance unit of ARB brought over a batch of samples for analysis. These samples were analyzed using the same procedures and method as outlined in the method section of this report. Samples arrived on 8/17/95 and were analyzed within 48-hours.

### Results

The results of the analysis from the initial samples submitted indicated that the values were less than the ARB fortified values. Subsequent ARB samples / standards were compared with TAL standards and inconsistencies were found. After further investigation, the problem was traced to the fact that the initial ARB standard, prepared in isooctane by Chem Service, was at fault. To prove this, TAL personnel weighed out a comparable standard in isooctane as was prepared by Chem Services personnel. The oxydemeton-methyl did not dissolve in the isooctane, even after sonification for a period of time. The conclusion was that oxydemeton-methyl is insoluble or only slightly soluble in isooctane in a very low concentration (less than 30 ng/ $\mu$ L).

However, phone conferences with Chem Service and TAL personnel indicated that Chem Service did not fully understand the importance of using a comparable solvent with polar compounds such oxydemeton-methyl.

Results of ARB's Quality Assurance audit samples are given in Table 11. These results are from a second batch of fortifications with an analytical standard that was made up by TAL personnel.

**Table 11. ARB's Quality Assurance Audit Samples Results (Total  $\mu$ g Found)<sup>1</sup>**

Sample ID	Oxydemeton- methyl			Dioxydemeton- methyl		
	Found ( $\mu$ g)	Amount Spiked	Percent Recovery	Found ( $\mu$ g)	Amount Spiked	Percent Recovery
Oxy-11	1.21	1.25	97	<0.25	----	----
Oxy-12	<0.25	----	----	3.49	3.125	112
Oxy-13	1.16	1.25	93	<0.25	----	----
Oxy-14	0.97	1.25	78	1.53	1.25	123
Oxy-15	<0.25	----	----	3.42	3.125	109

<sup>1</sup> Oxydemeton-methyl Percent Recovery for Concurrent Laboratory Validation run with ARB's Audit spike samples were 86%, 74%, 115%; Average 91%. For dioxydemeton-methyl: 115%, 134%, 116%, average: 122%.

The analytical results compared favorably with the ARB-QA assigned values for both oxydemeton-methyl and dioxydemeton-methyl.

### Recommendations

Many difficulties arise in the preparation of analytical standards of pesticides. Some of these problems include, but not limited to, solvent solubility/compatibility, oxidation, breakdown and photo degradation. Small amounts of water in the selected solvent may cause certain standards to hydrolyze. Other solvents may cause oxidation to another compound. Some pesticides, particularly organophosphates, can breakdown in "protic" solvents, solvents such as ethanol and methanol. Even acetone has been known to cause problems with certain compounds. Another problem is a small amount of water that may hydrolyze the analytical standard over the life of a project. However, it is important that the solvent chosen is compatible with the standard and the analytical system. Above all, solubility of the compound should be noted and a solvent that is compatible with the physicochemical properties of the particular compound is selected.

## VII PROJECT CONCLUSIONS

A method for oxydemeton-methyl and its transformation product, dioxydemeton-methyl, was developed for air samples using XAD-4 as a trapping medium. Laboratory recovery data for both compounds were quantitative. The average laboratory recovery for both compounds was greater than 95%.

Results of air trapping experiments concluded the following: 1) No breakthrough was observed in the backup traps; 2) With increased air temperature, volatility and trapping efficiency increases; 3) For the parent compound, the total average mass recovered from spiked air samples ranged from 60-80%; 4) Air trapping efficiencies experiments, at optimal conditions (40 °C), concluded that approximately 44% of the potential vaporized compound would be trapped by this method, and is comparable to other compounds with similar vapor pressures and polarities.

Samples from an ambient site study, collected by ARB personnel, were analyzed within 24-hours of receipt. Only three of the samples had trace residues which were above the detection limit of 0.05 micrograms/sample at any of the five sites, for the duration of the study. Trace amounts, quantities above the limit of detection but below the limit of quantitation, of oxydemeton-methyl and dioxydemeton-methyl were found in 14 of the 41 air samples, from a commercial ground application of oxydemeton-methyl. The residues may have been higher, during and right after the application, had the application been by air.

Quality assurance was kept to a maximum during the project by running three fortifications with each set of samples analyzed. Also, the ARB Quality Assurance Unit submitted blind-fortified samples for analysis. The results of these samples were well within the acceptable range.

In conclusion, oxydemeton-methyl and/or its transformation product, dioxydemeton-methyl, is not likely to be found in significant concentrations in air due to its low vapor pressure and high water solubility (Henry's Law). Volatilization is not likely to be a significant route of exposure. However, both the ambient and application sites were located in Monterey County, California where lower average temperatures would not provide the highest potential for volatilization.

## ACKNOWLEDGMENTS

We wish to acknowledge the technical assistance of Lynn Baker, Don Fitzell, Ruth Tomlin and Jane Pettit with the California Air Resources Board, and Matthew Hengel with the Department of Environmental Toxicology for their technical assistance. This study was supported by contract funds from the California Air Resources Board. Mention of proprietary products is made for identification purposes only and does not imply endorsement by ARB.

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## APPENDICES

### Appendix A. List of Chemicals and Solutions

1. Ethyl Acetate, Ultra Resi-Analyzed grade, J. T. Baker Co., Phillipsburg, NJ
2. Acetone, Ultra Resi-Analyzed grade
3. Chloroform, ACS Certified grade, Fisher Chemical Co., Fair Lawn, NJ
4. Potassium permanganate, ACS Certified grade, Fisher Chemical Co., Fair Lawn, NJ
5. Magnesium sulfate, Analytical Reagent Grade, Malenkrodt Chemical Co, St Louis, MO
6. XAD-4 Resin, Supelco
7. General laboratory glassware.

### Oxidation Solutions:

1. 20% Magnesium Sulfate solution:  
Add 100 grams of magnesium sulfate heptahydrate to 500 mL of deionized or distilled water.
2. 0.5 N Potassium Permanganate Solution:  
Add 15.8 grams of potassium permanganate to 1000 mL of deionized or distilled water.

## Appendix B. Preparation of XAD-4 Resin

1. Add ca 16 liters of XAD-4 resin (see note) was added to a 61 x 29 cm cylindrical Pyrex container (approx. 40L).
2. Wet the resin with one gallon of methanol (Resi-grade or equivalent. (Caution: The resin will expand in the presence of organic solvents. This prevented rapid expansion of the resin).
3. Remove "fines" by overfilling the container with deionized water with the hose placed at the bottom of the container and stirred vigorously.
4. Two liters of 0.25 N hydrochloric acid was added and stirred for 30 minutes.
5. Add water and vacuum off fines and water with an apparatus prepared with stiff tube covered at the inlet end with gauze and the outlet end connected to a large trap.
6. The container was re-filled with DI water and stirred.
7. Steps #5 and 6 were repeated until the water above the resin was clear and the pH is that of the deionized water.
8. Add 1 gallon of methanol and let stand overnight.
9. Transfer resin to a large Soxhlet extractor and extract resin with methanol for 24 hours.
10. Add fresh methanol and extract for another 24 hours.
11. Extract resin with ethyl acetate for 24 hours. Add fresh ethyl acetate and extract for an additional 24 hour.
12. Dry the resin in a vacuum oven (25") for 3-4 days at 65 °C or until all trace of ethyl acetate is gone from the resin.
13. Store resin in clean dry jars with Teflon® lined lids. Store at room temperature until time of use.

## Appendix C. Individual Ambient Site Results

**Table 12. Individual Ambient Site Results ( $\mu\text{g}/\text{Sample}$ )**

**Week One**

Sample Log #	Sample ID	Oxydemeton-methyl <sup>1</sup>	Dioxydemeton-methyl <sup>2</sup>
Log -1	1P	n.d. <sup>3</sup>	n.d.
Log -2	LJ-1	n.d.	n.d.
Log -3	LJ-2	n.d.	T <sup>4</sup>
Log -4	1C	n.d.	n.d.
Log -5	1S	n.d.	n.d.
Log -6	1G	n.d.	n.d.
Log -7	1B	n.d.	n.d.
Log -8	2P	n.d.	n.d.
Log -9	22LJ-1	n.d.	n.d.
Log -10	2LJ-2	n.d.	n.d.
Log -11	2C	n.d.	n.d.
Log -12	2S	n.d.	n.d.
Log -13	2G	n.d.	n.d.
Log -14	3P	n.d.	n.d.
Log -15	3LJ-1	n.d.	n.d.
Log -16	3LJ-2	n.d.	n.d.
Log -17	3C	n.d.	n.d.
Log -18	3S	n.d.	n.d.
Log -19	3G	n.d.	n.d.
Log -20	4P	n.d.	n.d.
Log -21	4LJ-1	n.d.	n.d.
Log -22	4LJ-2	n.d.	n.d.
Log -23	4C	n.d.	n.d.
Log -24	4S	n.d.	n.d.
Log -25	4G	n.d.	n.d.

1: Set Recoveries for oxydemeton-methyl: 79, 107, 102; Average: 96, Std Dev.: 14.8; Fort level: 1.0 $\mu\text{g}$

2: Set Recoveries for dioxydemeton-methyl: 122, 99, 122; Average: 114, Std Dev.:13.2; Fort Level: 1.0  $\mu\text{g}$

3: n.d. not detected, less than 0.05  $\mu\text{g}/\text{sample}$

4: T. Trace an estimated amount above 0.05  $\mu\text{g}/\text{sample}$  but less than the limit of quantitation of 0.25  $\mu\text{g}/\text{sample}$

Appendix C. Continued

Table 12. Continued

Week Two Ambient Site Results ( $\mu\text{g}/\text{Sample}$ )

Sample Log #	Sample ID	Oxydementon-methyl	Dioxydemeton-methyl
Log -26	5P	n.d. <sup>3</sup>	n.d.
Log -27	5LJ	n.d.	n.d.
Log -28	5C-1	n.d.	n.d.
Log -29	5C-2	n.d.	n.d.
Log -30	5S	n.d.	n.d.
Log -31	5G	n.d.	n.d.
Log -32	5B	n.d.	n.d.
Log -33	6P	n.d.	n.d.
Log -34	6LJ	n.d.	n.d.
Log -35	6C-1	n.d.	n.d.
Log -36	6C-2	n.d.	n.d.
Log -37	6S	n.d.	n.d.
Log -38	6G	n.d.	n.d.
Log -39	7P	n.d.	n.d.
Log -40	7LJ	n.d.	n.d.
Log -41	7C-1	n.d.	n.d.
Log -42	7C-2	n.d.	n.d.
Log -43	7S	n.d.	n.d.
Log -44	7G	n.d.	n.d.
Log -45	8P	n.d.	n.d.
Log -46	8LJ	n.d.	n.d.
Log -47	8C-1	n.d.	n.d.
Log -48	8C-2	n.d.	n.d.
Log -49	8S	n.d.	n.d.
Log -50	8G	n.d.	n.d.

1: Set Recoveries for oxydementon-methyl: 111, 67, 89; Average: 89, Std Dev.: 22.2; Fort level 2.5  $\mu\text{g}$ .

2: Set Recoveries for dioxydementon-methyl: 110, 127, 115; Average: 118, Std Dev: 8.95; Fort Level 2.5  $\mu\text{g}$

3: n.d. not detected, less than 0.05  $\mu\text{g}/\text{sample}$

Appendix C. Continued

Table 12. Continued

Week Three Ambient Sites Results

Sample Log #	Sample ID	Oxydementon-methyl	Dioxydemeton-methyl
Log -51	9P	n.d. <sup>3</sup>	n.d.
Log -52	9LJ	n.d.	n.d.
Log -53	9C-1	n.d.	n.d.
Log -54	9C-2	n.d.	n.d.
Log -55	9S	n.d.	n.d.
Log -56	9G	n.d.	n.d.
Log -57	9B	n.d.	n.d.
Log -58	10P	n.d.	n.d.
Log -59	10LJ	n.d.	n.d.
Log -60	10C-1	n.d.	n.d.
Log -61	10C-2	n.d.	n.d.
Log -62	10S	T <sup>4</sup>	n.d.
Log -63	10G	T	n.d.
Log -64	11P	n.d.	n.d.
Log -65	11LJ	n.d.	n.d.
Log -66	11C-1	n.d.	n.d.
Log -67	11C-2	n.d.	n.d.
Log -68	11S	n.d.	n.d.
Log -69	11G	n.d.	n.d.
Log -70	12P	n.d.	n.d.
Log -71	12LJ	n.d.	n.d.
Log -72	12C-1	n.d.	n.d.
Log -73	12C-2	n.d.	n.d.
Log -74	12S	n.d.	n.d.
Log -75	12G	n.d.	n.d.

1: Set Recoveries for oxydementon-methyl: 116,109, 92; Average:105, Std Dev.:12.3; Fort level 1.0 µg.

2: Set Recoveries for dioxydementon-methyl: 133, 135, 128; Average: 132, Std Dev: 3.8; Fort Level 1.0 µg.

3: n.d. not detected, less than 0.05 µg/sample

4: T. Trace an estimated amount above 0.05 µg/ sample but less than the limit of quantitation of 0.25 µg/sample

Appendix C. Continued

Table 12. Continued

Week Four Ambient Site Results

Sample Log #	Sample ID	Oxydementon-methyl	Dioxydemeton-methyl
Log -76	13P	n.d. <sup>3</sup>	n.d.
Log -77	13LJ	n.d.	n.d.
Log -78	13C	n.d.	n.d.
Log -79	13S-1	n.d.	n.d.
Log -80	13S-2	n.d.	n.d.
Log -81	13G	n.d.	n.d.
Log -82	13B	n.d.	n.d.
Log -83	14P	n.d.	n.d.
Log -84	14LJ	n.d.	n.d.
Log -85	14C	n.d.	n.d.
Log -86	14S-1	n.d.	n.d.
Log -87	14S-2	n.d.	n.d.
Log -88	14G	n.d.	n.d.
Log -89	15P	n.d.	n.d.
Log -90	15LJ	n.d.	n.d.
Log -91	15C	n.d.	n.d.
Log -92	15S-1	n.d.	n.d.
Log -93	15S-2	n.d.	n.d.
Log -94	15G	n.d.	n.d.

1: Set Recoveries for oxydementon-methyl: 93, 112, 115; Average:107, Std Dev. 12.2; Fort level 1.0 µg.

2: Set Recoveries for dioxydementon-methyl: 123, 124, 127; Average: 125, Std Dev: 2.3; Fort Level 1.0 µg

3: n.d. not detected, less than 0.05 µg/sample



## Appendix D. Application Site Results for Individual Samples

Table 13. Application Site Individual Sample Results

Sample Log #	Sample Period	Sample ID <sup>1</sup>	Oxydemeton-methyl	Dioxydemeton-methyl
Log -1	Background	0SE-1	n.d. <sup>2</sup>	n.d.
Log -2	Background	0SE-2	n.d.	n.d.
Log -3	Background	0E	n.d.	n.d.
Log -4	Background	0NW	n.d.	n.d.
Log -5	Background	0SW	n.d.	n.d.
Log -6	During App.	1NW	T <sup>3</sup>	n.d.
Log -7	During App	1E	n.d.	n.d.
Log -8	During App	1SE-1	T	n.d.
Log -9	During App.	1SE-2	T	n.d.
Log -10	During App.	1SW	T	n.d.
Log -11	2 hr sample	2NW	n.d.	n.d.
Log -12	2 hr sample	2E	n.d.	n.d.
Log -13	2 hr sample	2SE-1	n.d.	n.d.
Log -14	2 hr sample	2SE-2	n.d.	n.d.
Log -15	2 hr sample	2SW	n.d.	n.d.
Log -16	-----	2B	n.d.	n.d.
Log -17	4 hr sample	3NW	n.d.	n.d.
Log -18	4 hr sample	3E	n.d.	n.d.
Log -19	4 hr sample	3SE-1	T	n.d.
Log -20	4 hr sample	3SE-2	T	n.d.
Log -21	4 hr sample	3SW	T	n.d.
Log -22	12 hr sample	4NW	n.d.	n.d.
Log -23	12 hr sample	4E	n.d.	n.d.
Log -24	12 hr sample	4SE-1	n.d.	n.d.
Log -25	12 hr sample	4SE-2	T	n.d.

1: Reference positions corrected from Log sheets at request of ARB.

2: n.d. not detected, less than 0.05 µg/sample

3: T. Trace an estimated amount above 0.05 µg/ sample but less than the limit of quantitation of 0.25 µg/sample.

Appendix D Continued

Table 13. Continued

Sample Log #	Sample Period	Sample ID <sup>1</sup>	Oxydemeton-methyl	Dioxydemeton-methyl
Log -26	12 hr sample	4SW	Sample Lost	Sample Lost
Log -27	12 hr sample	5NW	T <sup>2</sup>	n.d. <sup>3</sup>
Log -28	12 hr sample	5E	T	n.d.
Log -29	12 hr sample	5SE-1	T	n.d.
Log -30	12 hr sample	5SE-2	T	n.d.
Log -31	12 hr sample	5SW	T	n.d.
Log -32	24 hr sample	6NW	n.d.	n.d.
Log -33	24 hr sample	6SE	n.d.	T
Log -34	24 hr sample	6SE-1	n.d.	T
Log -35	24 hr sample	6SE-2	n.d.	n.d.
Log -36	24 hr sample	6SW	n.d.	n.d.
Log -37	24 hr sample	7NW	n.d.	n.d.
Log -38	24 hr sample	7E	T	n.d.
Log -39	24 hr sample	7SE-1	n.d.	T
Log -40	24 hr sample	7SE-2	n.d.	T
Log -41	24 hr sample	7SW	n.d.	n.d.

1: Reference positions corrected from Log sheets at request of ARB.

2: T. Trace an estimated amount above 0.05 µg/ sample but less than the limit of quantitation of 0.25 µg/sample.

3: n.d. not detected, less than 0.05 µg/sample.

**Appendix E. Complete List of Resin Fortifications for the Entire Project**

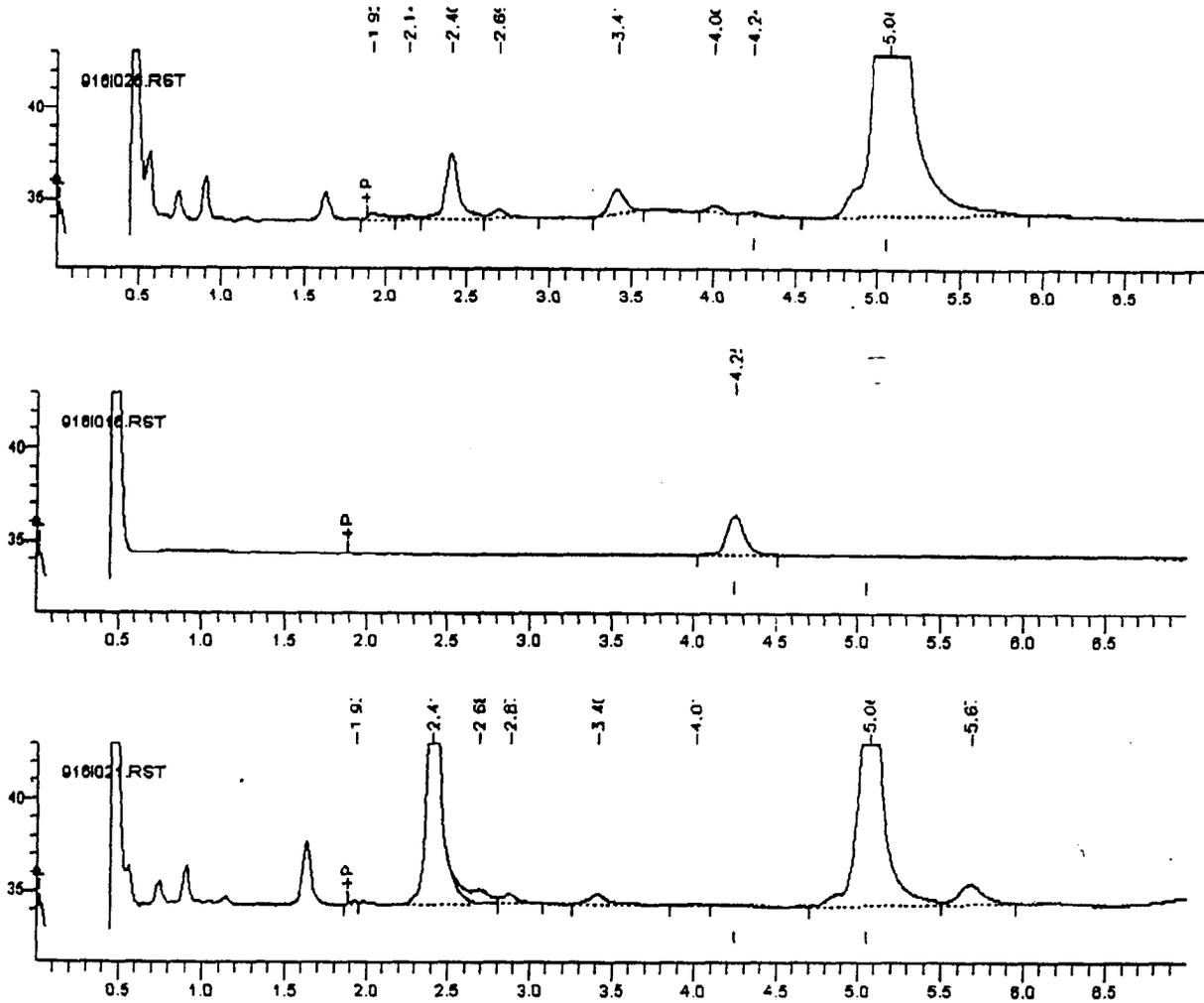
**Table 14. Project Fortification Levels and Percent Recovery**

Sample Type	Date	Fortification Level	Sample ID	Oxydemeton-methyl	Dioxydemeton -methyl
Method Validation	7/28/95	5.0 µg	non-oxidized dioxydemeton		108
Method Validation	7/28/95	5.0 µg	non-oxidized dioxydemeton		105
Method Validation	7/28/95	5.0 µg	non-oxidized dioxydemeton		112
Method Validation	7/28/95	5.0 µg	Oxidized oxydemeton	91	
Method Validation	7/28/95	5.0 µg	Oxidized oxydemeton	100	
Method Validation	7/28/95	5.0 µg	Oxidized oxydemeton	114	
Method Validation	7/28/95	5.0 µg	Oxidized Dioxydemeton-methyl		120
Method Validation	7/28/95	5.0 µg	Oxidized Dioxydemeton-methyl		104
Method Validation	7/28/95	5.0 µg	Oxidized Dioxydemeton-methyl		112
Trapping Efficiency	7/28/95	50 µg	Oxydemeton-methyl	80	
Trapping Efficiency	7/28/95	50 µg	Oxydemeton-methyl	88	
Trapping Efficiency	7/28/95	50 µg	Oxydemeton-methyl	71	
Trapping Efficiency	7/28/95	50 µg	Dioxydemeton-methyl		71
Trapping Efficiency	7/28/95	50 µg	Dioxydemeton-methyl		83
Trapping Efficiency	7/28/95	50 µg	Dioxydemeton-methyl		111

Table 14. Continued

Sample Type	Date	Fortification Level	Sample ID	Oxydemeton-methyl	Dioxydemeton - methyl
Ambient	week 1	1.0 µg	1.0R1	79	122
Ambient	week 1	1.0 µg	1.0R2	107	99
Ambient	week 1	1.0 µg	1.0R3	102	122
Ambient	week 2	2.5 µg	1.0R4	111	110
Ambient	week 2	2.5 µg	1.0R5	67	127
Ambient	week 3	1.0 µg	1.0R6	89	115
Ambient	week 3	1.0 µg	1.0R7	116	133
Ambient	week 3	1.0 µg	1.0R7	109	135
Ambient	week 3	1.0 µg	1.0R7	92	128
Ambient	week 4	1.0 µg	1.0R7	93	123
Ambient	week 4	1.0 µg	1.0R7	112	124
Ambient	week 4	1.0 µg	1.0R7	115	127
Application	Set 1	2.5 µg	2.5R7	87	110
Application	Set 1	2.5 µg	2.5R8	65	144
Application	Set 1	2.5 µg	2.5R9	75	134
Application	Set 2	0.25 µg	0.25R1	122	121
Application	Set 2	0.25 µg	0.25R2	86	144
Application	Set 2	0.25 µg	0.25R3	133	122
ARB-QA	----	2.5 µg	2.5R1	82	115
ARB-QA	----	2.5 µg	2.5R2	74	134
ARB-QA	----	2.5 µg	2.5R3	115	116

# Appendix F. Application Site Chromatograms



Top: Application site sample, Log #20 third period southeast site #2 oxydemeton-methyl (rt = 4.2 min) results: at limit of detection. Peak at 5.0 min is chlorpyrifos.

Middle: 0.096 ng of dioxydemeton-methyl (rt = 4.2 min) standard at limit of quantitation.

Bottom: Application site sample, Log #18 third period east site. None detected.

**APPENDIX IV**  
**QMOSB AUDIT REPORT**

**SYSTEM AUDIT REPORT  
OXYDEMETON METHYL  
MONITORING IN THE  
MONTEREY BAY UNIFIED  
APCD**

**STATE OF CALIFORNIA AIR RESOURCES BOARD  
MONITORING AND LABORATORY DIVISION  
QUALITY ASSURANCE SECTION**

**SYSTEM AUDIT REPORT**

**OXYDEMETON METHYL MONITORING IN THE  
MONTEREY BAY UNIFIED AIR POLLUTION CONTROL DISTRICT**

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OXYDEMETON METHYL MONITORING IN THE  
MONTEREY BAY UNIFIED AIR POLLUTION CONTROL DISTRICT

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ATTACHMENTS

1. Flow Rate Audit Procedures for Air Samplers Used in Pesticide Monitoring
2. Performance Audit Procedures for the Laboratory Analysis of Oxydemeton Methyl
3. Air Sampler Used in the Monitoring of Oxydemeton Methyl

## I. EXECUTIVE SUMMARY

During the months of August and September of 1995, the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) conducted a four-week ambient air monitoring program (Ambient Air Sampling) and a three-day source impacted ambient air monitoring program (Application Site Air Sampling) in Monterey County to document the airborne emissions of oxydemeton methyl and its primary breakdown product, dioxydemeton methyl in the vicinity of treated fields during and after an application. The samples were collected by ELB and analyzed by the Trace Analytical Laboratory (TAL) of the UC Davis Department of Environmental Toxicology.

The Quality Assurance Section (QAS) of the ARB's Monitoring and Laboratory Division (MLD) conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. During the method validation review, differences were found between the test conditions used for the TAL's trapping efficiency experiments and the actual field conditions. The TAL's trapping efficiency experiments were conducted to determine the total mass recoveries at extreme field conditions. The trapping efficiency test conditions differed from actual field conditions in that the field air flow rate was approximately one-half of the rate used to determine trapping efficiency. At these extreme field conditions, the total mass recoveries were acceptable. The system audit found that, in general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (California Air Resources Board, February 4, 1994).

Additionally, the QAS staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The difference between the reported and assigned flow rates averaged 9.2% with a range of 6.5% to 11.4% for Ambient Air Sampling. The difference between the reported and assigned flow rates for Application Site Air Sampling averaged 1.6% with a range of 0.0% to 2.9%.

To determine the effectiveness of the analytical procedure, laboratory performance audits were also conducted. On August 17, 1995, ten samples spiked with known amounts of oxydemeton methyl and dioxydemeton methyl were submitted to TAL for analysis. The samples were prepared from oxydemeton methyl and dioxydemeton methyl standard solutions obtained from Chem Service. The concentration of

the QAS audit samples were a minimum of five times the lower limit of detection. The difference between the assigned and the reported total mass was approximately -75% for both oxydemeton methyl and dioxydemeton methyl spiked solutions. The TAL staff investigated the problem and determined that inconsistencies were found when analyzing ARB's standard, prepared in isooctane by Chem Service, to the TAL's standard, prepared in ethyl acetate. After additional research, the TAL determined the oxydemeton methyl did not dissolve in the isooctane, even after sonification for a period of time. The conclusion was that oxydemeton methyl was insoluble or only slightly soluble in isooctane in a very low concentration (less than 30 ng/ul).

The ELB and TAL decided that the isooctane would be replaced with ethyl acetate. On August 23, 1995, five samples spiked with known amounts of oxydemeton methyl and dioxydemeton methyl were submitted to the laboratory for analysis. The samples were prepared from oxydemeton methyl and dioxydemeton methyl standard solutions in ethyl acetate obtained from the TAL. The difference between the assigned and the reported total mass of oxydemeton methyl averaged -10.9% with a range of -22.4% to -3.2%. For dioxydemeton methyl, the difference between the assigned and reported total mass averaged 14.5% with a range of 9.4% to 22.4%.

To verify the integrity of the standard solution fortified by the TAL, Chem Service supplied an oxydemeton methyl and dioxydemeton methyl standard in ethyl acetate solution to compare with the TAL's standard solution. The analysis conducted by the TAL indicated an average of 1.5% difference between the oxydemeton methyl standard solutions and an average of -1.5% difference between the dioxydemeton methyl standard solutions. The QAS decided to invalidate the August 17 audit samples based on the results from using oxydemeton methyl and dioxydemeton methyl in ethyl acetate during the audit conducted on August 23 and the standard solution validation study.

## II. CONCLUSIONS

The records for field operations, sample handling and storage procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring. The results of the reported flow rates were in good agreement with the actual flow rates measured by the QAS staff. The results of the August 23, 1995 analytical performance audit showed an average of -10.9% and 14.5% difference for oxydemeton methyl and dioxydemeton methyl, respectively. Based on

these results, the TAL and ELB determined that the results from the August 17, 1995 analytical performance audit were unreliable due to the use of isooctane as a solvent. The August 17, 1995 audit has been invalidated by the QAS.

For the three-day ambient application air monitoring and the four-week ambient air monitoring, none of the samples analyzed contained oxydemeton methyl or dioxydemeton methyl above the limit of detection. Had any of the samples been detected above the lower limit of detection, the effect of the positive flow biases for both compounds would be to under report mass concentrations. Additionally, the effect of positive and negative mass biases for dioxydemeton methyl and oxydemeton methyl would be to over and under report the mass concentrations for each compound, respectively.

### III. RECOMMENDATIONS

1. In order to ensure compatibility between the pesticide audit standard and the analytical system, the QAS should confirm that the laboratory providing the standard solution and the laboratory performing the analysis are in complete agreement concerning the solvent chosen for the pesticide standard. Specifically, the solubility of the compound should be noted and a solvent that is compatible with the physicochemical properties of the pesticide standard should be selected.
2. The flow rates used by the ELB during field sampling should match the flows used by the analytical laboratory during method development for trapping efficiencies. However, as long as the sampling flow rates are less than those used for trapping efficiencies, the trapping studies represent a "extreme field condition" situation.

### IV. INTRODUCTION

During the months of August and September of 1995, the ELB conducted a four-week Ambient Air Sampling and a three-day Application Site Air Monitoring in Monterey County to document the airborne emissions of oxydemeton methyl and its primary breakdown product, dioxydemeton methyl in the vicinity of treated fields during and after an application. The samples were collected by the ELB and analyzed by the TAL of the UC Davis Department of Environmental Toxicology. The QAS conducted a system audit of the field and

laboratory operations, and performance audits of the air samplers' flow rates and of the analytical method.

## V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (California Air Resources Board, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

## VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in August 1995 through a questionnaire submitted to the TAL staff. Also, the protocol for the ambient and application air monitoring of oxydemeton methyl and the laboratory sampling methodology for the analysis of oxydemeton methyl were reviewed. The following is a discussion of the audit findings.

### Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through a Teflon holder containing 30 ml of cleaned XAD-4 resin. The air samplers consisted of one sample holder, connected with Teflon tubing to an in-line rotometer, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Attachment 3). The samplers' rotometers were set to an indicated flow rate of 15 liters per minute (lpm) by adjusting the control valve on the rotometer.

Sampling was conducted following the schedule specified in the sampling protocol. After sampling, the XAD-4 resin was removed from the Teflon holder and transferred into a glass jar with a Teflon-lined lid. The jars were stored in an ice chest containing dry ice. During shipment, the samples were boxed, placed in a plastic cooler with dry ice, and wrapped with duct tape. Samples were stored in the field for up to four days prior to shipment and were determined to be stable for at least 29 days with negligible loss of parent or primary breakdown product during storage at -20 degrees Celsius.

Upon receipt at the laboratory, the samples were stored in their original boxes in a freezer for a maximum of two days until extraction and analyses were conducted.

### Sample Analysis

The analytical method was developed by TAL, and is described in a document titled "Method Development for Oxydemeton Methyl in Air Samples Using XAD-4 Resin as a Trapping Medium".

The method of extraction of oxydemeton methyl and dioxydemeton methyl involved the addition of ethyl acetate to resin sample jars and the samples were swirled for one hour, using a rotary platform shaker. Laboratory fortifications were spiked on control resin samples before the addition of extraction. Following extraction, the analysis for oxydemeton methyl and dioxydemeton methyl involved a two step process of direct analysis and an oxidation. For direct analysis, one fourth of the extract was quantitatively transferred to an appropriate size round bottom flask and concentrated just to dryness via rotor-evaporator with a water bath at approximately 40 degrees Celsius. To alleviate any residual ethyl acetate, acetone was added, and the sample was again evaporated to dryness. The sample was redissolved in acetone and then analyzed to determine the level of dioxydemeton methyl present in the sample.

For the analysis of the oxidation aliquot, the sample was evaporated to dryness and acetone was added to each flask and swirled. The sample was oxidized to dioxydemeton methyl by first adding magnesium sulfate followed by potassium permanganate. The oxidized sample was transferred to separatory funnel and partitioned three times with pesticide grade chloroform. The organic layer (bottom layer) was dried with anhydrous sodium sulfate and drained into flasks. The sodium sulfate was rinsed with chloroform. The sample was taken to dryness, rinsed with acetone, and taken to dryness and brought up in acetone. The oxidation aliquot was then analyzed for combined dioxydemeton methyl (any originally in the sample plus any oxydemeton methyl present which would be oxidized to the breakdown product, dioxydemeton methyl).

The level of oxydemeton methyl was calculated by subtracting the evaporation results from the oxidation results in the same sample. The analyses were performed on a Hewlett Packard (HP) model 5890A gas chromatograph equipped with a nitrogen-phosphorous detector and a HP-GC System Injector-autosampler. Analysis of samples was quantified by using 4-point external linear regression

standard curve for dioxydemeton methyl. Each sample was injected twice and the standard(s) were interdispersed between samples during each analysis (set). Precision checks of the data were less than  $\pm 10\%$  difference.

Quality control activities performed to monitor and document the quality of the data included analysis of a field control blank with every sample set, laboratory spikes of three replicates per set of samples. For the Ambient Air Sampling, the recovery for the twelve oxydemeton methyl laboratory validation samples were an average recovery of 99.8% and a standard deviation of 15.3%. For the twelve dioxydemeton methyl laboratory samples the average recovery were 122% with a standard deviation of 10.0%. For the Application Site Air Sampling, the percent average recovery for the four oxydemeton methyl samples were 113% with a standard deviation of 5.5% while the percent recovery for dioxydemeton methyl was 124% and a standard deviation of 8.7%. Field duplicates from collocated sites were collected once each sampling day. A portion of the samples were analyzed by GC/Mass Spectroscopy Selective Ion monitoring to confirm the identity of the analyte.

#### Method Validation

The limit of detection (LOD) was determined by injecting known quantities of external standards into a GC. The LOD was calculated as 0.25 ug per sample. TAL's trapping efficiency experiments were conducted to determine the total mass recoveries at extreme field conditions. Trapping efficiency was determined as 80% total mass recovery for oxydemeton methyl and an average of 88% total mass recovery for dioxydemeton methyl at an approximate temperature of 32 degrees Celsius. The trapping efficiency at an approximate temperature of 40 degrees Celsius was 60% total mass recovery for oxydemeton methyl and 111% total mass recovery for dioxydemeton methyl. The laboratory trapping efficiency study conditions differed from field conditions in that the field air flow was approximately one-half of the rate used to determine trapping efficiency. This test condition was in accordance with ELB's acceptable testing requirements. The ELB trapping efficiency test flow rates are conducted at rates equal or greater than the field flow rates. Also, for trapping efficiencies, primary and backup traps were used. Backup traps were not used for the application site samples. There was no breakthrough in any of the replicates using mass load of 50 ug over 12 hours at a flow rate of 25-35 lpm.

Sample stability studies were conducted and verified the integrity of the sample to be 93% with the standard deviation of 3.9% for oxydemeton methyl and 102% with a standard deviation 2.5% for dioxydemeton methyl. Samples are stable for at least 29 days.

#### Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were received by the TAL. The information recorded on the field data sheets included sampler location, sampling date, start and stop times, log number, identification number, description, job name, date, job number, and initials of the field technician.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, date of analysis, results of analysis, and analyst.

The raw analytical data were recorded on electronic files and will be kept indefinitely by the ELB.

### **VII. PERFORMANCE AUDITS**

#### Flow Rate Audit

The flow rate of each sampler used for the monitoring was audited on August 4, 1995 and September 25, 1995 following the procedures outlined in Attachment I. The audit was conducted with a 0 to 30 lpm mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the Ambient Air Sampling reported and true flow rates averaged 9.2% and ranged from 6.5% to 11.4% (Table 1). For the Application Site Air Monitoring, the difference between the reported and true flow rates averaged 1.6% and ranged from 0.0% to 2.9% (Table 2).

Due to the nature of the mass concentration ratio (mass/volume), the effect of the positive flow biases would be to over calculate the total volume used in the mass concentration calculation. Consequently, the mass concentration would be under reported.

Table 1  
Results of the Flow Audit of the Samplers  
Used in the Ambient Air Sampling  
Monitoring of Oxydemeton Methyl

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1	14.6	13.11	11.4
2	14.6	13.20	10.6
3	14.6	13.71	6.5
4	14.6	13.44	8.6
5	14.6	13.41	8.9
6	14.6	13.41	8.9

Table 2  
Results of the Flow Audit of the Samplers  
Used in the Application Site Air Monitoring  
of Oxydemeton Methyl

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1	14.4	14.0	2.9
2	14.4	14.2	1.4
3	14.4	14.4	0.0
4	14.4	14.2	1.4
5	14.4	14.3	0.7
6	14.4	14.0	2.9

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

#### Laboratory Performance Audit

The accuracy of the analytical method was evaluated by submitting for analysis a set of ten QAS audit samples spiked with known amounts of oxydemeton methyl and dioxydemeton methyl. The pesticide standard solutions were prepared by Chem Services and samples spiked by the QAS staff on August 17, 1995 following the procedures outlined in Attachment II. The concentration of the QAS audit samples were a minimum of five times the lower limit of detection. The audit samples were analyzed by TAL and the results for samples Oxy-1 to Oxy-10 were 25% of the expected assigned mass values. TAL's staff investigated the problem and determined that inconsistencies were found when analyzing ARB's standard solution, prepared in isooctane by Chem Service, to TAL's standard solution prepared in ethyl acetate. The TAL determined the Chem

Service standard solution was 40% - 60% lower than their standard solution. After additional research, TAL determined the oxydemeton methyl did not dissolve in the isooctane, even after sonification for a period of time. The conclusion was that oxydemeton methyl is insoluble or only slightly soluble in isooctane in a very low concentration (less than 30 ng/ul). Chem Service was notified and asked to verify their standards. Chem Service analyzed the dioxydemeton methyl against a freshly prepared standard in isooctane and against a freshly prepared standard in ethyl acetate. The results of Chem Service's analysis indicates that there was agreement between the standards. Based on the analysis, Chem Service says the standards were prepared correctly. Chem Service did not analyze the oxydemeton methyl solution, but feels that it was prepared correctly also.

TAL prepared a new standard solutions in ethyl acetate. On August 23, 1995 ARB's QAS spiked five samples. The concentration of the QAS audit samples were a minimum of five times the lower limit of detection. These samples were designated as Oxy-11 through Oxy-15. The difference between the assigned and the reported total mass of oxydemeton methyl averaged -10.9% with a range of -22.4% to -3.2% (Table 3). For dioxydemeton methyl, the difference between the assigned and reported total mass averaged 14.5% with a range of 9.4% to 22.4% (Table 4). Again, due to the nature of the mass concentration ratio (mass/volume), the effect of the positive and negative mass biases would be to over and under report the mass concentrations.

New audit standard solutions in ethyl acetate were ordered from Chem Service to verify the integrity of the standard solution fortified by TAL. ARB supplied this Chem Service standard solution to TAL for comparison with their standard solution. The analysis conducted by TAL indicated an average of 1.5% difference between the oxydemeton methyl standard solutions (Table 5) and an average of -1.5% difference between the dioxydemeton methyl standard solutions (Table 6). The QAS decided to invalidate the August 17 audit samples based on the results from using oxydemeton methyl and dioxydemeton methyl in ethyl acetate during the audit conducted on August 23 and the standard solution validation study.

Table 3  
Results of Analyses of the Oxydemeton Methyl  
Audit Samples

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
Oxy-11	1.25	1.21	-3.2
Oxy-13	1.25	1.16	-7.2
Oxy-14	1.25	0.97	-22.4

Table 4  
Results of Analyses of the Dioxydemeton Methyl  
Audit Samples

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
Oxy-12	3.125	3.49	11.7
Oxy-14	1.25	1.53	22.4
Oxy-15	3.125	3.42	9.4

Table 5  
Results of Analyses Comparing Chem Service and  
TAL Oxydemeton Methyl Standard Solutions

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
Rep 2	12.5	12.50	0.0
Rep 3	12.5	12.88	3.0

Table 6  
Results of Analyses Comparing Chem Service and  
TAL Dioxydemeton Methyl Standard Solutions

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
Rep 2	12.5	12.25	-2.0
Rep 3	12.5	12.38	-1.0

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

**FLOW RATE AUDIT PROCEDURES FOR AIR SAMPLERS  
USED IN PESTICIDE MONITORING**

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST-traceable flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.

4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

**PERFORMANCE AUDIT PROCEDURES  
FOR THE  
LABORATORY ANALYSIS OF OXYDEMETON METHYL**

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory to measure the ambient concentrations of oxydemeton methyl and its primary breakdown product, dioxydemeton methyl. The audit is conducted by submitting audit samples spiked with known concentrations of oxydemeton methyl and dioxydemeton methyl. The analytical laboratory reports the results to QAS, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Oxydemeton methyl 0.125 ug/ul in ethyl acetate, Trace Analytical Laboratory, Oxydemeton methyl, Lot #136-151A, Purity:95%.
2. Dioxydemeton methyl 0.125 ug/ul in ethyl acetate, Trace Analytical Laboratory, Dioxydemeton methyl, Lot #151-146B, Purity 99%.
3. Glass jars with Teflon-lined lids, 30 ml XAD-4 resin.

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Preparation of Audit Samples

Prepare seven audit samples by spiking the XAD-4 resin contained in the glass jars with the volume of oxydemeton methyl and dioxydemeton methyl solution indicated in the table below. Using a microsyringe, slowly expel the solution into the glass jar, move the syringe so that the solution is not landing in the same place on the resin. Touch the tip of the syringe to the side of the glass jar to expel the last bit of solution.

Sample ID (ul)	Oxydemeton Methyl Total Spiking Solution Volume (ul)	Dioxydemeton Methyl Total Spiking Solution Volume
Oxy-11	1.25	----
Oxy-12	----	3.125
Oxy-13	1.25	----
Oxy-14	----	1.25
Oxy-15	1.25	3.125

AIR SAMPLER USED IN MONITORING OXYDEMETON METHYL

