

APPENDIX I  
REQUEST FOR MONITORING

## OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT

MEMORANDUM

TO: Genevieve Shiroma, Chief  
Toxic Air Contaminant  
Identification Branch  
California Air Resources Board  
P.O. Box 2815  
Sacramento, California 95812

FROM: Richard A. Jackson, M.D., M.P.H.  
Hazard Identification and  
Risk Assessment Branch  
2151 Berkeley Way  
Berkeley, California 94704

DATE: April 6, 1992

SUBJECT: Air Monitoring for Molinate during the 1992 Use Season

*Jim Stratton/for*

Recently, you were notified by the California Department of Pesticide Regulation (DPR) that the Hazard Identification and Risk Assessment Branch (HIRAB) of the Office of Environmental Health Hazard Assessment requested air monitoring for molinate during the 1992 use season. This memorandum is to inform you of our reasons for requesting the air monitoring.

Recent worker monitoring suggested that volatile molinate vapors released when the bags of the pesticide are first opened are as much of a problem as dust (ICI Americas, Inc., 1991). In an effort to reduce potential exposure, the use of 1500-pound bags has been approved by DPR for the 1992 use season. With the concentration of the mixer/loader activity into relatively few sites, due to the logistics of the heavy equipment needed to handle the 1500-pound bags, the mixer/loader sites could act as stationary point sources. These sites should be monitored accordingly to determine if this is true. Additionally, monitoring should take into account the hours of operation at the site.

HIRAB is concerned that community exposure to molinate could be occurring. Molinate has been shown to cause adverse reproductive effects in rodents. Residents living in homes that are surrounded by rice fields may be at highest risk from potential reproductive effects because they could be getting high, short-term exposures to molinate from potential point sources (e.g., mixer/loader sites), as well as lower, longer-term exposures from large area sources (e.g., treated fields).

Genevieve Shiroma, Chief  
April 6, 1992  
Page Two

We are aware that some air monitoring of molinate was done in the Sacramento Valley in 1986 by Seiber et al. (1989), but we believe that the study is insufficient for the following reasons. The study targeted methyl parathion use, rather than molinate; therefore, the data was collected from mid-May to mid-June, three to four weeks past the peak molinate season which occurs in mid- to late-April. The Seiber et al. monitoring sites (located in towns) were not as close to the rice fields as many homes are. Furthermore, the highest molinate values were obtained on day one of the study and declined steadily thereafter, so the peak concentrations undoubtedly were missed. Additionally, because of recent changes in application techniques and field practices (e.g., increased holding times of field water before draining into the Sacramento River), the 1986 field data may no longer be applicable to the current use scenario.

Because of these reasons, we recommend that additional community monitoring be performed. In fact, the conclusions of the Seiber study, published in 1989, that "molinate levels are in a concentration range that is comparable to that observed for many other organic pollutants in ambient air" and that the health risk of airborne residues to populations "does warrant further attention" seem to support our recommendations.

Because reproductive toxicity may occur from peak, short-term exposures, sampling should characterize peak and short-term levels in addition to the usual longer-term time-weighted average approach. We recommend that stations be set up among fields in a large treatment area during and immediately following molinate application. Obvious choices for monitoring sites would be homes that are located among the rice fields, since residents of those homes would be at highest risk from adverse reproductive effects. If the molinate values there appear to be acceptable from a public health perspective, then they should be acceptable in communities located further away. Because molinate is so volatile, attention should be paid to the effect of ambient temperature, solar effects, wind speed and air stability on monitored levels.

We realize that the 1992 molinate use season is quickly approaching. We hope that every effort can be made to commence monitoring in mid-April. If you have any further questions, please contact me or Dr. Michael DiBartolomeis at 510-540-3063.

Thank you.

cc: Lynn Baker, Air Resources Board  
Michael J. DiBartolomeis, Ph.D.  
Anna M. Fan, Ph.D.  
Donald C. Mengle, M.S.  
James W. Stratton, M.D., M.P.H.  
Joy A. Wisniewski, Ph.D.  
George Alexeeff, Ph.D.

Jim Wells, Director, DPR  
Larry Nelson, Ph.D., DPR  
Doug Okumura, DPR  
Ron Oshima, Ph.D., DPR  
John Ross, Ph.D., DPR

APPENDIX II  
PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

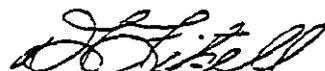
Air Monitoring for Molinate in Sutter  
or Colusa County during May 1992

Engineering Evaluation Branch  
Monitoring and Laboratory Division

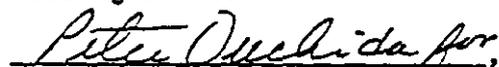
Project No. C92-042

Report Date: May 11, 1992

APPROVED:

  
\_\_\_\_\_, Project Engineer  
Testing Section

\_\_\_\_\_, Manager *pho*  
Testing Section

  
\_\_\_\_\_, Chief  
Engineering Evaluation Branch

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 Molinate Monitoring in Sutter  
or Colusa County during May 1992

I. Introduction

The Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA) has requested that the Air Resources Board (ARB) conduct air monitoring for the herbicide molinate (Attachment A). In response to this request, staff of the ARB will conduct a 4-day source impacted ambient monitoring program for molinate in Sutter or Colusa County following an aerial application of molinate. In addition, ARB staff will collect air samples during the opening of a 1,500 pound bag of granular molinate and the loading operation of a hopper or airplane tank.

Molinate is a selective herbicide used to control watergrass in rice fields. Its peak use in California is in Colusa, Butte, Glenn, and Sutter Counties during the spring months (usually April and May.) Molinate is applied as a granular formulation. Results of the monitoring will be evaluated by staff of the OEHHA and the Department of Pesticide Regulation.

II. Sampling

Air sampling will be coordinated with the Sutter and Colusa County Offices of the Agricultural Commissioner, and an applicator in one of the counties. Prior to application, background samples will be taken to establish if any molinate is 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-2 adsorbent tubes. Ambient air will be pulled through the sampling tubes at a flow rate of approximately 2 liters per minute using battery powered pumps. A few duplicate samples will be collected from each sampler for quality assurance purposes. (Duplicates at each sampling location will not be collected due to analytical constraints.) A sketch of the pesticide monitoring apparatus is presented in Attachment B.

Calibrated rotameters will be used to control sample flow rates. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. A field log book will be used to record sample start and stop times, duration of the aerial application and tank loading operation, sample IDs, any change in the flow rates, and other pertinent information.

A. Aerial Application

Two samplers will be used: one 15-20 yards upwind of the field and one 15-20 yards downwind. These distances are approximate and dependent on the physical obstacles surrounding the field. Information on field size, application rate, and formulation will be noted in the log book. The sampling schedule is listed in the following table. (The sampling design and schedule were prepared based on recommendations from staff of OEHHA and differs somewhat from the application sampling schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring," enclosed as Attachment C.)

Sampling Schedule - Application Site\*

Day 1

Background sample (1 hr. sample prior to application)

Application + 1 hr. after application (combined sample)

2 hr. sample (from 1 to 3 hrs. after application)

6 hr. sample (from 3 to 9 hrs. after application, or to early evening)

12 hr. sample (to 24 hrs. after application beqaq)

Day 2

12 hr. sample (early morning to early evening)

12 hr. sample (early evening to early morning)

Day 3

12 hr. sample (early morning to early evening)

12 hr. sample (early evening to early morning)

Day 4

12 hr. sample (early morning to early evening)

12 hr. sample (early evening to early morning)

\* Schedule subject to modifications depending on time and day of week of application.

#### B. Bag Opening and Tank Loading

Battery-powered samplers will be set up prior to opening of a 1,500 pound bag of granular molinate. Air samples will be collected from the time the bag is opened until the loading of a hopper or airplane tank is completed. Two to four samplers will be set up approximately 15-20 yards upwind and downwind of the tank loading operation. Air samples will be collected during two loading operations.

#### III. Analysis

All samples will be stored in an ice chest or freezer until analysis. Analysis of samples will be performed by the Department of Environmental Toxicology, U C Davis. The analytical method is gas chromatography using a nitrogen/phosphorus detector. The analytical procedure is described in Attachment D and will be fully documented in the final report.

#### IV. Quality Assurance

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample collection efficiency, stability, and recovery will also be verified based on spiked samples. Sampler flow rates will be calibrated prior to and after sampling in the field. Blank sampling tubes will accompany each batch of samples from the field to the lab prior to analysis. A chain of custody sheet will accompany all samples.

#### V. Personnel

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

State of California

MEMORANDUM

To : Peter Ouchida *PO*  
Manager,  
Testing Section

Date : May 21, 1992  
Subject : Amendment to Molinate  
Protocol

Don Fitzell *DF*  
Assoc. Air Pollution Spec.

From : Air Resources Board

Lynn Baker has asked to modify the molinate protocol after meeting with DPR and OEHHA. UCD has agreed to analyze up to 50 samples now, so the request is reasonable.

The changes result in the following sampling program:

Application Monitoring

Two samplers, one 15 yds. upwind, one 15 yds. downwind of the field.

	# of <u>samples</u>
Background sample (1 hour sample prior to application)	2
Application + 1 hour sample	2
2 hr. sample (from 1 to 3 hours after application)	2
6 hr. sample (from 3 to 9 hours after application)	2
12 hr. sample (to 24 hours after application began)	2
12 hr. samples from then until study is completed 96 hours (four days) after application began.	12
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Two samplers, one 150 yds. upwind, One 150 yds. downwind of the field.

	# of <u>samples</u>
Background sample (1 hour prior to application)	2
Application + 1 hour sample	2
2 hr. sample (from 1 to 3 hours after application)	2
6 hr. sample (from 3 to 9 hours after application)	2
12 hr. sample (to 24 hours after application began)	2
24 hr. samples from then until study is completed 96 hours (four days) after application began.	6
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Ambient Air Monitoring

We have been asked to set up two ambient air monitors, one in Williams and one in Maxwell. Both will be AC powered and 24-hour long. Two sets will be taken the week of May 18-22 and three sets during the week of May 26-29.

Williams  
Maxwell

# of  
samples  
5  
5  
10

APPENDIX III  
LABORATORY REPORT

UNIVERSITY OF CALIFORNIA, DAVIS

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COLLEGE OF AGRICULTURAL AND  
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(916) 752-1142  
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DEPARTMENT OF ENVIRONMENTAL TOXICOLOGY  
DAVIS, CALIFORNIA 95616

July 10, 1992

Mr. Lynn Baker  
California Air Resources Board  
Toxics Pollutant Branch  
P. O. Box 2815  
Sacramento, CA 95812

Dear Lynn,

Please find enclosed the results of the molinate-XAD resin air samples. Also included are the ARB resin spikes, pre-extraction recovery spikes, run spike and the original protocol.

The results of the ARB resin samples are located in Table 1. The ARB resin spikes are in Table 2. while the pre-extraction lab spikes are in Table 3.

There were only a few samples that 2-oxo-molinate was found above the limit of detection ( $<0.06 \mu\text{g}/\text{sample}$ ). These results were insignificant and are not reported. However, they are available on request.

There are some modifications made in the original protocol and are noted in Section 5 of the include protocol. The column used for analysis was a DB-5 15 m X 0.53 mm capillary column purchased from J & W Scientific, Folsom, CA. Column temperature was programmed from 140 °C to 160 °C @ 4 °C/min

Please give me a phone call if you have any questions.

Best regards,

*Michael M. McChesney*  
Michael M. McChesney  
Staff Research Associate

enclosures

CC: J. N. Seiber

Table 1. Sample Results (total  $\mu\text{g}$  in sample)

SAMPLE	Molinate ( $\mu\text{g}$ )			Average	Standard Deviation
	REP 1	REP 2	REP 3		
1-N-1	< 0.06	< 0.06	< 0.06	< 0.06	0.00
1-S-1	0.21	0.22	0.22	0.22	0.01
1-S-2	< 0.06	< 0.06	< 0.06	< 0.06	0.00
2-N-1	2.08	2.06	2.05	2.06	0.01
2-N-1-2	2.15	2.15	2.04	2.12	0.05
2-N-2	< 0.06	< 0.06	< 0.06	< 0.06	0.00
2-N-2	< 0.06	< 0.06	< 0.06	< 0.06	0.00
2-S-1	0.60	0.60	0.57	0.59	0.01
2-S-2	0.09	0.10	0.07	0.09	0.01
2-S-1-2	0.61	0.63	0.62	0.62	0.00
2-S-2-2	0.13	0.14	0.13	0.13	0.00
3-N-1	2.50	2.51	2.43	2.48	0.03
3-N-2	< 0.06	< 0.06	< 0.06	< 0.06	0.00
3-S-1	0.79	0.80	0.80	0.80	0.00
3-S-2	0.06	0.07	0.06	0.06	0.00
4-N-1	6.96	6.69	6.38	6.67	0.24
4-N-2	< 0.06	< 0.06	< 0.06	< 0.06	0.00
4-S-1	1.20	1.20	1.11	1.17	0.04
4-S-2	< 0.06	< 0.06	< 0.06	< 0.06	0.00
5-N-1	14.27	14.33	14.19	14.26	0.06
5-N-2	0.85	0.85	0.83	0.84	0.01
5-S-1	3.78	3.73	3.68	3.73	0.04
5-S-2	0.82	0.80	0.77	0.80	0.02
6-N-1	11.61	11.31	11.26	11.39	0.15
6-N-2	0.86	0.82	0.75	0.81	0.04
6-S-1	2.65	2.78	2.65	2.69	0.06
6-S-2	2.33	2.37	2.31	2.34	0.02
7-N-1	3.38	3.45	3.47	3.43	0.04
7-S-1	5.10	5.18	4.11	4.80	0.49
8-N-1	0.43	0.46	0.47	0.46	0.02
8-N-2	1.26	1.25	1.21	1.24	0.02
8-S-1	9.23	9.31	8.77	9.10	0.24
8-S-2	7.35	7.48	6.91	7.25	0.24
9-N-1	2.14	2.15	2.13	2.14	0.01
9-S-1	9.69	9.17	8.89	9.25	0.33
10-N-1	0.15	0.17	0.15	0.16	0.01
10-N-2	4.06	4.17	3.93	4.05	0.10
10-S-1	7.79	8.09	7.45	7.78	0.26
10-S-2-2	10.44	10.60	9.99	10.34	0.26
10-S-2	9.73	8.96	9.95	9.55	0.43
11-N-1	5.91	6.14	4.76	5.60	0.60
11-N-1	5.97	6.01	5.68	5.88	0.15
11-S-1	11.89	11.81	9.35	11.02	1.18

Table 1. Sample Results (total  $\mu\text{g}$  in sample)

SAMPLE	Molinate ( $\mu\text{g}$ )			Average	Standard Deviation
	REP 1	REP 2	REP 3		
1-M	1.74	1.74	1.73	1.74	0.01
1-W	2.07	2.12	1.63	1.94	0.22
2-M	5.78	5.78	4.69	5.42	0.52
2-W	0.94	0.91	0.97	0.94	0.02
3-B	< 0.06	< 0.06	< 0.06	< 0.06	0.00
3-M	5.96	5.83	5.92	5.90	0.05
3-M-2	6.73	6.75	6.34	6.60	0.19
3-W	2.57	2.57	2.48	2.54	0.04
4-M	2.78	2.82	2.67	2.76	0.06
4-W	2.74	2.69	2.48	2.64	0.11
4-W-2	2.76	2.80	2.74	2.77	0.02
5-M	3.57	3.60	3.45	3.54	0.06
5-W	1.48	1.45	1.47	1.47	0.01

Table 2. ARB Spike Results (total  $\mu\text{g}$  in sample)

SAMPLE	Molinate ( $\mu\text{g}$ )			Average	St Dev
	REP 1	REP 2	REP 3		
MO-1	0.49	0.50	0.48	0.49	0.01
MO-2	0.27	0.28	0.25	0.264	0.01
MO-3	< 0.06	< 0.06	< 0.06	< 0.06	0.00
MO-4	0.96	0.97	0.95	0.96	0.01
MO-5	0.28	0.30	0.26	0.28	0.01

Table 3. Molinate Spike and Blank Resin

(spiked, extracted and run with samples)

SAMPLE	Molinate ( $\mu\text{g}$ )			Average	St Dev
	REP 1	REP 2	REP 3		
2.0 $\mu\text{g}$ AR	1.79	1.81	1.73	1.78	0.04
RES BLNK	< 0.0.1	< 0.0.1	< 0.0.1	< 0.0.1	< 0.0.1

Table 4. Pre extraction Recovery Study Spiked at 0.25  $\mu\text{g}$

(percent recovery)

1	2	3	4	5	Average	Std. Deviation
86.6	91.0	90.8	96.2	97.6	92.4	3.7

J. N. Seiber  
Envir. Tox  
U. C. Davis

Protocol for Molinate Air Samples with Commercial Sampling Tubes

1. Storage

Store all samples at -20 °C until the time of extraction.  
Record all sample labels in notebook.

2. Extraction

1. Break open top part of glass sampling tube.
2. Remove glass wool and add to 15 ml centrifuge tube.
3. Add contents of sampling tube, including foam partition to centrifuge tube.
4. Add 3 ml ethyl acetate to centrifuge tube and vortex for 2 minutes.
5. Transfer ethyl acetate to a second graduated centrifuge tube with a disposable pipet.
6. Repeat steps 4 & 5 3-times.
7. Concentrate combined ethyl acetate extracts to an appropriate volume for analysis, using a nitrogen evaporator.
8. Include a solvent blank and resin blank.
9. Include spikes, 3 replicates, at 1.0 ug molinate, if extra control resin is provided.

3. Analysis

1. Range find using a Hewlett-Packard 5710 gas chromatograph with a nitrogen-phosphorous(N/P) detector and a 30 DB-1 megabore column.
2. Record the total volume of each sample.
3. Transfer 1 ml of each sample to Hewlett-Packard 7673 autosampler vials.
- 4. Analyze each sample using a Hewlett-Packard 5890 series II gas chromatograph with a N/P detector and an appropriate 30 meter megabore column.

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5. analyze each sample 3 times using a 5-point external standard curve, using a linear regression, in the following manner:
  - a. The total number of samples will be divided into three groups (groups A, B and C).
  - b. Standard curve checks will be run after every fourth sample.
  - c. Each group, with the appropriate number of standard curve checks, will be analyzed with three different standard curves, in the following manner:
    - 1). run standard curve.
    - 2). analyze group A, first time.
    - 3). replace standard curve
    - 4). analyze group A, second time.
    - 5). replace standard curve
    - 6). analyze group A, third time.
  - d. repeat for groups B and C.
  - e. The analysis of each sample will be considered valid if 1) the correlation coefficient value is greater than 0.999 and 2) the standard curve check has less than 5% variation from the standard curve.
6. Check each sample for the presence of 2-oxo-molinate.
7. Quantitate the amount of 2-oxo-molinate, if found.

#### 4. Report

1. The total number of micrograms of molinate in each sample, average of three replicates, will be reported.
2. report the percent recovery for spikes, if resin was provided.
3. Report the amount of 2-oxo-molinate, in micrograms, if present.

#### 5. Deviations from Protocol

Section 2-8. There was no solvent blank run during sample analysis. Only solvent blank to be run was

J. N. Seiber  
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during the pre-extraction lab spike and recovery study done 12 hours prior to the extraction of the samples.

- Section 2-9 A spiking study of 5 replicates spiked at 0.25  $\mu\text{g}$  in each sample was done 12 hours prior to sample extraction.
- Section 3-5 Samples were analyzed using a 7-point linear regression standard curve rather than the stated 5-point standard curve.
- Section 3-7 Samples were analyzed for 2-oxo-molinate. However, the quantity found was less than 0.2  $\mu\text{g}$  total in each sample and those results are not included in this report.

APPENDIX IV  
ANALYTICAL METHOD VALIDATION

## AIRBORNE RESIDUES RESULTING FROM USE OF METHYL PARATHION, MOLINATE AND THIOBENCARB ON RICE IN THE SACRAMENTO VALLEY, CALIFORNIA

JAMES N. SEIBER,\* MICHAEL M. MCCHESENEY and JAMES E. WOODROW  
Department of Environmental Toxicology, University of California, Davis, California 95616

(Received 11 August 1988; Accepted 5 January 1989)

**Abstract**—In connection with requirements of California's Toxic Air Contaminant Act, 24-h ambient air samples were collected using an XAD-4 resin trap technique capable of simultaneously collecting methyl parathion, methyl paraoxon, molinate and thiobencarb. Sampling was conducted on rooftops of public buildings located in four towns in two counties where methyl parathion, molinate and thiobencarb were used in significant quantities, and at a background site located in a county where no use occurred, for four intervals each week for 5 weeks during the springtime application period of 1986. Satisfactory recoveries (greater than 66%) were obtained from dynamic spiking experiments, and the precision from field replicates was consistently less than 50% relative standard deviation using a protocol designed to accommodate a large number of samples. Daily maximum average concentrations (and the range in averages for all sites over the 19 and 20 sampling days in the two-county use area) were 25.7 ng/m<sup>3</sup> (0.2–6.2 ng/m<sup>3</sup>) for methyl parathion, 3.1 ng/m<sup>3</sup> (<0.5–0.8 ng/m<sup>3</sup>) for methyl paraoxon, 1,720 ng/m<sup>3</sup> (60–650 ng/m<sup>3</sup>) for molinate and 250 ng/m<sup>3</sup> (12.9–67.8 ng/m<sup>3</sup>) for thiobencarb. Concentrations correlated well with reported uses of methyl parathion and molinate in the general vicinity of the sampling sites. The likely sources of observed residue levels, based upon the method of application and pesticide physicochemical properties, were spray drift during application for methyl parathion, vapor-phase oxidation of parent thion for methyl paraoxon, and postapplication volatilization from field water for molinate and thiobencarb.

**Keywords**—Methyl parathion    Methyl paraoxon    Molinate    Thiobencarb    Rice  
Pesticides

### INTRODUCTION

Pesticides may enter the atmosphere as drift during application and by volatilization or wind erosion of deposited residues. Quantitation of these routes of environmental entry to the air, though difficult, has revealed a dependence on such factors as the method of application, type of formulation, pesticide physicochemical properties and meteorological conditions at the application site [1–4]. For surface-applied pesticides that are relatively volatile and stable, volatilization is often the most significant dissipation process in residue decline [5,6]. The ambient distribution and persistence of airborne residues has received less attention,

particularly over broad geographic areas of heavy use. Most published examples—2,4-D [7], various insecticides [8–10], DEF [11], atrazine [12] and MCPA [13]—have relied on a relatively small number of samples and/or sampling sites to generalize about temporal or geographic trends in airborne residue concentrations. The expense of collecting and analyzing large sets of air samples and the nonpoint nature of the source limit the amount and quality of published data.

There has been renewed interest in California in the subject of airborne levels of toxic chemicals, including pesticides, as reflected in the recent passage of the Toxic Air Contaminant Act (AB 1807). This measure includes a requirement for determining which pesticides are toxic air contaminants and the appropriate degree of control measures needed [14]. To fulfill this requirement of AB 1807, state regulatory agencies must conduct sampling of candidate pesticides in geographic areas of significant use to ascertain atmospheric concentrations and

\*To whom correspondence may be addressed.

The statements and conclusions in this report are those of the authors 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 either an actual or an implied endorsement of such products.

distribution patterns in relation to potential human exposure, and then conduct risk assessments based on these results and toxicological data. The design and performance of a sampling program capable of fulfilling AB 1807 requirements for pesticides are the general subjects of this report.

The AB 1807 target pesticide in this pilot study was methyl parathion (*O,O*-dimethyl *O-p*-nitrophenyl phosphorothioate), an organophosphate insecticide used to control shrimp in rice fields in the Sacramento Valley. Air sampling was designed to include molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate) and thiobencarb (*S*-[4-chlorobenzyl]*N,N*-diethylthiocarbamate), thiocarbamate herbicides that are applied to control graminaceous weeds in rice during the same springtime period and over a similar geographic area as for methyl parathion. Four-year annual use data for these three chemicals on rice, which reflect primarily uses in the Sacramento Valley, are listed in Table 1. For molinate and thiobencarb, Table 1 shows essentially all of the use of these chemicals in the Sacramento Valley, because their only application in the Valley is on rice. For methyl parathion, the usage on rice (Table 1) represents an estimated one quarter of all uses in the Sacramento Valley throughout the year, but a major use of this chemical is in the May-June period.

Specific objectives were to (a) design sampling and analytical procedures for quantifying these three pesticides, along with the oxon conversion product (*O,O*-dimethyl *O-p*-nitrophenyl phosphate) of methyl parathion, in a large number of 24-h interval air samples; (b) develop quality assurance protocols to provide confidence in the resulting data; and (c) test the methods in an area-wide surveillance by which levels of exposure could be determined for eventual use in risk assessment. We were aiming for methods, results and data interpretation that could be applied to other pesticides in other locales of interest in the AB 1807 process and, potentially, to other trace organic air contaminants.

## METHODS

### Site selection

The highest density of flooded rice fields likely to be treated with methyl parathion during the 1986 growing season, during which sampling was to be conducted, was determined to be in Colusa and Sutter Counties, based on use records from prior years (Pesticide Use Reports, 1983-1985 [15]). Sampling sites were considered in each county using the criteria that they be within significant population centers, near rice-growing areas, accessible to project personnel, free of large obstructions that might void the U.S. Environmental Protection Agency's ambient monitoring criteria (40 CFR 58 [16]) and capable of providing electrical power outlets. Of approximately 12 candidate sites, 2 were selected in Colusa County (rooftops of the high school in Maxwell, and of the city hall in Williams) and two in Sutter County (rooftops of the elementary school in Robbins, and East Nicolaus High School in Trowbridge). A background site that was at least 20 km from rice fields likely to be treated with methyl parathion, molinate or thiobencarb was established on the rooftop of a utility building on the University of California-Davis (UCD) campus in Yolo County. A map indicating the location of the five sampling sites in relation to rice growing areas is shown in Figure 1.

### Sampling equipment

Each sampling site was equipped with a mast consisting of a 2-m aluminum rod (1.27 cm diameter Labrack) attached to a ring stand and secured with guy wires. Fixed to the vertical rod was a horizontal 2-m length of aluminum rod, to the ends of which were attached sampling cups (described below) and in-line flow meters (Model VFA-21, Dwyer Instruments, Michigan City, IN) as shown in Figure 2. Each sampling cup-flow meter combination was attached with 1.25 cm (o.d.) Tygon tubing to an acrylic plastic manifold fitted to the intake of a high-volume sampling

Table 1. Reported uses of molinate, methyl parathion and thiobencarb on rice in California

	Methyl parathion		Molinate		Thiobencarb	
	ha	kg	ha	kg	ha	kg
1983	31,174	24,062	90,688	421,766	36,032	159,354
1984	43,725	33,596	158,300	695,074	36,437	160,262
1985	28,745	21,338	117,409	516,198	48,988	215,650
1986	29,150	19,068	120,243	549,340	39,271	175,244

Data from ref. 15.

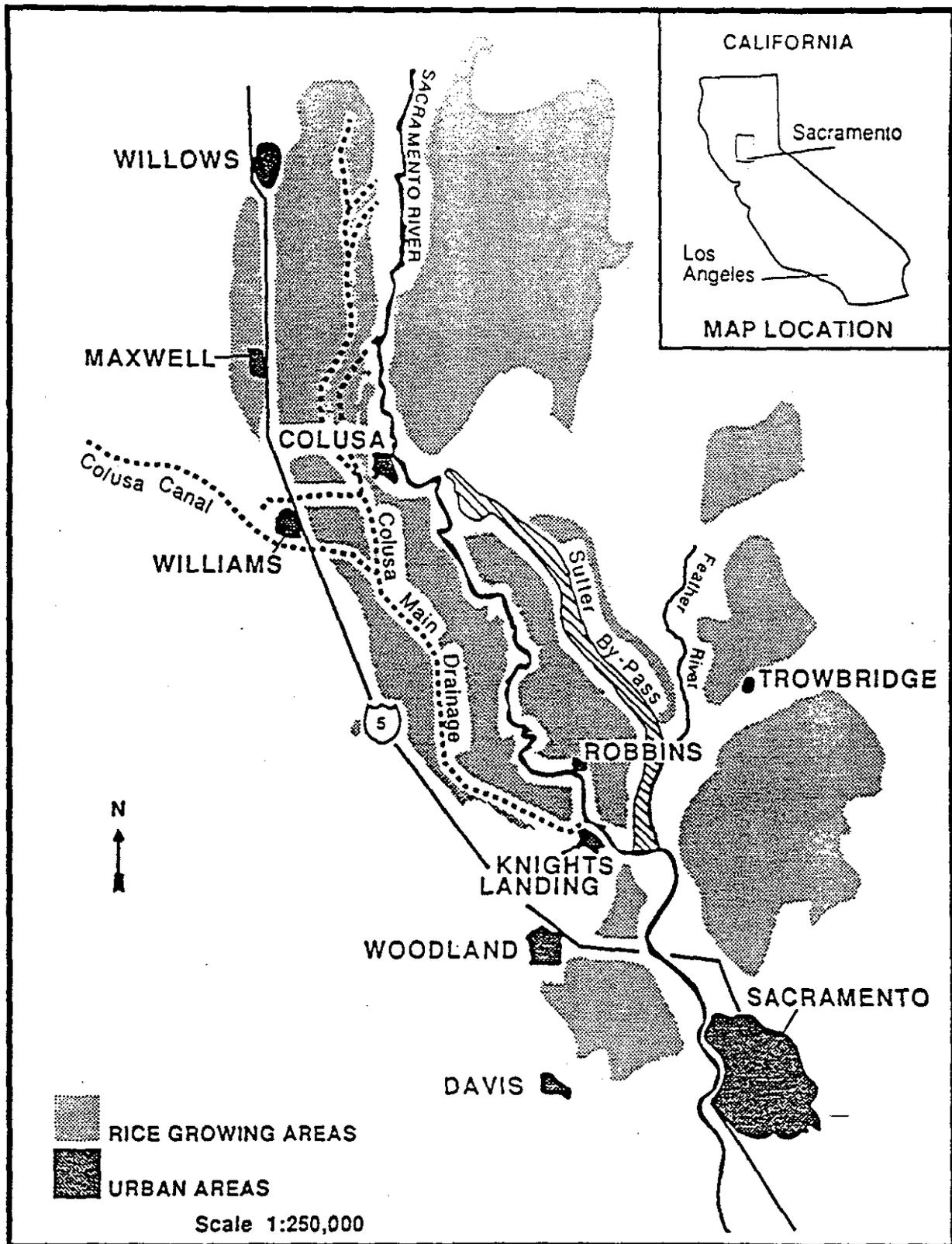


Fig. 1. Map of rice growing area of the Sacramento Valley, California, showing locations of principal canals and rivers, and of the locations of Maxwell, Williams, Robbins, Trowbridge, and Davis, where air samples were collected.

pump (either a Model U-1/AT from BGI, Inc., Waltham, MA, or a standard model from Bendix Corp., Baltimore, MD). The manifold had three or more outlet ports, at least one of which was left

open or unused to provide an unobstructed air inlet to cool the motor. Air flows were set to approximately 50 L/min through each sampling cup by adjusting the flow meters.

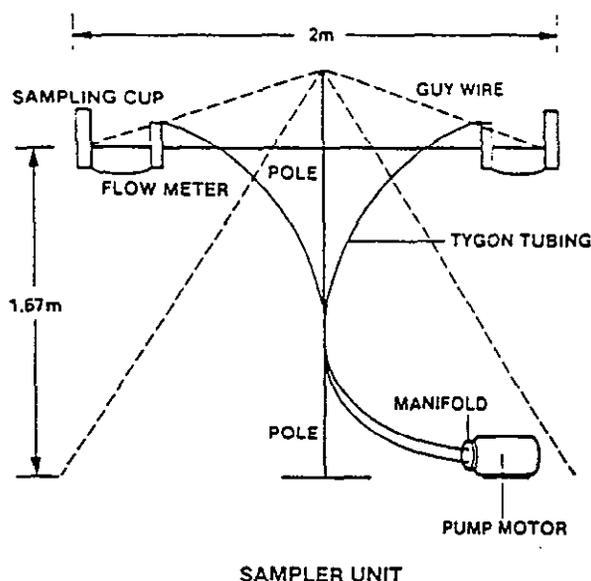


Fig. 2. Schematic of mast assembly used for simultaneously collecting two air samples.

The mast at the Maxwell site was configured to support three rather than two sampling cups 2 m equidistant from each other. This site also had some meteorological equipment for wind direction and windspeed measurements (Wind Profile Register System, Model 104-LED-LM-DC CWT-1791, Thornthwaite and Associates, Elmer, NJ) and a temperature probe (Model 107, Campbell Scientific, Logan, UT) connected to a Model CR-21X Microdata Logger (Campbell Scientific). This site also had a separate sampling mast used for dynamic spiking-recovery experiments.

#### Sampling cups

Each sampling cup consisted of a 6.0 cm × 12.1 cm Teflon cartridge (Savillex Co., Minnetonka, MN). A 100-mesh stainless steel screen pressed into one end of the trap served to retain the sampling medium, which was 60 cm<sup>3</sup> of XAD-4 macroreticular resin (Rohm and Haas, Philadelphia, PA). The resin was cleaned prior to use by washing continuously with deionized water to remove fines, by washing with 0.25 N hydrochloric acid followed by rinsing with several bed volumes of distilled water until the pH of the rinse was about 5, and by successive 24-h Soxhlet extractions with methanol (2×), ethyl acetate and methylene chloride. The resin was then dried for 48 h in a vacuum oven at room temperature.

Some spiking-recovery experiments (see below) were carried out using a Teflon sampling cup charged with either a single 60-cm<sup>3</sup> portion of resin or two 30-cm<sup>3</sup> portions and with a wad of

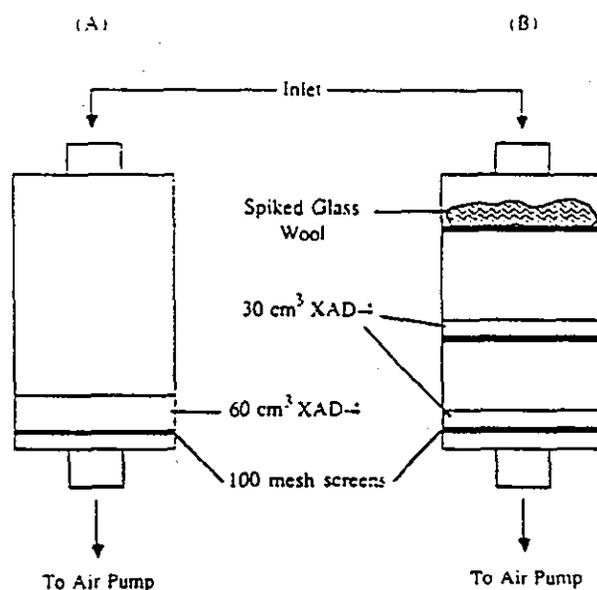


Fig. 3. Schematic of Teflon sampling cups used for normal field sample collection (A) and for determining trapping efficiencies of spiked standards under dynamic conditions (B).

glass wool near the inlet to receive the spiking solution (Fig. 3).

#### Sampling protocol

Normal operation consisted of emptying the 60 cm<sup>3</sup> of XAD-4 resin, used for the prior 24-h sampling interval, from each cup at a given sampling site into glass jars, which were then sealed, labeled and placed in a dry ice chest for eventual transport to a deep freeze (−20°C) at UCD. The cups were then rinsed with acetone, air-dried and recharged with 60 cm<sup>3</sup> of fresh resin. Glass wool was placed on top of the resin to prevent turbulent mixing, the cups were sealed with a Teflon cap that had a 1-cm opening, and air flow was begun. The 1-cm inlet was sealed momentarily to check for leaks, and then the flow was adjusted to a specific value between 40 and 60 L/min, as indicated by the in-line flow meters. An accurate measurement of the flow was then made by momentarily fixing a calibrated flow meter (Model F-1500, Gilmont Instruments, Great Neck, NY) to the cup inlet. This measurement operation was repeated at the end of the sampling interval as well. The entire operation took about 15 min, and was completed between 6:00 and 9:00 a.m. (Pacific Daylight Time) at each site on a schedule that took into account the time for UCD personnel to travel from site to site. An additional operation at the Maxwell site included setting up a separate sampler to receive the dynamic air spike.

### Spiking-recovery tests

To determine extraction recoveries, 60 cm<sup>3</sup> of XAD-4 resin was spiked with a known amount of methyl parathion, methyl paraoxon, molinate or thiobencarb delivered from stock solutions. After thoroughly mixing the resin by tumbling, it was then extracted and analyzed. To test for freezer stability, the same operations were carried out, except that the spiked and mixed resin was placed in a freezer (-20°C) for 11 weeks prior to extraction.

To determine recoveries from air (trapping efficiency), two types of tests were run. In Method A, either a single 60-cm<sup>3</sup> or two 30-cm<sup>3</sup> portions of XAD-4 resin were placed in the Teflon sampling cup. The glass wool at the cup inlet was spiked with a known amount of the chemical(s) of interest. Air was then drawn through the cup at a known rate (about 50 L/min) for 24 h. The air temperature was recorded continuously (a usual 24-h cycle ranged from 18 to 30°C).

In Method B, designed for use at the field sampling sites, a small wad of glass wool, placed inside a piece of curved 15 cm × 1 cm (o.d.) glass tubing, was spiked. The tubing was immediately connected at the downstream end to the Teflon sampling cup and at the upstream end to a glass drying tube (12.8 cm × 1.6 cm o.d.; Bantamware) filled to a 3-cm depth with XAD-4 resin. This latter tube cleaned the incoming air of any chemical residues that might have interfered with the recovery test. Flow was established as before.

In both types of tests (Methods A and B), the glass wool that received the initial spiking solution, the tubing walls and the resin bed were separately extracted. Trapping efficiency was calculated as follows:

% trapping efficiency

$$= \frac{(\text{amount in resin}) \times 100}{\left( \begin{array}{c} \text{amount} \\ \text{spiked} \end{array} \right) - \left( \begin{array}{c} \text{amount remaining} \\ \text{in glass wool} \end{array} \right)}$$

### Extraction

The XAD-4 resin was extracted in the following manner: Ethyl acetate (90 ml) was added to the resin in a 250-ml Erlenmeyer flask and then swirled for 30 min. The solvent was decanted and filtered through Whatman No. 1 filter paper into a 500-ml sample storage container. Fresh solvent (60 ml) was added to the flask and then swirled for 15 min. The solvent was then transferred and 50 ml of additional fresh solvent was added and the

flask was swirled once more for 10 min. Samples were concentrated to approximately 4 ml on a steam bath using a Kuderna-Danish apparatus. Further reduction of solvent, if necessary, was accomplished using a three-ball micro Snyder column. Samples were first analyzed for molinate and thiobencarb when the sample volume was 4 ml and then for methyl parathion and methyl paraoxon at reduced volumes.

### Gas chromatography

Molinate, thiobencarb, methyl parathion and the oxon of methyl parathion were analyzed using a Hewlett-Packard Model 5710A gas chromatograph equipped with a nitrogen-phosphorus detector. The column was a 30-m DB-5 megabore (J&W Scientific, Rancho Cordova, CA). Flows for helium, air and hydrogen gases were, respectively, 6, 70 and 3 ml/min, and helium make-up gas flow was 19.5 ml/min. Temperatures for injector, column and detector were 250, 210 and 250°C, respectively.

A Tracor Model MT-220 gas chromatograph equipped with a flame photometric detector with phosphorus filter (526 nm) was also used for methyl parathion analysis when there was a question of interference or need of confirmation for those samples that approached the limit of detection. A 1.8 m × 0.32 cm glass column packed with 3% OV-210 on 80-100 mesh Chrom W HP was used. Flow rates (ml/min) for nitrogen (carrier), air and hydrogen were 55, 80 and 60, respectively.

Some recovery samples were analyzed for methyl parathion using a Varian Model 2100 gas chromatograph equipped with a 1.8 m × 3 mm (i.d.) glass column packed with 100/120 mesh Supelcoport, coated with 1.5% SP 2250 and 1.95% SP 2401, and an alkali flame ionization detector. Column oven temperature was maintained at 175°C and the carrier (nitrogen) flow was 35 ml/min.

In all cases, a four- or five-point standard curve was made using a variable volume injection technique. Samples were then doubly injected and the average of the two areas used to calculate concentrations. A standard was injected after every other sample and compared with the original standard curve. The analysis was considered valid if the standard was within 3% of the original standard curve.

The minimum detectable limit (MDL) for methyl parathion was calculated to be 0.2 ng/m<sup>3</sup> (0.02 ppt) based on the following: 0.10 ng was detectable in a 6-μl injection from a total sample volume of 0.5 ml derived from an air sample of 50 m<sup>3</sup>.

The MDL for methyl paraoxon was 0.5 ng/m<sup>3</sup>, while for molinate and thiobencarb it was 1.4 ng/m<sup>3</sup> and 2 ng/m<sup>3</sup>, respectively.

## RESULTS

We collected 24-h ambient air samples using an XAD-4 resin trap technique capable of simultaneously collecting the four chemicals of interest—methyl parathion, methyl paraoxon, molinate and thiobencarb. Four ambient sampling sites were established in two counties where methyl parathion, molinate and thiobencarb were expected to be used in significant quantities on rice, while a background site was placed in a location in a third county where no use was expected. Sampling was carried out for four 24-h intervals (Monday morning through Friday morning) for five weeks (12 May through 12 June, 1986) during the period selected to represent the highest uses in the two counties. This represented some guesswork based upon application data from prior years.

### Spike/recoveries

When methyl parathion, methyl paraoxon, molinate or thiobencarb were spiked to XAD-4 resin and then immediately extracted, recoveries were essentially quantitative (Table 2). When extraction was carried out after 11 weeks of storing the spiked resin in a freezer, recoveries were still quite good for methyl parathion, but the recovery for methyl paraoxon dropped to 66.5%. Molinate and thiobencarb were not checked for freezer stability, but other studies indicate they are stable. When methyl parathion was spiked dynamically, by volatilizing

a deposit of the chemical on glass wool directly into the incoming air over a 24-h period outdoors (Method A), recovery (i.e., trapping plus extraction efficiency) was 85% when 60 cm<sup>3</sup> of resin was used and 82% when 30 cm<sup>3</sup> of resin was used, with no significant conversion of thion to oxon in either case. Molinate recovery from Method A spiking was 67% on 30 cm<sup>3</sup> of resin, with no breakthrough to a second 30 cm<sup>3</sup> portion of resin. Thiobencarb recovery was 96.5% for 24-h sampling through 30 cm<sup>3</sup> of XAD-4 resin. The lower recovery for molinate was probably due to incomplete extraction of resin-bound residue, or to some loss during concentration of the extract. In sum, these spiking experiments indicated that the resin trapped and retained the chemicals satisfactorily during 24-h runs, and released them satisfactorily by a simple solvent extraction. After concentration, the extract could be analyzed by gas chromatography without significant resin-derived interferences. No cleanup of extracts was needed for either spiked or field samples.

When dynamic spiking was done by volatilizing a deposit of the chemical contained in a glass tube attached to the inlet of the sampling cup (Method B), average recoveries of methyl parathion and molinate dropped considerably to 37 and 30%, respectively (Table 2); precision was poor and significant conversion of the thion to the oxon (up to 82% of the volatilized thion) occurred. These results were most likely due to the technique of spiking; the glass spiking tubes were not shielded from direct sunlight, which could have caused some photolysis or thermal breakdown of the

Table 2. Results of tests for trapping, extraction and storage recoveries (percent  $\pm$  SD)

Method	Methyl parathion	Methyl paraoxon	Molinate	Thiobencarb
Spike to resin/extract <sup>a</sup>	111.0 $\pm$ 6.1 (n = 3)	86.7 $\pm$ 22.0 (n = 3)	92.3 $\pm$ 8.3 (n = 3)	84.2 $\pm$ 7.2 (n = 3)
Spike to resin/freeze 11 weeks/extract				
2,000 ng	97.6 $\pm$ 6.8 (n = 3)	—	—	—
200 ng	86.2 $\pm$ 4.2 (n = 3)	66.5 $\pm$ 6.0 (n = 3)	—	—
Dynamic (Method A <sup>b</sup> )				
60 cm <sup>3</sup> resin	85.0 $\pm$ 1.0 (n = 3)	—	—	—
30 cm <sup>3</sup> resin (1st)	82.0 $\pm$ 1.0 (n = 3)	—	67 $\pm$ 1 (n = 3)	96.5 $\pm$ 23.6 (n = 6) <sup>c</sup>
30 cm <sup>3</sup> resin (2nd)	0 (n = 3)	—	0 (n = 3)	—
Dynamic (Method B <sup>d</sup> )				
60 cm <sup>3</sup>	37 (n = 16)	—	30 $\pm$ 12 (n = 10)	—

<sup>a</sup>100 ng, except for thiobencarb (2,000 ng).

<sup>b</sup>800 ng spiked, 60 L/min, 24 h.

<sup>c</sup>50  $\mu$ g spiked, 24 h.

<sup>d</sup>2,000 ng spiked, 60 L/min, 24 h.

spiked deposits. There was about 5 cm of unshielded glass tubing through which vapors had to pass before entering the sampling cup—a zone for potential breakdown of vapors or of material adsorbed to the tubing walls. The Method B results are included here to point out the need for careful design when field spiking is to be done, and to indicate a point where improvement is needed in extending this protocol to other applications. In fact, we believe that Method A would be the correct choice for future design, and that Method A spiking be done at least once a week at the same sites where samples are to be collected.

### Field results

**Background samples.** A total of 20 sampling days were employed, with duplicate samples taken at four locations (Trowbridge, Robbins, Williams, and UCD background) and triplicate samples taken at one location (Maxwell) for a total of approximately 200 samples requiring analysis for the four chemicals. The UCD background samples showed, with one exception, no methyl parathion or methyl paraoxon above the detection limits (0.2 and 0.5 ng/m<sup>3</sup>, respectively). The single exception was a sample from 15 May, which had 0.39 ng/m<sup>3</sup> of methyl parathion, for which the duplicate was less than 0.2 ng/m<sup>3</sup>. No molinate or thiobencarb was recorded in any of the background samples above the detection limit (1.4 and 2.0 ng/m<sup>3</sup>, respectively).

**Methyl parathion and methyl paraoxon.** The higher air concentrations of these two chemicals were obtained from samples collected at Maxwell High School—the site that also had triplicate collection cups. The highest daily average thion values occurred early in the study, on 13 May (25.7 ng/m<sup>3</sup>) and 14 May (21.5 ng/m<sup>3</sup>), with a gradual decrease through the remainder of May, after which time values were near or below the detection limit (Table 3). Oxon concentrations were low throughout, with the maximum occurring on 22 May (3.1 ng/m<sup>3</sup>). The thion/oxon ratios averaged about 10:1 at Maxwell over the month of May, although ratios as low as 2:1 were recorded on a few days (Table 3).

Replication of thion values was generally good, with most relative standard deviations (RSD) being less than about 50%, except for very low concentrations, which gave poorer precision. RSDs for the oxon were generally higher than for the thion. Agreement between duplicates at the other sites was similar to that for the results from Maxwell. Concentration averages and samples above the detection limit were generally in the order: Maxwell > Williams > Trowbridge ≈ Robbins > UCD (negligible).

**Molinate.** The Maxwell site again yielded generally higher air concentrations of molinate (Table 4), with the highest daily average (1.7 µg/m<sup>3</sup>) recorded on the first day of sampling (12 May). Concentrations decreased during the re-

Table 3. Average methyl parathion and methyl paraoxon concentrations in air (ng/m<sup>3</sup>)<sup>a</sup>

Date	Trowbridge		Robbins		Maxwell		Williams	
	Thion	Oxon	Thion	Oxon	Thion	Oxon	Thion	Oxon
5/12/86	0.53	<0.5	0.72	<0.5	6.65	<0.5	1.03	<0.5
5/13/86	1.05	<0.5	0.50	<0.5	25.67	2.32	4.69	1.14
5/14/86	0.54	<0.5	0.50	<0.5	21.53	0.83	21.75	0.75
5/15/86	<0.2	<0.5	0.37	<0.5	13.80	<0.5	5.56	0.87
5/19/86	<0.2	<0.5	<0.2	<0.5	14.90	1.14	5.31	<0.5
5/20/86	<0.2	<0.5	<0.2	<0.5	5.01	0.68	5.22	0.93
5/21/86	1.10	<0.5	<0.2	<0.5	13.97	<0.5	4.74	0.98
5/22/86	<0.2	<0.5	<0.2	<0.5	7.72	3.07	1.45	<0.5
5/27/86	<0.2	<0.5	— <sup>b</sup>	— <sup>b</sup>	2.13	<0.5	1.34	<0.5
5/28/86	<0.2	<0.5	<0.2	<0.5	5.73	1.15	1.82	0.72
5/29/86	<0.2	<0.5	<0.2	<0.5	2.84	0.65	— <sup>b</sup>	— <sup>b</sup>
5/30/86	<0.2	<0.5	<0.2	<0.5	1.43	<0.5	— <sup>b</sup>	— <sup>b</sup>
6/10/86	<0.2	<0.5	<0.2	<0.5	<0.2	<0.5	0.32	<0.5
6/11/86	— <sup>b</sup>	— <sup>b</sup>	<0.2	<0.5	0.71	<0.5	0.66	<0.5
6/12/86	0.50	<0.5	<0.2	<0.5	<0.2	<0.5	0.34	<0.5

<sup>a</sup>Samples collected on 2–9 June, and on all the sampling days but one at the background site (Davis), showed less than the minimum detectable limit for the thion (0.2 ng/m<sup>3</sup>) and the oxon (0.5 ng/m<sup>3</sup>).

<sup>b</sup>No samples taken.

Table 4. Average molinate and thiobencarb concentrations in air (ng/m<sup>3</sup>)<sup>a</sup>

Date	Trowbridge		Robbins		Maxwell		Williams	
	Molinate	Thiobencarb	Molinate	Thiobencarb	Molinate	Thiobencarb	Molinate	Thiobencarb
5/12/86	280	— <sup>b</sup>	28	— <sup>b</sup>	1,720	25.5	141	<2.0
5/13/86	247	4.32	40.5	<2.0	885	17.5	113	5.16
5/14/86	137	4.08	104	2.42	1,183	37.7	415	8.03
5/15/86	<1.4	<2.0	2.4 <sup>c</sup>	<2.0	295 <sup>d</sup>	<2.0	76	6.28
5/19/86	102	82.8	44.5	8.80	947	26.1	216	23.3
5/20/86	84.5	250	142 <sup>c</sup>	7.67 <sup>c</sup>	389	7.10 <sup>d</sup>	77.5	23.0
5/21/86	162	27.6	87	40.8	314	7.36 <sup>d</sup>	195 <sup>c</sup>	4.64
5/22/86	200	80.2	93.5	17.4	614	18.2	105	21.8
5/27/86	71.9	50.6	— <sup>b</sup>	— <sup>b</sup>	561	27.1	100	16.6
5/28/86	171	119	48.5	13.0	240	59.2	82.4	18.4
5/29/86	84	43.2	70	17.7	266 <sup>d</sup>	64.5	— <sup>b</sup>	— <sup>b</sup>
5/30/86	43.8	16.4	25.4	5.66 <sup>c</sup>	145	28.7	— <sup>b</sup>	— <sup>b</sup>

<sup>a</sup>All samples collected on 2-12 June, and on all sampling days at the background site (Davis), showed less than the minimum detectable limit for molinate (1.4 ng/m<sup>3</sup>) and thiobencarb (2.0 ng/m<sup>3</sup>).

<sup>b</sup>No samples taken.

<sup>c</sup>One replicate only.

<sup>d</sup>Two replicates only.

mainder of May and by early June approached the detection limit. RSDs for replicates were similar to those for methyl parathion, that is, generally below 50%. The Williams and Trowbridge samples were generally lower in concentration, and the Robbins samples were lower still (Table 4). Even at these three sites, however, average molinate concentrations still far exceeded the highest methyl parathion values.

*Thiobencarb.* Replication of values was quite good for 7 of the 11 d for which data were collected at the Maxwell site (Table 4). The highest 19-sampling-day average air concentration for thiobencarb was recorded at Trowbridge (67.8 ng/m<sup>3</sup>), but this average included two days (20 and 28 May) when very high concentrations were recorded. We suspect that thiobencarb was applied to rice fields located within 0.5 km of this site during those two days; chemical applications were observed then, although they were not confirmed to be thiobencarb. Subtracting these two days' results from the average, the overall concentration averages from the four sites near rice fields differed little, ranging from 12.9 ng/m<sup>3</sup> at Williams to 39 ng/m<sup>3</sup> (average minus the data for 20 and 28 May) at Trowbridge. Concentrations at all sites fell to below detectable limits from 2 June to the end of sampling.

#### Correlation with use data

California statutes require that the location, acreage treated and application rate be supplied

with the application permit when any chemical, especially restricted-use pesticides such as methyl parathion, molinate or thiobencarb, is to be applied by a commercial applicator. This information was searched manually over the period of sampling (i.e., 10 May through 12 June) for methyl parathion and molinate in areas within approximately 16 km of the sampling sites. Because thiobencarb was not included in our original experimental design, use data for it were not obtained. For both methyl parathion and molinate, the heaviest use was in the Maxwell-Williams area, and the least use was in the Robbins-Trowbridge area. The low use in the latter areas was due, at least in part, to the lack of a significant rice shrimp pest problem in Sutter County in 1986.

Correlation of use data with air concentrations was done for the Maxwell site only, assuming that since this site had the highest air concentrations of methyl parathion and molinate and was near the heaviest use there was a better chance of seeing clear-cut trends. In attempting to correlate use data with air concentrations for methyl parathion at the Maxwell site (Fig. 4), a trend was apparent toward higher concentrations during periods of heaviest use and lower to negligible concentrations after reported uses ceased (i.e., after 23 May). The correlation was crude, at best, because our sampling was conducted for only 4 d each week while applications could take place on all days of the week, and the correlation did not differentiate between applications made very close to or distant

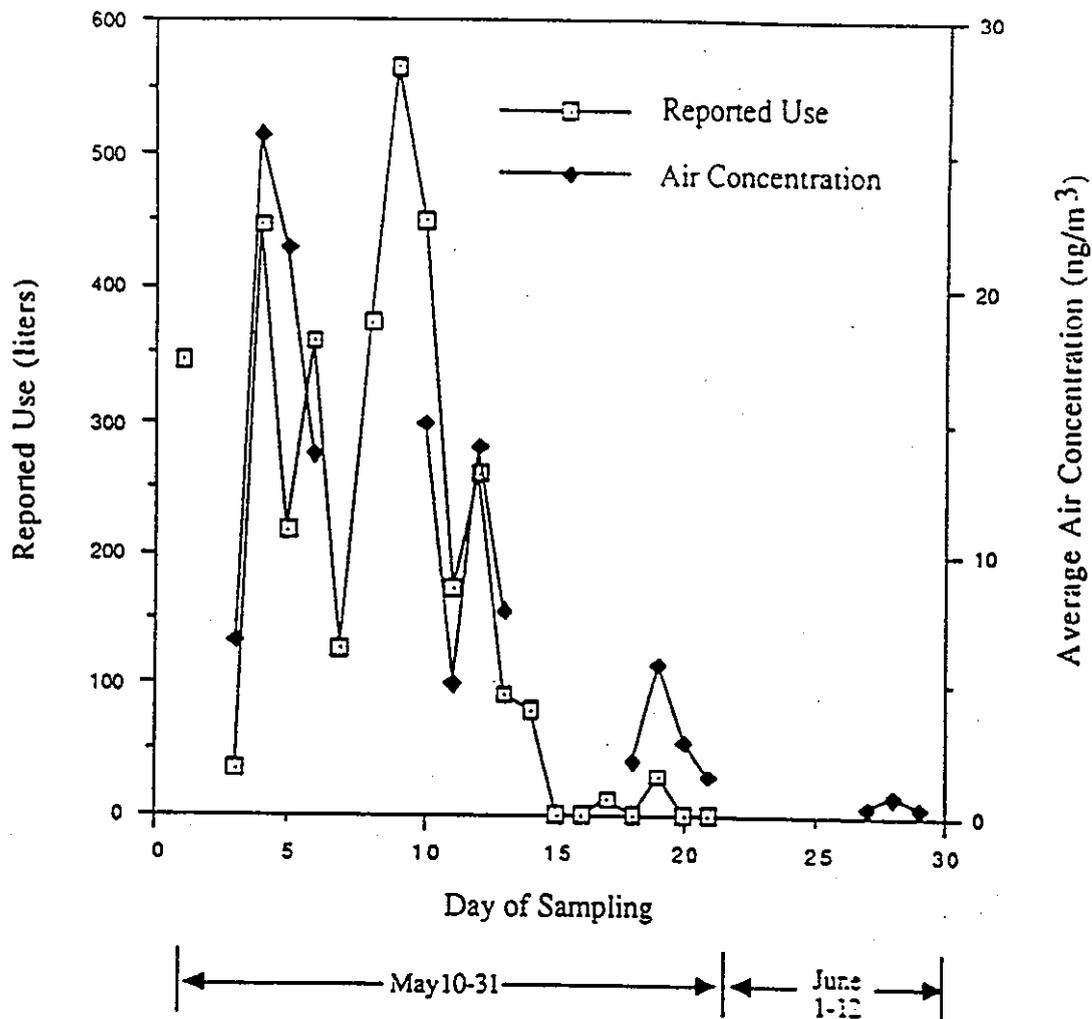


Fig. 4. Plot of methyl parathion air concentrations at Maxwell and reported usage of methyl parathion in the Maxwell vicinity, 10 May to 12 June 1986.

from the sampling sites, or between those made upwind or downwind from the sampling sites.

The correlation for molinate at Maxwell (Fig. 5) showed the highest concentrations and highest uses at the initiation of the sampling period, suggesting that use had begun before sampling was under way. Here again, however, there was a decrease in air concentrations through the sampling period corresponding to the decrease in reported usage, although significant air concentration persisted well beyond cessation of molinate applications on approximately 27 May.

#### DISCUSSION

Methyl parathion, molinate and thiobencarb are applied exclusively by air directly to rice field water. However, there are major differences between the manner of use and the physicochemical properties that might influence air concentrations of the three chemicals observed in the area of use. Methyl parathion is applied as a water-based emul-

sifiable spray, while molinate and thiobencarb are applied as granular formulations. Thus drift during application might be expected to be greater for methyl parathion, and the correlation curves may reflect this (Figs. 4 and 5). Methyl parathion concentrations correlated better, at least qualitatively, with the usage on individual days of sampling, and the concentrations fell off abruptly when usage ceased. This is more consistent with an immediate release as spray drift (as either vapors or fine particulate aerosol—our sampling method did not discriminate between the two) rather than a slower postapplication volatilization of residue dissolved in field water.

In fact, the volatilization tendencies of the three chemicals are markedly in favor of molinate (Table 5). The vapor pressure of molinate is considerably higher (factor of about 300), as is the Henry's Law constant, the governing property in water, air distribution (factor of about 10). In a separate study, we measured the volatilization flux of methyl

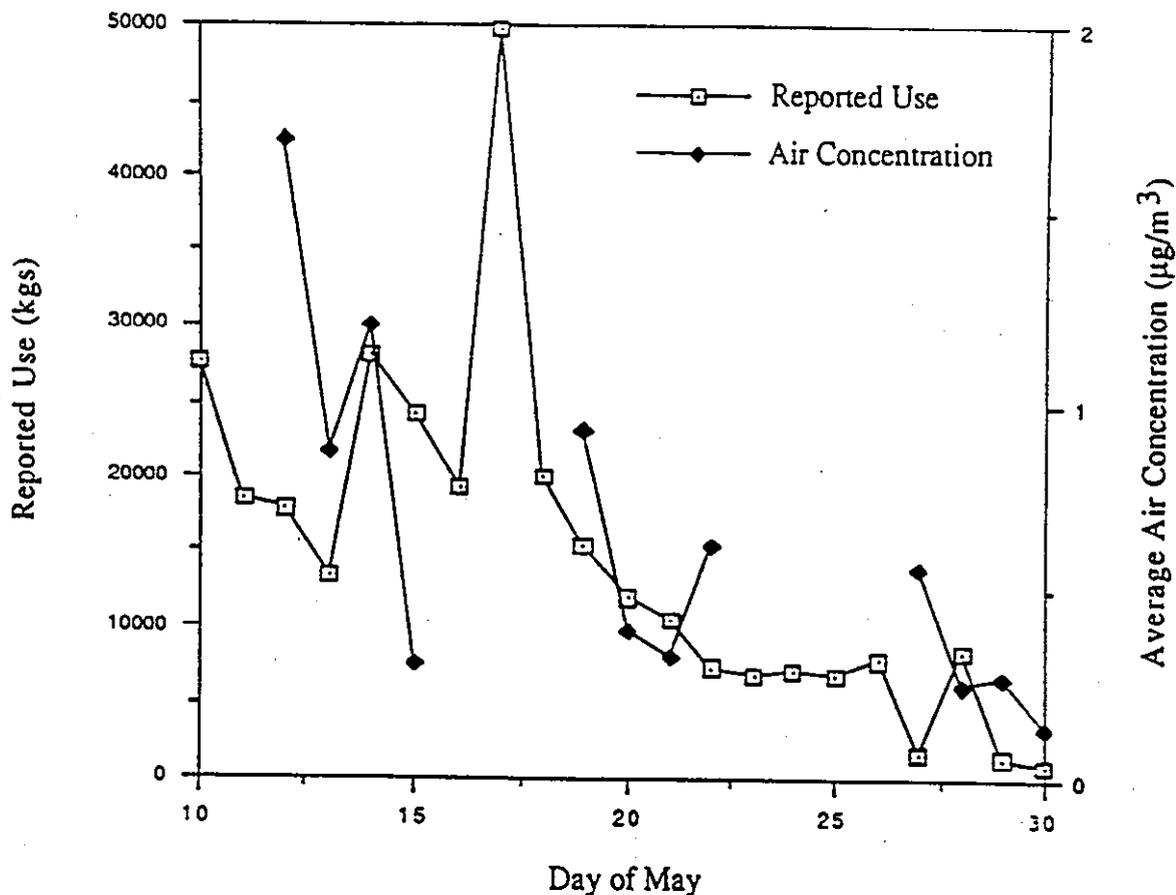


Fig. 5. Plot of molinate air concentrations at Maxwell and reported usage of molinate in the Maxwell vicinity, 10 May to 30 May 1986.

Table 5. Physical properties and dissipation behavior of methyl parathion, molinate and thiobencarb in a flooded rice field

	Methyl parathion	Molinate	Thiobencarb
<b>Physical properties</b>			
Water solubility	37.7 mg/L (22°C)	800 mg/L (20°C)	30 mg/L (20°C)
Vapor pressure	$1.5 \times 10^{-6}$ kPa (22°C)	$4.1 \times 10^{-4}$ kPa (20°C)	$2.0 \times 10^{-6}$ kPa (20°C)
Henry's Law constant	$1.0 \times 10^{-7}$ m <sup>3</sup> ·atm/mol	$9.7 \times 10^{-7}$ m <sup>3</sup> ·atm/mol	$1.7 \times 10^{-7}$ m <sup>3</sup> ·atm/mol
<b>Dissipation data from rice field water</b>			
Half-life in water	44 h <sup>a</sup>	84 h <sup>a</sup>	6-9 d <sup>c</sup>
Major loss route <sup>a,b</sup>	Chemical/microbial breakdown in water —	Volatilization from water	Adsorption to soil, and chemical/microbial breakdown
Volatilization rate <sup>a,b</sup>	<0.01 kg/ha/d	1.1 kg/ha (1st 4 d)	0.07 kg/ha (1st 4 d)

<sup>a</sup>From Seiber and McChesney [17].

<sup>b</sup>From Seiber et al. [19].

<sup>c</sup>Yusi and Ishikawa [24].

parathion and molinate from the same rice field and found that the normalized flux (i.e., flux normalized on water concentration) of molinate was about 10 times that of methyl parathion [17]. The absolute flux for molinate was over 100 times that of methyl parathion due to its higher rate of application and thus higher water concentrations.

Methyl parathion dissolved in rice field water is primarily lost by chemical and microbial breakdown (hydrolysis and possibly oxidation to the oxon followed by hydrolysis). Molinate, however, is relatively stable in rice field water [18] and dissipates primarily by volatilization, which may release approximately 1.1 kg/ha to the air over the

first 4 d after application at a typical 4 kg/ha rate [19,20]. The rate of volatilization can be particularly high when the field water warms in the late afternoons and under windy conditions, leading to several-fold hourly and diurnal variations in volatilization rates.

Thiobencarb represents an intermediate situation. Its stability toward hydrolysis in rice field water is similar to that of its chemical relative molinate, but its Henry's Law constant is very close to that of methyl parathion. At a given application rate, a much larger percentage is adsorbed to sediment and thus a much lower percentage is dissolved in water than for the more water-soluble molinate [20]. In a prior experiment, we observed that maximum rice field water concentrations of thiobencarb were about 20% those of molinate [19]. Thus, volatilization of thiobencarb from water could occur at as little as 2% of the rate for molinate, and this factor could account for the observed differences in air concentrations for the two chemicals. The lower overall quantity of thiobencarb used in 1986 (about 33% that of molinate) also would influence observed air concentrations, but this could not be directly correlated with concentrations observed in the present study because we were unable to document thiobencarb use data in the vicinity of the four sampling sites located in the rice-growing regions of the Sacramento Valley.

Thus, while methyl parathion may have the greater drift potential, which could lead to measurable downwind air concentrations close to a field undergoing treatment, the overriding factor affecting the observed differences in the average concentrations of the three chemicals appears to be the rate of postapplication volatilization from field water. Not only does molinate have a much higher rate of volatilization, and a prolonged period during which it can occur, but the usage of molinate in the sampled areas was much greater than that of methyl parathion and, apparently, of thiobencarb. Another factor, not estimable from data at hand, is the potentially greater stability of molinate and thiobencarb in air as compared with methyl parathion, which would allow a longer residence of volatilized molinate or thiobencarb and thus a greater likelihood of occurrence. Woodrow et al. [21] showed that ethyl parathion is converted to ethyl paraoxon in field air and provided indirect evidence of further conversion to *p*-nitrophenol. Airborne molinate has not been shown to photodecompose in the field, although it does so slowly upon vapor-phase irradiation in the laboratory [22]. In fact, a number of our air samples contained 2-oxomolinate, a potential oxidation

product of molinate, but the concentrations of this product were generally lower than those for the parent molinate. We are unaware of published data on the vapor-phase stability of thiobencarb.

With regard to methyl paraoxon residues observed at the sampling sites, it is very unlikely that these originate by volatilization from water because the Henry's Law constant of the oxon is less than that for the thion, due to the oxon's much greater water solubility [23]. Also, hydrolysis of the oxon is considerably faster than that of the thion. Rather, atmospheric oxidation of thion vapors to oxon is more likely, with the example provided by the earlier study of ethyl parathion showing the feasibility of this route. Apparently it was not a major route in this study, however, because oxon residue levels were always much less than the thion levels.

The observed ambient concentrations of molinate averaged over the study period are approximately an order of magnitude lower than predicted from a uniform distribution of vapors in the Sacramento Valley. The assumptions, and calculations, are as follows: Assume that volatilization is the only dissipation pathway for molinate (i.e., all of the applied molinate eventually volatilizes), that volatilization occurs over a 30-d period with each day contributing 1/30th of the total (i.e.,  $1/30 \times 549,340 \text{ kg} = 18,311 \text{ kg/d}$ ), that the total volume of air in the Sacramento Valley is about 17,000 km<sup>3</sup> (70 km  $\times$  240 km  $\times$  1 km), and that there is no route of escape for uniformly distributed airborne molinate from the Sacramento Valley within a 24-h period but also that there is no carryover of airborne residue from one day to the next. These assumptions lead to a calculated uniform air concentration of about 1  $\mu\text{g}/\text{m}^3$  in the Sacramento Valley atmosphere, compared with the 20-sampling-day average concentrations of 0.06 to 0.65  $\mu\text{g}/\text{m}^3$  at the Sutter and Colusa County sampling sites in the present study (Table 4). In terms of risk assessment for human exposure, this range of average concentrations represents a chronic exposure for the general population during the application season. However for margin-of-safety considerations, transient elevated concentrations (such as the ones observed early in this study) close to sources are of particular importance. Knowing the worst-case scenario, or highest possible concentrations, for residents in a treatment area allows the determination of a "safe" exposure, or equivalently, a "safe" distance from a particular source.

Airborne pesticide vapors are undoubtedly continually dissipated by transport out of the Valley, by dry deposition or exchange to water, vegetation

and soil surfaces, and perhaps by slow degradation. But these loss routes are apparently slow enough, at least for molinate, to allow for some accumulation in air over the 1-month period of heaviest use. While these factors await future study, we do know from the present work that pesticide vapors are measurably present in the Valley's atmosphere, that the concentrations of airborne molinate are much higher than those of methyl parathion and thiobencarb, and that molinate levels are in a concentration range that is comparable to that observed for many other organic pollutants in ambient air. Whether these airborne residues represent a health risk for exposed populations is unlikely, but the question does warrant further attention.

*Acknowledgement*—We thank the following individuals and agencies for help with various phases of this project: Lynn Baker and Tom Parker of the California Air Resources Board, who serve as Project Officers for the contract (ARB No. A5-169-43) under which this study was conducted, and Vince Schmidt and Kathy Orr of the University of California-Davis, who helped with the laboratory analyses.

#### REFERENCES

- Lewis, R.G. and R.E. Lee, Jr. 1976. Air pollution from pesticides: Sources, occurrence, and dispersion. In R.E. Lee, Jr., ed., *Air Pollution from Pesticides and Agricultural Processes*. CRC Press, Cleveland, OH, pp. 5-50.
- Taylor, A.W. 1978. Post application volatilization of pesticides under field conditions. *J. Air Pollut. Control Assoc.* 28:922-927.
- Seiber, J.N., G.A. Ferreira, B. Hermann and J.E. Woodrow. 1980. Analysis of pesticidal residues in the air near agricultural treatment sites. In J. Harvey, Jr., and G. Zweig, eds., *Pesticide Analytical Methodology*. American Chemical Society Symposium Series No. 136. Washington, DC, pp. 177-208.
- Taylor, A.W. and D.E. Glotfelty. 1988. Evaporation from crops and soils. In R. Grover, ed., *Environmental Chemistry of Herbicides*, Vol. 1. CRC Press, Boca Raton, FL, pp. 89-129.
- Spencer, W.F., W.T. Farmer and M.M. Cliath. 1973. Pesticide volatilizations. *Residue Rev.* 49:1-47.
- Seiber, J.N., S.C. Madden, M.M. McChesney and W.L. Winterlin. 1979. Toxaphene dissipation from treated cotton field environments: Component residual behavior on leaves and in air, soil, and sediment determined by capillary gas chromatography. *J. Agric. Food Chem.* 27:284-291.
- Que Hee, S.S., R.G. Sutherland and M. Vetter. 1975. GLC analysis of 2,4-D concentrations in air samples from central Saskatchewan in 1972. *Environ. Sci. Technol.* 9:62-66.
- Arthur, R.D., J.D. Cain and B.F. Barrentine. 1976. Atmosphere levels of pesticides in the Mississippi delta. *Bull. Environ. Contam. Toxicol.* 15:129-134.
- Kutz, F.W., A.R. Yobs and H.S.C. Yang. 1976. National pesticide monitoring programs. In R.E. Lee, Jr., ed., *Air Pollution from Pesticides and Agricultural Processes*. CRC Press, Cleveland, OH, pp. 95-136.
- Baunok, I. 1984. Analysis of airborne pesticides at selected sites in South Africa. *Suid-Afrik. Tydskrif vir Wetenskap.* 80:277.
- Kilgore, W., C. Fischer, J. Rivers, N. Akesson, J. Wicks, W. Winters and W. Winterlin. 1984. Human exposure to DEF merphos. *Residue Rev.* 91:71-102.
- Glotfelty, D.E. 1985. Pathways of pesticide dispersion in the environment. In J.L. Hilton, ed., *Agricultural Chemicals of the Future*. Beltsville Symposium in Agricultural Research, Vol. 8. Rowan and Allanheld, Totowa, NJ, pp. 425-435.
- Seiber, J.N. and J.E. Woodrow. 1984. Airborne residues and human exposure. In M. Siewierski, ed., *Determination and Assessment of Pesticide Exposure*. Elsevier, New York, NY, pp. 133-146.
- Tanner. *Air Pollution: Toxic Air Contaminants*. AB 1807. 1984. Chapter 1047 California Assembly Record. Legislative Counsel's Digest, Sacramento, CA, March 27.
- Pesticide Use Reports. 1983, 1984, 1985 and 1986. Annual Summaries, Department of Food and Agriculture, Sacramento, CA.
- 40 CFR 58. 1986. Appendix E. Code of Federal Regulations, Washington, DC.
- Seiber, J.N. and M.M. McChesney. 1987. Measurement and computer model simulation of the volatilization flux of molinate and methyl parathion from a flooded rice field. Final Report to Department of Food and Agriculture, Sacramento, CA.
- Soderquist, C.J., J.B. Bowers and D.G. Crosby. 1977. Dissipation of molinate in a rice field. *J. Agric. Food Chem.* 25:940-945.
- Seiber, J.N., M.M. McChesney, P.F. Sanders and J.E. Woodrow. 1986. Models for assessing the volatilization of herbicides applied to flooded rice fields. *Chemosphere* 15:127-138.
- Ross, L.J. and R.J. Sava. 1986. Fate of thiobencarb and molinate in rice fields. *J. Environ. Qual.* 15:220-225.
- Woodrow, J.E., J.N. Seiber, D.G. Crosby, K.W. Moilanen, C.J. Soderquist and C. Mourer. 1977. Airborne and surface residues of parathion and its conversion products in a treated plum orchard environment. *Arch. Environ. Contam. Toxicol.* 6:175-191.
- Woodrow, J.E., D.G. Crosby and J.N. Seiber. 1983. Vapor-phase photochemistry of pesticides. *Residue Rev.* 85:111-125.
- Bowman, B.T. and W.K. Sans. 1979. The aqueous solubility of twenty-seven insecticides and related compounds. *J. Environ. Sci. Health B14:625-634*.
- Yusi, Y. and K. Ishikawa. 1977. Disappearance of benthocarb herbicide in irrigation water. In M. Soerjani, D. E. Barnes, and T. O. Robson, eds., *Proceedings of the Sixth Asian-Pacific Weed Science Society Conference*, Vol. 2. Asian-Pacific Weed Science Society, Jakarta, Indonesia, pp. 596-602.

APPENDIX V  
QUALITY ASSURANCE PLAN

State of California  
Air Resources Board

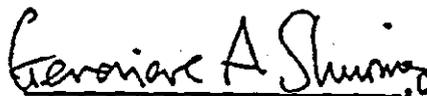
Quality Assurance Plan  
for Pesticide Monitoring

Prepared by the

Monitoring and Laboratory Division  
and  
Stationary Source Division

September 28, 1990

APPROVED:

  
\_\_\_\_\_, Chief,  
Toxic Air Contaminant  
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\_\_\_\_\_, Chief,  
Quality Management and  
Operations Support Branch  
Monitoring and Laboratory Division

  
\_\_\_\_\_, Chief,  
Engineering Evaluation Branch  
Monitoring and Laboratory Division

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 view 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 Food and Agriculture (DFA), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. Short-term (one month) ambient monitoring will be conducted in the area of, and during the season of, peak pesticide applications. In addition, monitoring of a field during and after application (up to 72 hours) will occur. The purpose of this document is to specify quality assurance activities for sampling and laboratory analysis of the pesticide.

## II. Quality Assurance Policy Statement

It is the policy of the ARB to provide DFA with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

## III. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: 1) to establish the necessary quality control activities relating to site selection, sample collection, sample analysis, and data validation, and 2) assessment of data quality in terms of precision, accuracy and completeness.

## IV. Siting

Siting criteria for ambient pesticide monitoring are listed in TABLE 1. 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. Background sites should be located away from any applications.

Siting criteria for placement of samplers near a pesticide application for collection of short-term samples are: 1) fifteen yards upwind of the field, 2) fifteen yards downwind of the field, and 3) 150 yards downwind of the field. These are only guidelines, since conditions at the site will dictate the placement of monitoring stations. Data on wind speed and direction will be collected during application monitoring. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed. Field application monitoring will follow the schedule outlined in TABLE 2. This schedule and study design are consistent with requests from DFA for monitoring near a pesticide application.

## A. Monitoring Site Description

The protocol for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions).

Similarly, a map or sketch of the monitoring stations should be made with respect to the application field.

## V. Sampling

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. Sampling will be conducted following the Environmental Protection Agency (EPA) ambient monitoring guidelines of 40 CFR 58 for calibration, precision, accuracy and data validation. The ARB Quality Assurance Section upon request will review quality assurance/quality control procedures and will evaluate pesticide monitoring activities.

### A. Protocol

Prior to conducting any pesticide monitoring a protocol will be written that describes the overall monitoring program and includes the following topics:

1. Identification of the sample site locations.
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. Description of the analytical method.
4. Quality assurance/quality control plan for sampling, including calibration procedures for flow meters.
5. Test schedule.
6. Test personnel.

Specific sampling methods and activities will be described in a monitoring plan (protocol) for review by ARB and DFA. Criteria which apply to all sampling are: 1) chain of custody forms will accompany all samples (APPENDIX I.), 2) light and rain shielding will be used for samples during monitoring and, 3) samples will be stored in an ice chest 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 this specific pesticide.

## B. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample type (e.g., charcoal tube), 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. Field blanks should be included with each batch of samples submitted to the lab for analysis. The average of the initial and final flow rates for the sampling period will be used if a flow controller is not used.

## C. Collocation

For ambient monitoring, sampling precision or the standard deviation of the data set will be calculated from at least 2 samples collocated at a site. The collocated sampler will be rotated between sampling sites so that at least three duplicate samples are collected at each site. 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. One sample will be designated as the primary sample and the other sample will be designated as the duplicate.

## D. Calibration

If elapsed time meters are used, rather than noting beginning and ending times, the meters should be checked and calibrated to within  $\pm 5$  minutes for a 24-hour period. Samplers operated with an automatic on/off timer should be calibrated so that the sampling period is 24 hours  $\pm 15$  minutes.

Flow meters, flow controllers or critical orifices should be calibrated against a referenced flow meter prior to a monitoring period.

Sampling flows should be checked in the field and noted before and after each sampling period. Before flows are checked, the sampling system should be leak checked. The initial flow should be within  $\pm 10\%$  if a calibrated pressure transducer is used to check the flows, or within  $\pm 15\%$  if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of those control limits.

## E. 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 MONITOR SITING CRITERIA SUMMARY

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

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
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. APPLICATION SAMPLING SCHEDULE

The sampling schedule for each station is as follows:

	<u>Samples per Site*</u>		
	<u>-15 yds up- wind</u>	<u>-15 yds down- wind</u>	<u>-150 yds down- wind</u>
- Background sample (1 hr. sample: prior to application).	2	2	2
- Application + 1 hr. after application combined sample.	2	2	2
- 2 hr. sample from 1 to 3 hours after the application.	2	2	2
- 4 hr. sample from 3 to 7 hours after the application.	2	2	2
- 8 + hr. sample from 7 to 15+ hours after the application.	2	2	2
- 9 + hr. sample from 15 to 24+ hours after the application.	2	2	2
- 1st 24 hour sample starting at the end of the 9+ hr. sample.	2	2	-
- 2nd 24 hour sample starting 24 hrs after the end of the 9+ hr. sample.	2	2	-

\* duplicate collocated samples at each site.

## VI. Analysis

Analytical audits should be conducted by spiking the sample medium with the reference standard. These can then be carried into the field and handled as actual samples (trip spike) or run at the background site for ambient monitoring (field spike) prior to delivery to the laboratory for analysis. At least one spike per monitoring period is required and one spike per week is recommended for ambient monitoring.

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. should include: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures.

### A. Standard Operating Procedures

#### 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 monitoring 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 gas 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 Assurance

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits 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 lab 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 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. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked tubes 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.

## VII. Data Reduction and Reporting

The mass of pesticide (microgram, ug) found in each sample will be used along with the sample air volume 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 ug/m<sup>3</sup> as well as ppb or ppt (as appropriate). Wind speed and direction data will also be reported for application site monitoring.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum detection limit), total number of samples and number of samples above the minimum detection limit. For this purpose, collocated samples are averaged and treated as a single sample.

### A. Quality Assurance

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final data summary. The quality assurance report will include a summary of the average data precision, accuracy, and completeness.

## 1. Precision and Accuracy

The average precision or standard deviation will be reported based on the comparison of the collocated sampling data. Accuracy data to be reported includes the results of the analyses of spiked samples and the results of any flow audits.

## 2. Data Completeness

Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample time cannot be verified, or if any of the sampling medium is lost during sampling, shipment or analysis.

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 #: \_\_\_\_\_

ACTION	DATE	TIME	INITIALS	
Sample Collected				
			GIVEN BY	TAKEN BY
Transfer				
Transfer				
Transfer for Analysis				

ID #	LOG #	DESCRIPTION

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

APPENDIX VI  
QA AUDIT REPORT

State of California

MEMORANDUM

To : George Lew, Chief  
Engineering Evaluation Branch

Date : September 11, 1992

Subject : Molinate Monitoring  
Audit

  
for Alice Westerinen, Manager  
Quality Assurance Section  
From : Air Resources Board

Thank you for reviewing the draft Quality Assurance audit report on the Molinate monitoring project conducted in Colusa County by the Air Resources Board's Engineering Evaluation Branch and the Department of Environmental Toxicology of the University of California, Davis.

Since you or your staff do not have any comments that need to be incorporated into the report, please consider the draft dated August 26, 1992, to be the final document. A new cover sheet is enclosed to reflect this change.

If you have any questions, please contact Gabriel Ruiz of my staff at 327-0885.

Enclosure

cc: Gabriel Ruiz

September 11, 1992

AUDIT REPORT  
MOLINATE MONITORING IN COLUSA COUNTY

SUMMARY

In May of 1992, the California Air Resources Board's Engineering Evaluation Branch conducted ambient air sampling for Molinate in Colusa County, California. The samples were analyzed by the Department of Environmental Toxicology of the University of California, Davis.

On May 5, staff of the Quality Assurance Section of the Air Resources Board conducted flow rate audits of the air samplers used by the Engineering Evaluation Branch in the monitoring of Molinate. The audits were conducted with a NIST traceable mass flow meter. The difference between the reported and true flow rates averaged 0.6% with a range of -1.6% to 3.3%.

A system audit of the Environmental Toxicology laboratory was conducted to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that these were consistent with good practice. The only deficiencies noted were the lack of response factor plots, field spikes, and specific breakthrough data.

On May 28, five samples spiked with known amounts of Molinate were submitted to the laboratory for analysis. The samples were prepared from a 97% pure Molinate sample obtained from Chem Service. The difference between the assigned and the reported Molinate mass averaged -3.7% and ranged from -10.3% to 0%.

State of California

MEMORANDUM

To : George Lew, Chief  
Engineering Evaluation Branch

Date : August 26, 1992

Subject : Molinate Monitoring  
Audit

From : Alice Westerinen, Manager  
Quality Assurance Section  
Air Resources Board

*Alice*

Please find attached a draft Quality Assurance audit report on the Molinate monitoring project conducted by the Air Resources Board's Engineering Evaluation Branch and the Department of Environmental Toxicology of the University of California, Davis. The report consists of three parts: the results of a flow rate audit of the air samplers, the results of a system audit, and the results of an analytical performance audit.

Please review the report and feel free to comment on any areas that may need further discussion. We would like to receive your comments by Friday, September 4, 1992.

If you have any questions, please contact Gabriel Ruiz of my staff at 327-0885.

Attachment

cc: Jeff Cook  
Gabriel Ruiz

Air Resources Board  
**RECEIVED**  
AUG 26 1992

Monitoring & Laboratory Division

DRAFT

DRAFT

DRAFT

DRAFT

August 26, 1992

## AUDIT REPORT

### MOLINATE MONITORING IN COLUSA COUNTY

#### SUMMARY

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## AUDIT REPORT

### MOLINATE MONITORING IN COLUSA COUNTY

#### INTRODUCTION

In May of 1992, the California Air Resources Board's (ARB) Engineering Evaluation Branch (EEB) conducted ambient air sampling for Molinate in Colusa County, California. Ambient air was passed at measured rates through XAD-2 resin adsorbant tubes during several days surrounding an application. The samples were later analyzed by the Department of Environmental Toxicology (DET) of the University of California, Davis. Gabriel Ruiz of the ARB's Quality Assurance (QA) Section conducted a flow rate audit of the air samplers, a system audit of the field and laboratory operations, and a performance audit of the laboratory method for the analysis of Molinate.

#### FLOW RATE AUDIT

On May 5, 1992, a flow rate audit of the five air samplers used by the EEB in the monitoring of Molinate was conducted at the EEB's shop in Sacramento, before the samplers were deployed in the field.

Each sampling apparatus consisted of two XAD-2 resin adsorbant tubes, each connected with Teflon tubing to a rotameter, which was then connected with latex tubing to a double-headed pump, so that the flows did not interfere with each other. The sampling assembly was supported with a two meter section of aluminum tubing. The adsorbant tubes were covered with a plastic hood to protect them from sunlight.

Don Fitzell of the EEB calibrated the samplers by connecting a bubble meter to the inlet of the sampler and adjusting the valve on the rotameter so that the flow rate indicated by the rotameter was 2.0 liters per minute (lpm). The actual flow was then measured with the bubble meter, and the average of the flow rates measured for all five samplers was reported as the sample collection flow rate.

After the calibration, a flow rate audit of each sampler was conducted with a NIST traceable 3 lpm Matheson mass flow meter (MFM), following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged 0.6% and ranged from -1.6% to 3.3% (Table 1).

Table 1. Results of the flow rate audits of the air samplers used in the monitoring of Molinate.

<u>Sampler</u>	<u>Rotameter</u>	<u>Set Flow (lpm)</u>	<u>Reported Flow (lpm)</u>	<u>True Flow (lpm)</u>	<u>Percent Difference</u>
2	2A	2.0	1.90	1.90	0
	2B	2.0	1.90	1.89	0.5
4	4A	2.0	1.90	1.89	0.5
	4B	2.0	1.90	1.87	1.6
6	6A	2.0	1.90	1.89	0.5
	6B	2.0	1.90	1.93	-1.6
7	7A	2.0	1.90	1.87	1.6
	7B	2.0	1.90	1.92	-1.0
8	8A	2.0	1.90	1.84	3.3
	8B	2.0	1.90	1.89	0.5

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

## SYSTEM AUDIT

A system audit of the laboratory operations was conducted through a telephone conversation with Mike McChesney of the DET. The audit consisted of a review of the sample handling and storage procedures, analytical methodology, and method validation. The following is a discussion of the audit findings.

### Sample Handling and Storage

Sampling was conducted by staff of the ARB's EEB, following the schedule specified in the sampling protocol. After sampling, the exposed XAD-2 resin tubes were collected and placed inside screw-cap glass culture tubes. The tubes were then stored in an ice chest, until they were delivered to the laboratory at the end of the sampling period. Upon receipt at the DET laboratory, the samples were logged in and stored in a freezer at  $-20^{\circ}\text{C}$  for about three weeks before analysis.

### Sample Analysis

The analytical method was developed by laboratory staff and is described in a document entitled "Protocol for Molinate Air Samples with Commercial Sampling Tubes." The method entails extraction of the XAD-2 resin with ethyl acetate, and analysis by gas chromatography (refer to the protocol available in the QA office for further details). Analyses were performed with a Hewlett Packard 5890 II gas chromatograph equipped with a nitrogen-phosphorus detector and an integrator.

Immediately after extraction, the samples were placed in an autosampler for analysis. The analyses were conducted in triplicate, with three different 7-point calibration curves. The calibration standards were prepared on the day of analysis and had concentrations of 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ug/ml.

Quality control activities performed to monitor and document the quality of the data included analysis of five laboratory spikes, one control sample every four samples, one method blank, one solvent blank, one field blank, and seven duplicate samples. The study did not include field spikes.

### Method Validation

The limit of detection (LOD) was determined as the total mass equivalent to the concentration of the lowest calibration standard. The LOD was calculated as 0.06 ug/tube.

The method recovery rates were determined by spiking sample tubes in triplicate with Molinate at 2.0 ug/tube. The recovery rates averaged 89.0%.

Stability studies were not conducted specifically for this project. However, the DET laboratory had investigated the stability of Molinate in XAD-2 resin in previous studies. In one study, samples were stored for six months at  $-20^{\circ}\text{C}$ , and the recovery ranged from 85% to 95%. Furthermore, the laboratory audit samples were stored with the ambient monitoring samples, and the results showed recovery rates greater than 89% after three weeks at  $-20^{\circ}\text{C}$  (Table 2).

A study which showed no breakthrough for sampling tubes containing 30 ml of XAD-2 resin at a flow rate of 30 lpm was conducted by the DET laboratory for previous projects. However, no breakthrough data were available for the actual sample collection flow rate of 1.9 lpm.

#### Documentation

All the samples received at the DET laboratory were accompanied by ARB's chain-of-custody records. The samples were logged into the laboratory book using the sample numbers assigned in the field.

Field data sheets containing the sample collection information were retained by the EEB staff. The information included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

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, and analyst. The raw analytical data and the results of the analyses were stored in an electronic spreadsheet. Hard copies of the data were pasted onto the laboratory book. The chromatograms and integrator printouts were saved in an accessible form.

## LABORATORY AUDIT

The accuracy of the DET's analytical method was evaluated by submitting for analysis a set of five audit samples spiked with known amounts of Molinate. The samples were prepared on May 28, 1992, following the procedures outlined in Attachment II, from a 97% pure Molinate sample obtained from Chem Service (lot #63-106A). The samples were delivered to the DET's laboratory on May 29, 1992, where they were extracted and analyzed three weeks later.

The difference between the assigned and the reported Molinate mass for the samples averaged -3.7% and ranged from -10.3% to 0%. The results of duplicate samples MD-2 and MD-5 indicate a high degree of precision for the method (Table 2).

Table 2. Results of DET's analyses of Molinate audit samples.

<u>Sample ID</u>	<u>Assigned Mass (ug)</u>	<u>Reported Mass (ug)</u>	<u>Percent Difference</u>
MD-1	0.49	0.49	0
MD-2	0.29	0.26	-10.3
MD-3	0	ND	N/A
MD-4	0.97	0.96	-1.0
MD-5	0.29	0.28	-3.4

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ND = Not Detected

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

## CONCLUSIONS

In general, good quality control practices were observed during the study. The records for field operations were appropriate; the flow rates reported were in good agreement with the actual flow rates measured by the QA staff; the sample handling and storage procedures, the analytical methodology, and the method validation were appropriate; and the results of the analytical performance audit were in excellent agreement with the expected values.

The only deficiencies noted were the lack of control charts or response factor plots, field spikes, and specific breakthrough data. Response factor plots would allow the analyst to monitor the instrument's sensitivity over time, so that changes such as column, detector, or standard degradation could be detected. Field spikes should be included with each batch of samples submitted to the laboratory to monitor sample recovery. Finally, breakthrough studies should be conducted under conditions that duplicate the actual sample collection parameters.

Flow Audit Procedure 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 Brooks automatic flow calibrator. The audit device is placed in series with the sampler's inlet 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 fitting.
5. 1/4" to 5/16" Teflon union.

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 teflon tubing to the outlet port of the audit device with the Swagelock fitting.
3. Connect the free end of the teflon tubing to the sampler inlet with the Teflon union.
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 Procedure  
For The Laboratory Analysis Of Molinate

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Molinate. The audit is conducted by submitting audit samples prepared by spiking adsorbant tubes with known concentrations of Molinate. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Molinate, 97% pure, Chem Service Lot #63-106A.
2. Ethyl Acetate, nanograde.
3. XAD-2 resin Adsorbant Tubes
4. 50 ul Microsyringe

Safety Precautions

Overall toxic data for Molinate has been thoroughly investigated. Avoid direct physical contact. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

4 mg/ml Molinate Stock Solution: Weigh about 40 mg of Molinate into a clean 10 ml volumetric flask and dilute with ethyl acetate to the mark. Correct for the purity of Molinate and record the concentration.

0.02 mg/ml Molinate Spiking Solution: Transfer 50 ul of the 4 mg/ml Molinate stock solution to a clean 10 ml volumetric flask and dilute with ethyl acetate to the mark. Record the concentration.

ATTACHMENT II (Cont.)

Sample Preparation

Prepare five audit samples from the 0.02 mg/ml Molinate spiking solution according to the following table:

<u>Sample</u>	<u>0.02 mg/ml Molinate Volume (ul)</u>
1	25
2	15
3	0
4	50
5	15

1. Break off the inlet end of the sample tube.
2. Insert the syringe needle into the adsorbant bed of the primary section of the tube, and slowly inject the appropriate volume of Molinate solution. Do not allow the liquid to run down the sides of the tube.
3. Cap the open end of the tube with the plastic cap provided.
4. Label each tube with its assigned number and store in a freezer until ready for analysis.