APPENDIX VI

Q.A. SECTION AUDIT REPORT

State of California

M E M O R A N D U M

To : Gabriel Ruiz
Quality Assurance Section

Date : February 25, 1993

Subject : Naled Application
Monitoring Audit

Don Fitzell
Testing Section
From : Air Resources Board

I have reviewed the Naled audit and would like to make a few comments regarding the problems determined by your laboratory audit. I don't recall if I informed you at the time, but I did do additional work after the audit to try to resolve the question of the negative bias for Naled and the positive bias for Dichlorvos.

Initially I repeated the analysis (9/11/93) reported to you for the audit with the following results:

	Naled		Dichlorvos	
	9/11/92	9/23/93	9/11/92	9/23/92
DN-1	0.34	0.46	1.10	1.04
DN-2	0.76	0.72	0.94	0.86
DN-3	1.75	1.94	0.18	0.28
DN-4	0.40	0.50	1.30	1.22
DN-5	ND	0.44	2.54	3.56
DN-6	0.72	0.72	0.68	1.46

The repeat of the Naled analysis resulted in average values 113% of the original numbers and the Dichlorvos resulted in average values 132% of the original numbers.

Approximately one month later (10/1-2/92) I was able to compare the standards used for the analysis and fresh standards recently purchased. A one microgram per milliliter (1 ug/ml) solution of each was prepared from the neat compounds. Replicate (five each) injections were made and averaged. For Naled, the old standard was found to be 89% of the new standard; for Dichlorvos, the old standard was found to be 102% of the new standard. Considering the standard deviation of the replicate injections (approx. 6% for Dichlorvos and 32% for Naled) the bias detected in the audit cannot be attributed to degradation of the original standard.

If I recall correctly, we had to use the same neat standards for my analysis and preparation of your audit samples. If this is correct, the degradation of the neat compound would not explain the bias since I analyzed the audit samples within 24-hours of their preparation, so overall breakdown of the standards should not affect our relative results. Also, I would like to point out that I did have significant interferences with the Naled peak which would cause a positive bias, not negative as found.

I have no explanation for the results I obtained or the follow up analysis I did. I don't know how much, if any, of this information you might like to include in your audit report, but I feel you should be made aware of these facts.

Airborne Concentrations of Methidathion and Methidaoxon in Central Tulare County from Sampling Conducted in June and July 1991

Prepared for California Air Resources Board
Contract No: A032-094

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JUNE 24, 1993

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CALIFORNIA STATE UNIVERSITY, FRESNO

DISCLAIMER

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ACKNOWLEDGEMENTS

The study presented in this report was supported by contract funds under ARB Research Contract No. A032-094, Monitoring Pesticides in Air. The authors of this report desire to acknowledge the valuable assistance provided by the staff of the Air Resources Board, particularly Lynn Baker, Ruth Tomlin, Ralph Propper, and Don Fitzell. We also thank personnel of the Tulare County Agriculture Commissioner's Office for the valuable information provided to us regarding pesticide application.

TABLE OF CONTENTS

Summary

The monitoring conducted in this study has been carried out at the request of the Department of Pesticide Regulation in support of their Toxic Air Contaminant Program. Both ambient and application monitoring for methidathion and its oxidation product, methidaoxon, were performed in Tulare County during June and July of 1991. Both methidathion and methidaoxon were detected at all five ambient monitoring sites and during the application monitoring period. Table 1 contains a summary of the findings. Appendices A, B and C contain a more detailed presentation of the monitoring data.

Table 1. Summary of Methidathion Results

Site	Highest Value	Second Highest Value	Mean of Results >LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	<LOQ	<LOQ	—	0	17
Jefferson Elementary School	0.56	0.30	0.16	6	17
Exeter Union High School	0.070	<LOQ	0.070	1	15
UC Lindcove Field Station	<LOQ	<LOQ	—	0	15
ARB Monitoring Station, Visalia	<LOQ	<LOQ	—	0	17

NOTE: LOQ for methidathion is 0.03 µg/m³

Table 2. Summary of Methidaoxon Results

Site	Highest Value	Second Highest Value	Mean of Results >LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	.092	<LOQ	.092	1	17
Jefferson Elementary School	0.10	<LOQ	0.10	1	17
Exeter Union High School	<LOQ	<LOQ	—	0	15
UC Lindcove Field Station	<LOQ	<LOQ	—	0	15
ARB Monitoring Station, Visalia	<LOQ	<LOQ	—	0	17

NOTE: LOQ for methidaoxon is 0.09 µg/m³

Detectable level of methidathion were found during all application monitoring sampling periods except the initial background period, while methidaoxon was found only during the last three sampling periods. The peak concentrations were found in samples 5N (3.16 $\mu g/m^3$) and 4SW1 (0.36 $\mu g/m^3$) for methidathion and methidaoxon, respectively.

INTRODUCTION

Very low flow volume (4 *lpm*) ambient air samples were collected at five sites (including background site) in Tulare County for analysis of an organophosphate insecticide, methidathion (*O, O-dimethyl phosphorodithioate S-ester with 4(mercaptomethyl)-2-methoxy-delta-2-1,3,4-thiadiazolin-5-one*), a restricted use pesticide which is the active ingredient in a product formulated as an emulsifiable concentrate. The location and time period for sampling were based on reported applications of methidathion in recent years. Tulare County was selected as the study area since within California it had a history of having the largest applications of methidathion (70,532 pounds active ingredient in 1988). Typically, peak usage in Tulare County occurs in the June-July period when methidathion is applied to orange trees, the principal use of this insecticide. Other crops to which methidathion is also applied in large quantities include almonds, alfalfa, cotton, and artichokes.

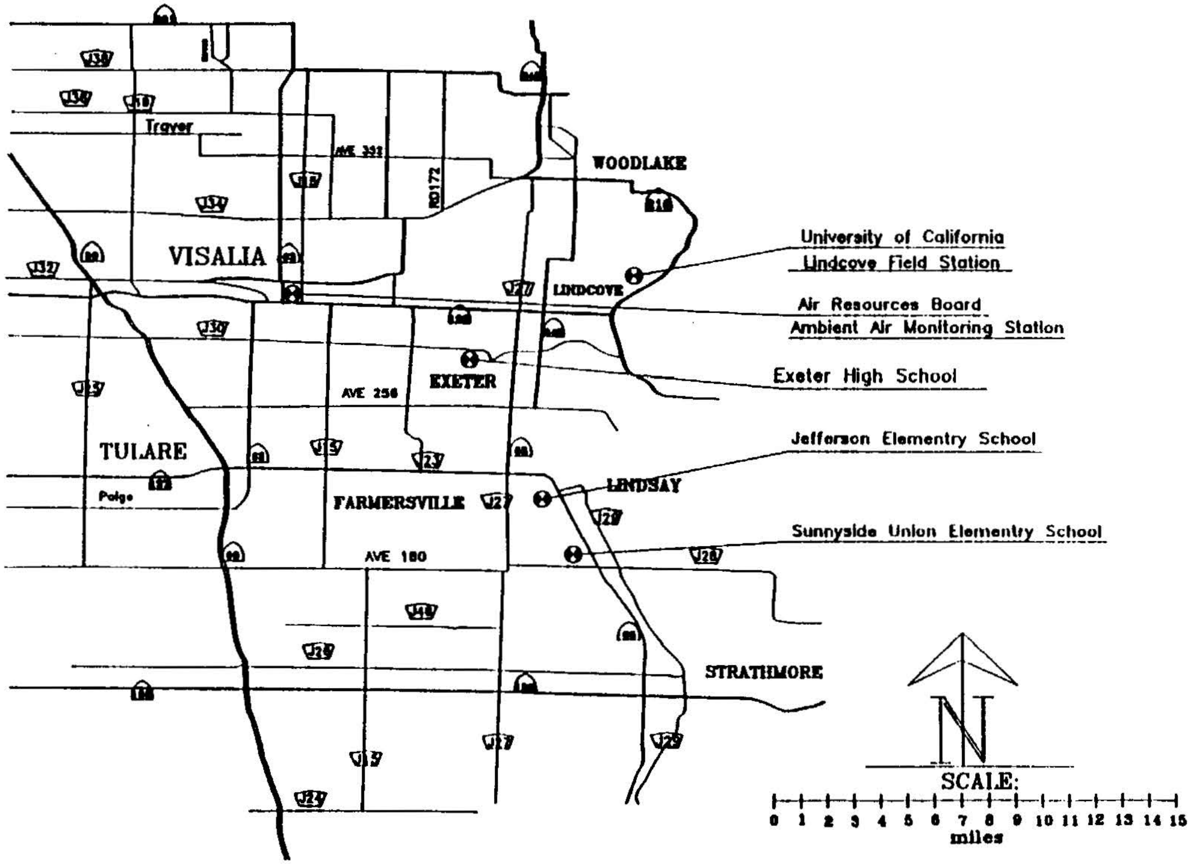
SITE DESCRIPTION

Five sampling sites were chosen by California Air Resources Board (ARB) personnel from an area of Tulare County where orange orchards are predominant. With the exception of the ARB Monitoring Station, the sampling sites selected are within the citrus fruit production area of Tulare County. These sites have citrus groves within one-quarter miles of their boundaries in which methidathion application were expected. Site selection criteria also included considerations for both accessibility and security of the sampling equipment. The five selected sites were the following locations: Sunnyside Union Elementary School, Strathmore; Jefferson Elementary School, Lindsay; Exeter Union High School, Exeter; the University of California (UC) Lindcove Field Station, Exeter; and the ARB Ambient Air Monitoring Station, Visalia (Figure 1). The latter site was the site used for monitoring background concentration. Samplers were located on the roof of a building at each site except at the Lindcove Field Station. The Lindcove Field Station is a citrus study facility and the sampler was positioned in an open area near the meteorological station located on-site. Both elementary schools are located within one-quarter mile of orange orchards. The orange groves nearest to Exeter Union High School are located one-quarter mile north of the school. No orange groves are in existence near the City of Visalia where the background monitoring site was set up.

The samples were collected by California State University, Fresno (CSUF) personnel over a four week period from June 27 - July 25, 1991. Samples were transported to CSUF for analysis.

SAMPLING

Ambient samplers consisted of a glass tube (8*mm* x 110*mm*) containing two sections of XAD-2 resin (400 *mg* primary section with 200 *mg* backup section) connected by Teflon tubing to a



HIGHWAYS

ROADS

SAMPLE LOCATIONS

METHIDATHION
AMBIENT AIR MONITORING
DRAWN
BY:
CALIFORNIA STATE
UNIVERSITY FRESNO
E.R.I.
FOR
CALIFORNIA AIR
RESOURCES BOARD

This map was drawn by digitizing a portion of Tulare County map (In California) published by Automobile Club of Southern California.

FIGURE 1. Site Map

flowmeter and a sampling pump. Each sampling pump had two resin tubes attached to it with the air flow through each tube being monitored by an independent flowmeter. A diagram of the sampling apparatus is presented in Figure 2. Flow rates for each sampling tube were measured at the beginning and at the end of each sampling period. Sampling periods were nominally 24 hours and varied from approximately 23 to 25 hours. The sampling data are presented in Appendix A. At the end of the sampling period, each resin tube was removed from the sampling apparatus and capped, labeled, and placed in a screw cap glass culture tube. The culture tubes with their contents were then placed on ice in an ice chest. The samples were stored in the ice chests until delivery at the end of each sampling day to CSUF for analysis. At CSUF samples were stored in a freezer at -15°*C* until extracted for analysis.

Application monitoring was conducted by the ARB Evaluation Branch during the month of July. The report for this monitoring is at Appendix B.

LABORATORY ANALYSIS

All samples for ambient and application monitoring were prepared for analysis within seven days of sampling. All samples were warmed to room temperature before extraction. The primary section of resin in each sample was extracted in 2.0 *mL* of toluene by sonicating for 30 minutes. The backup section of the resin was not extracted based upon breakthrough studies conducted during the method evaluation. No breakthrough was demonstrated for either compound at levels up to 100 μg. The extract was allowed to settle, filtered through a plug of glass wool, and transferred to a 4 *mL* vial for gas chromatographic analysis. No additional cleanup was required.

The samples were analyzed on a Varian 3400 gas chromatograph equipped with a Ni^{63} electron capture detector and a Varian model 4290 integrator. A J&W Scientific DB-5 megabore column (30*m* x 0.53*mm* ID) provided the separation. The table below contains the instrument conditions.

Table 3. Instrument Conditions

Temperatures		Column Program					Gas Flows (mL/min)	
Injector °C	Detector °C	Initial °C	Hold *min*	Ramp °C/min	Final °C	Hold *min*	Carrier N_2	Make Up N_2
220	280	200	1	10	250	6	8	22

PESTICIDE SAMPLING APPARATUS

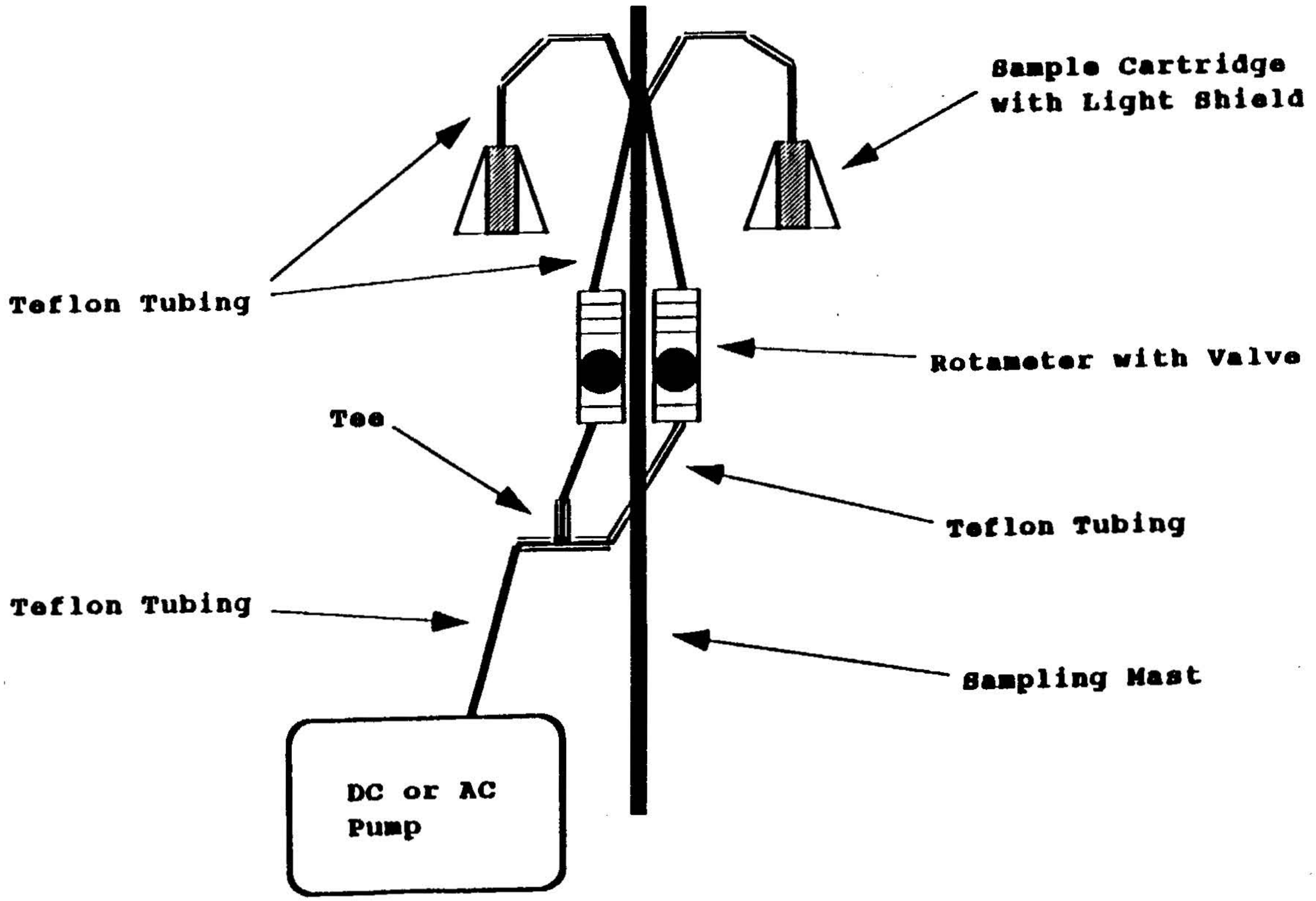


Figure 2 SAMPLING APPARATUS

A four point calibration curve was prepared by injecting 2 *µL* of each of the working standards into the gas chromatograph. A second-order equation for the standard curve was generated from the resulting peak area data using Cricket Graph™. Two microliters of each sample were injected into the gas chromatograph for comparison to the standards.

The analytical results for methidaoxon and methidathion are found in Appendix C at the end of this report.

An example using the chromatograms and equations for one set of standard curves can be found in Appendix D.

QUALITY CONTROL/QUALITY ASSURANCE

Sampling and analysis were conducted according to the project quality assurance plan. Collocated replicate samples were collected at each sampling site for each sampling period. Replicate samples from one site each week (20% of the samples) were analyzed as part of the quality control requirements. In addition, control spikes were analyzed with each extraction set to monitor extraction efficiencies. When detectable levels of the study compound were identified, the replicate sample was also extracted and analyzed.

The limit of detection (LOD) was determined to be three times the standard deviation of replicate injections of the lowest standard. The limit of quantitation (LOQ) is three times the LOD. The limit of detection (LOD) for methidathion and its oxidation product, methidaoxon, in air are 0.01 and 0.03 $\mu g/m^3$, respectively. The LOQ is 0.03 and 0.09 $\mu g/m^3$ for methidathion and methidaoxon, respectively.

A set of control samples was prepared and submitted to CSUF by Gabriel Ruiz (ARB) during the monitoring period. These were analyzed and the data returned to ARB for analysis and a separate report was prepared by Gabriel Ruiz (Appendix E).

During the method validation, a number of parameters were evaluated. The parameters studied include extraction efficiency, sampling recovery, and storage stability. The data for these parameters are presented in Appendix F.

During the retention efficiency studies, a low-level background for methidaoxon was identified. This background was also found in the field blanks. The average background value for the retention blanks, the samples of the backup section of the breakthrough studies, and the field blanks is $0.13 \pm 0.02\ \mu g$ of methidaoxon. This corresponds to a concentration of $0.023\ \mu g/m^3$. The background appears be an artifact of the sampling process. It may be either a low-level material extracted from the XAD-2 resin or possibly an interfering substance in the ambient air.

RESULTS AND DISCUSSION

Figures 3-1 and 3-2 through figures 7-1 and 7-2 show methidaoxon and methidathion data, respectively, as a function of the day of the study for the five study sites. The methidaoxon and methidathion data for the Sunnyside Union Elementary School site are shown in figures 8-1 and 8-2, respectively, as a function of the probability of occurrence (a statistical measure of the probability the concentration of the pesticide in the sample equalled or exceeded a selected concentration given that the sample population is normally distributed). Likewise, the methidaoxon and methidathion data for the Jefferson Elementary School site are shown in figures 9-1 and 9-2, respectively, as a function of the probability of occurrence. The plotted data are not blank corrected (0.024 and 0.001 $\mu g/m^3$ for methidaoxon and methidathion, respectively).

The five sampling sites, including the intended background site (the Air Resources Board Monitoring Station in Visalia) had positive results for methidathion and its oxidation product, methidaoxon, during part of the ambient monitoring period. Results ranged from below the LOD to a high of 0.56 $\mu g/m^3$ for methidathion at the Jefferson Elementary School site (figure 4-2), and a high of 0.12 $\mu g/m^3$ for methidaoxon at the Exeter Union High School site (figure 5-1).

Both methidaoxon and methidathion were consistently detected at the Sunnyside Union Elementary School site (figures 3-1 and 3-2) above the LOD with maximum values detected being 0.092 and 0.029 $\mu g/m^3$, respectively.

The most extreme values for methidathion in air occurred at the Jefferson Elementary School site (figure 4-2). Of particular note is the two week period of July 10-23, 1992 (study days 15-27). During this period the methidathion concentration peaked at 0.56 $\mu g/m^3$ and averaged 0.13 $\mu g/m^3$. The methidaoxon concentration at this site during the early part of this time period was also elevated having a peak concentration of 0.11 $\mu g/m^3$ on July 10, 1991 (study day 15). However, another high methidaoxon concentration at the Jefferson Elementary School site occurred on July 2, 1991 (study day 6) and no apparent increase of methidathion, the precursor compound, is noted.

The remainder of the data shown on figures 5-1, 5-2, 6-1, 6-2, 7-1, and 7-2 are generally near the LOD. A correlation does not appear to exist for the occurrence of detectable quantities of methidaoxon as a function of detectable quantities of methidathion. An investigation of this must include consideration of particle transport in air, meteorological conditions, and the ambient oxidation rates of methidathion.

The fact that methidaoxon and methidathion were detected eight and two times, respectively, at the Air Resource Board Monitoring Station in Visalia (figures 7-1 and 7-2) is significant since this site is located in a downtown area and not in the immediate area of a known use of methidathion (the County Agricultural Commissioner has stated that no known applications of methidathion occurred in the immediate area of downtown Visalia during this time period). These compounds appear to persist sufficiently long to be transported into populated areas from the region in which the application takes place.

Figures 3-1, 4-1, 5-1, and 7-1 show relatively high concentrations of methidaoxon for July 25, 1991 (study day 29). The samples from which these data were determined were analyzed together with standards, external quality assurance samples, control samples, and samples from application monitoring and day 28 ambient monitoring. After reviewing these data the results are deemed to be valid.

In the preparation of the data for figures 8-1, 8-2, 9-1, and 9-2, all the data including the data points for data below the LOD were used to calculate the probability interval. An evaluation of these figures show the data to be generally normally distributed. Significant outliers are found with the Jefferson Elementary School data (figures 9-1 and 9-2) for the few very high data points. These data are significantly above the LOQ's for methidaoxon and methidathion, respectively, and they have a low probability of occurrence.

CONCLUSIONS

All data presented in this report for methidaoxon and methidathion have been determined and accepted subject to a rigorous quality assurance program. Most data are below, at, or slightly above the LOD's for both methidaoxon and methidathion, and few data were above the LOQ's for these compounds.

Methidaoxon and methidathion can persist for extended periods of time at elevated concentrations at sites near where application of an insecticide having methidathion as the active ingredient is being carried out. The persistence of these compounds may be responsible for their detection at the Air Resources Board Monitoring Station site which is located in an urban area and not in the immediate locale of known application of methidathion.

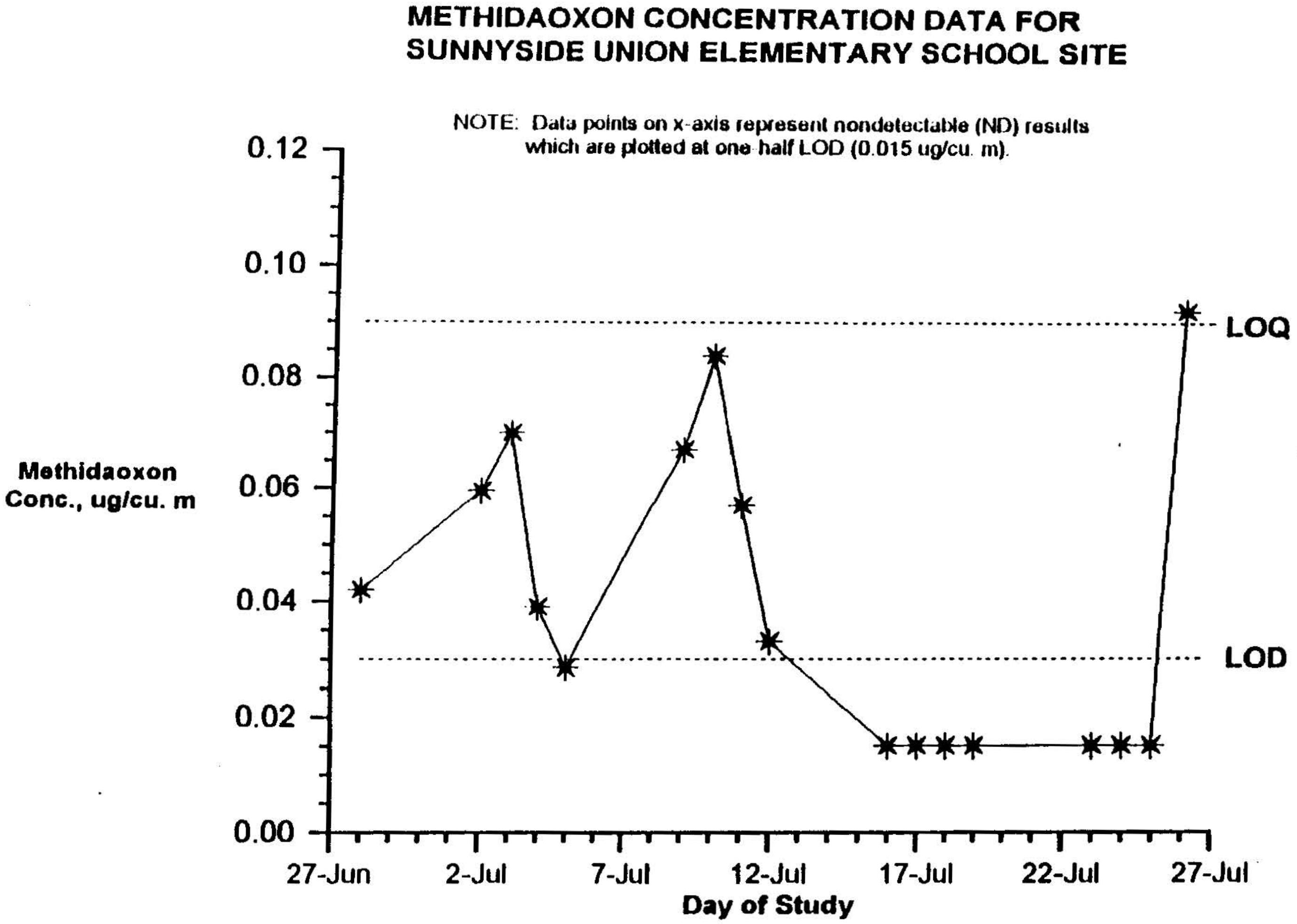


Fig. 3-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the Sunnyside Union Elementary School site during the June 27 - July 25, 1991 sampling period.

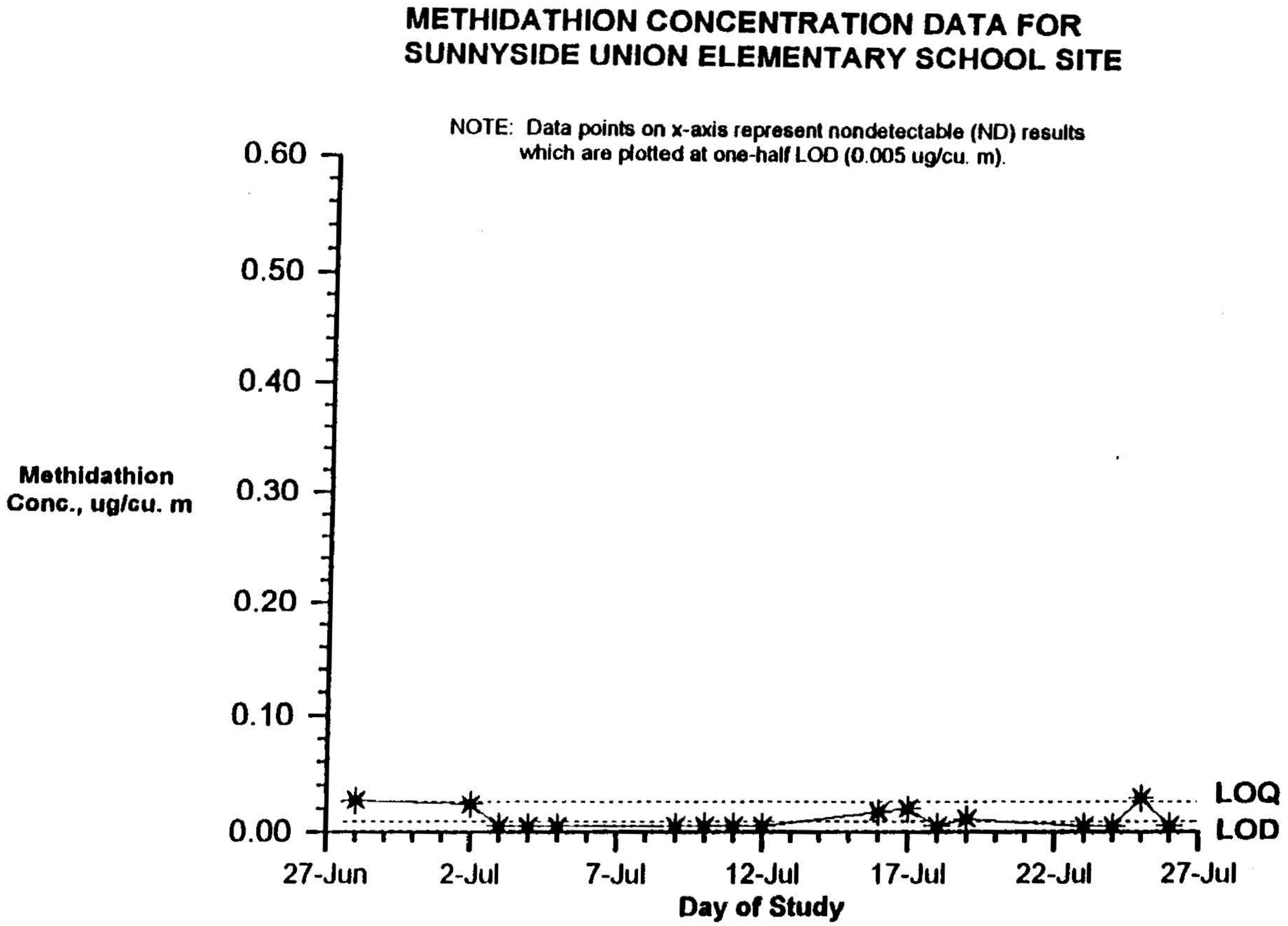


Fig. 3-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the Sunnyside Union Elementary School site during the June 27 - July 25, 1991 sampling period.

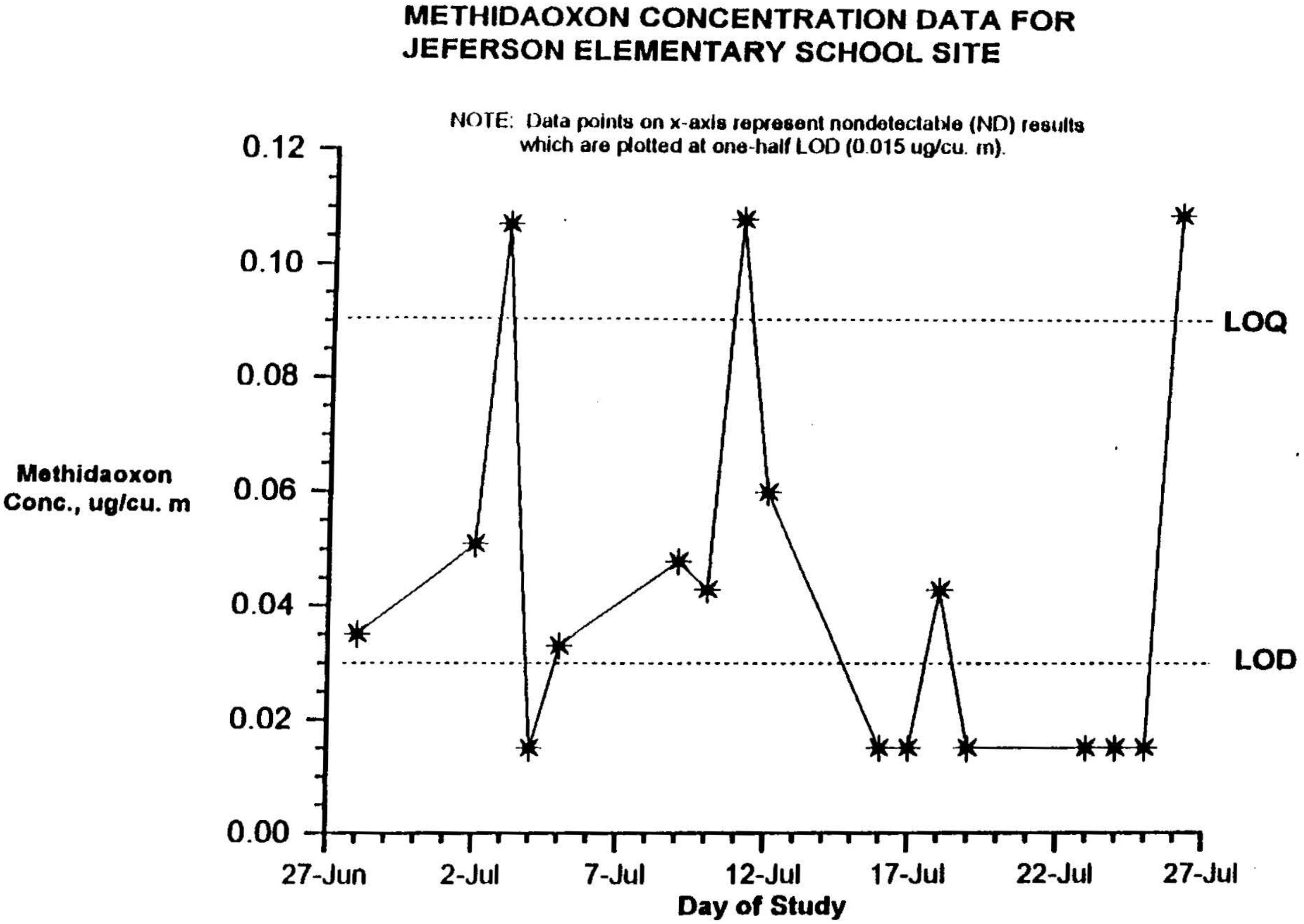


Fig. 4-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the Jefferson Elementary School site during the June 27 - July 25, 1991 sampling period.

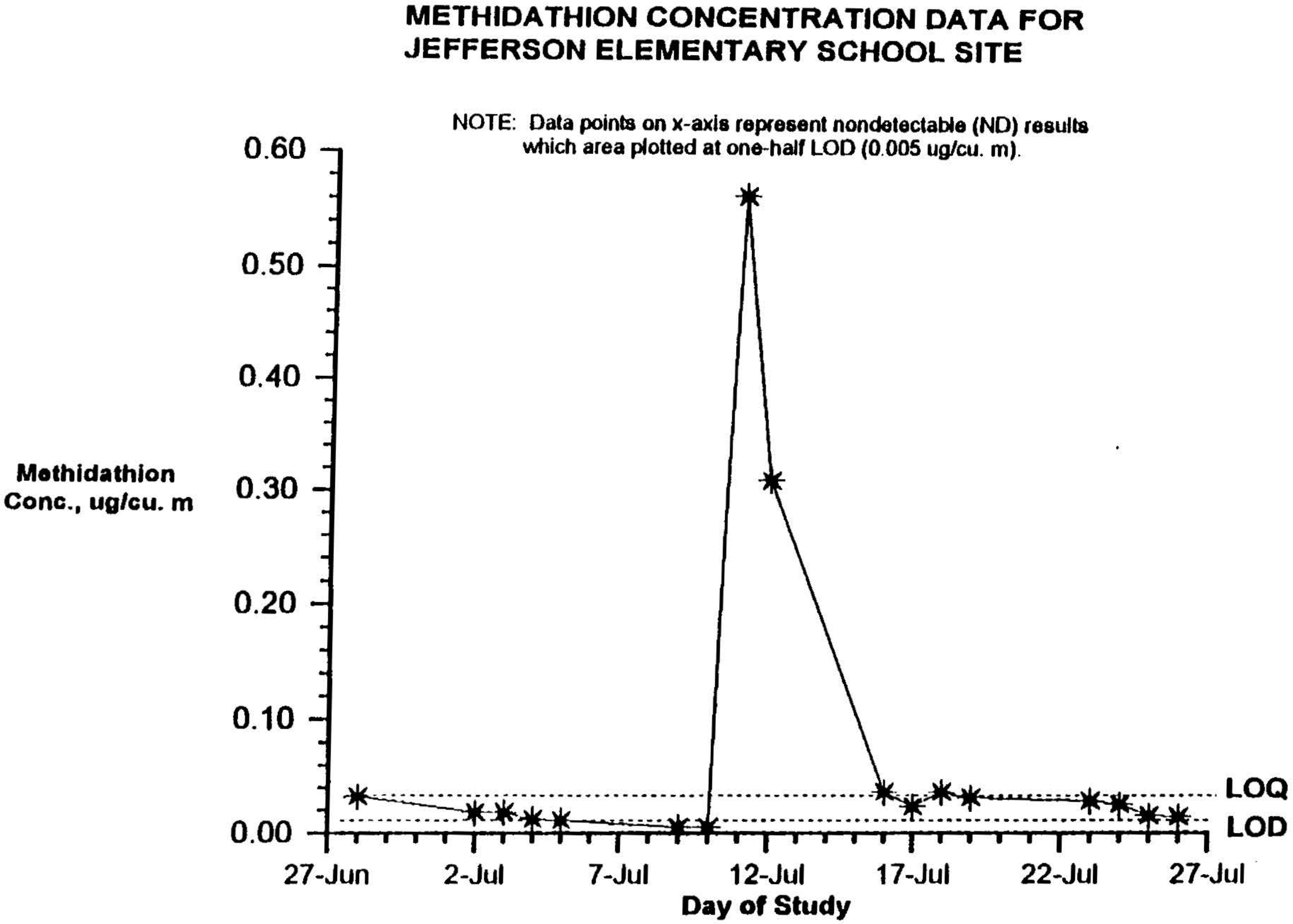


Fig. 4-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the Jefferson Elementary School site during the June 27 - July 25, 1991 sampling period.

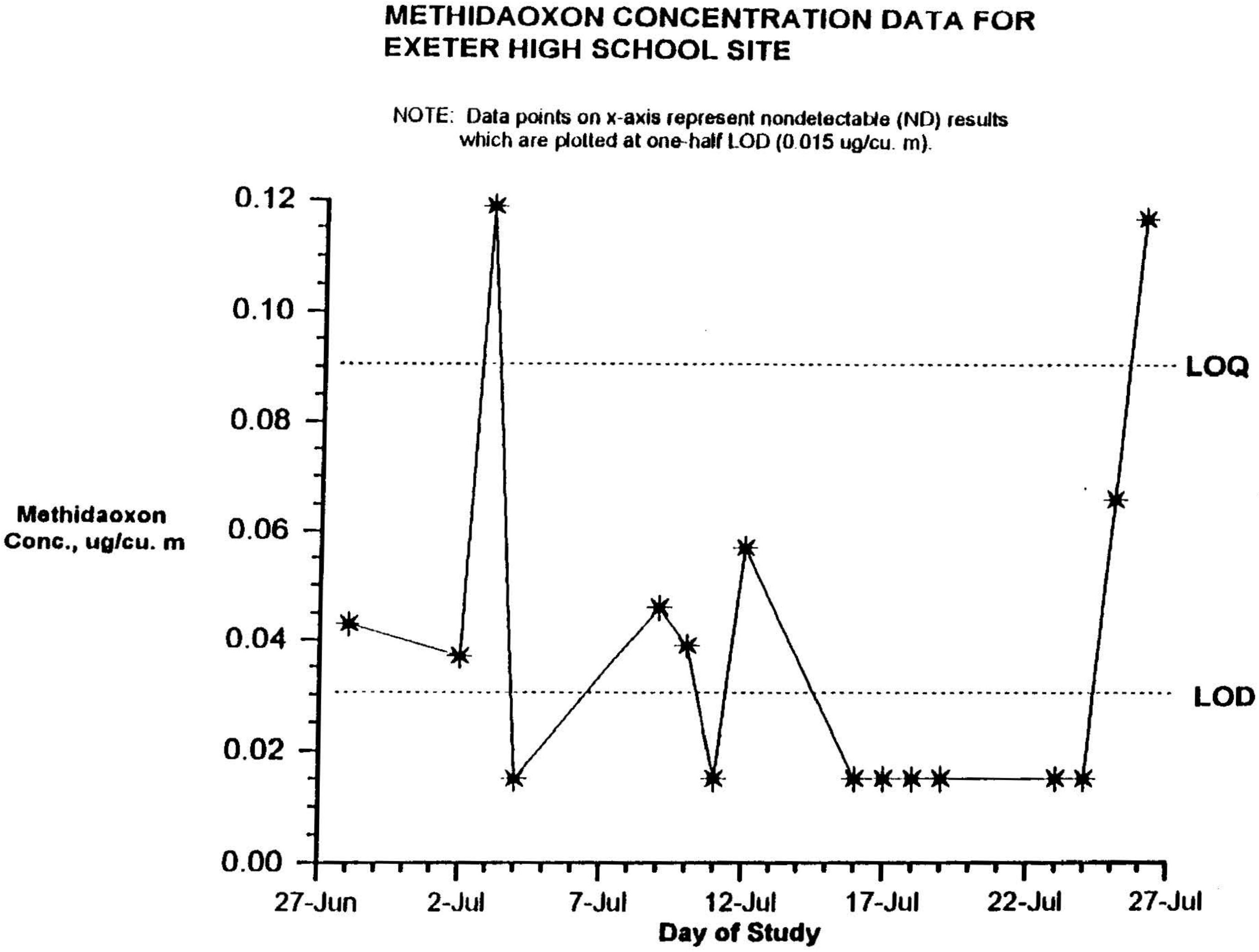


Fig. 5-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the Exeter Union High School site during the June 27 - July 25, 1991 sampling period.

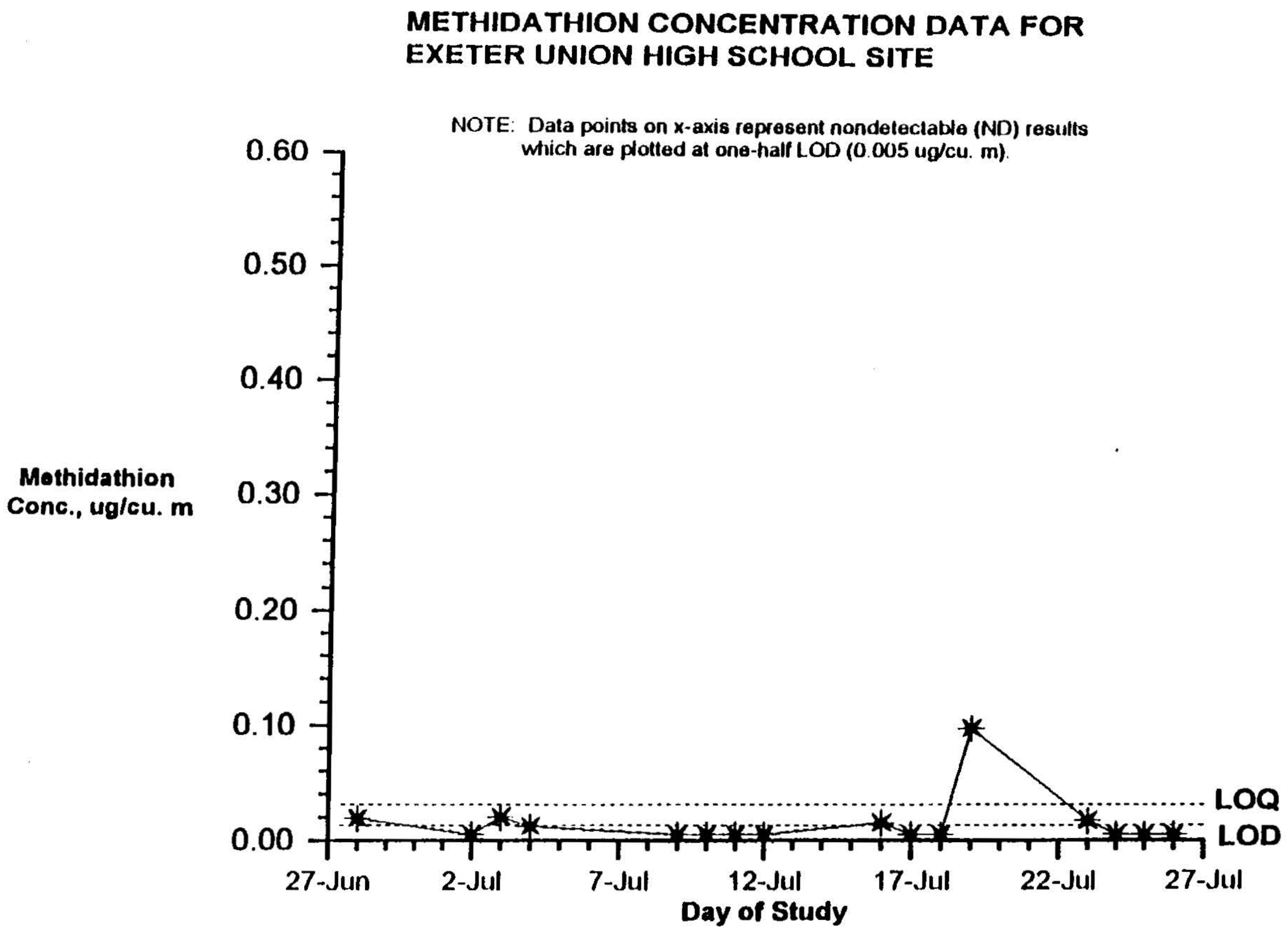


Fig. 5-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the Exeter Union High School site during the June 27 - July 25, 1991 sampling period.

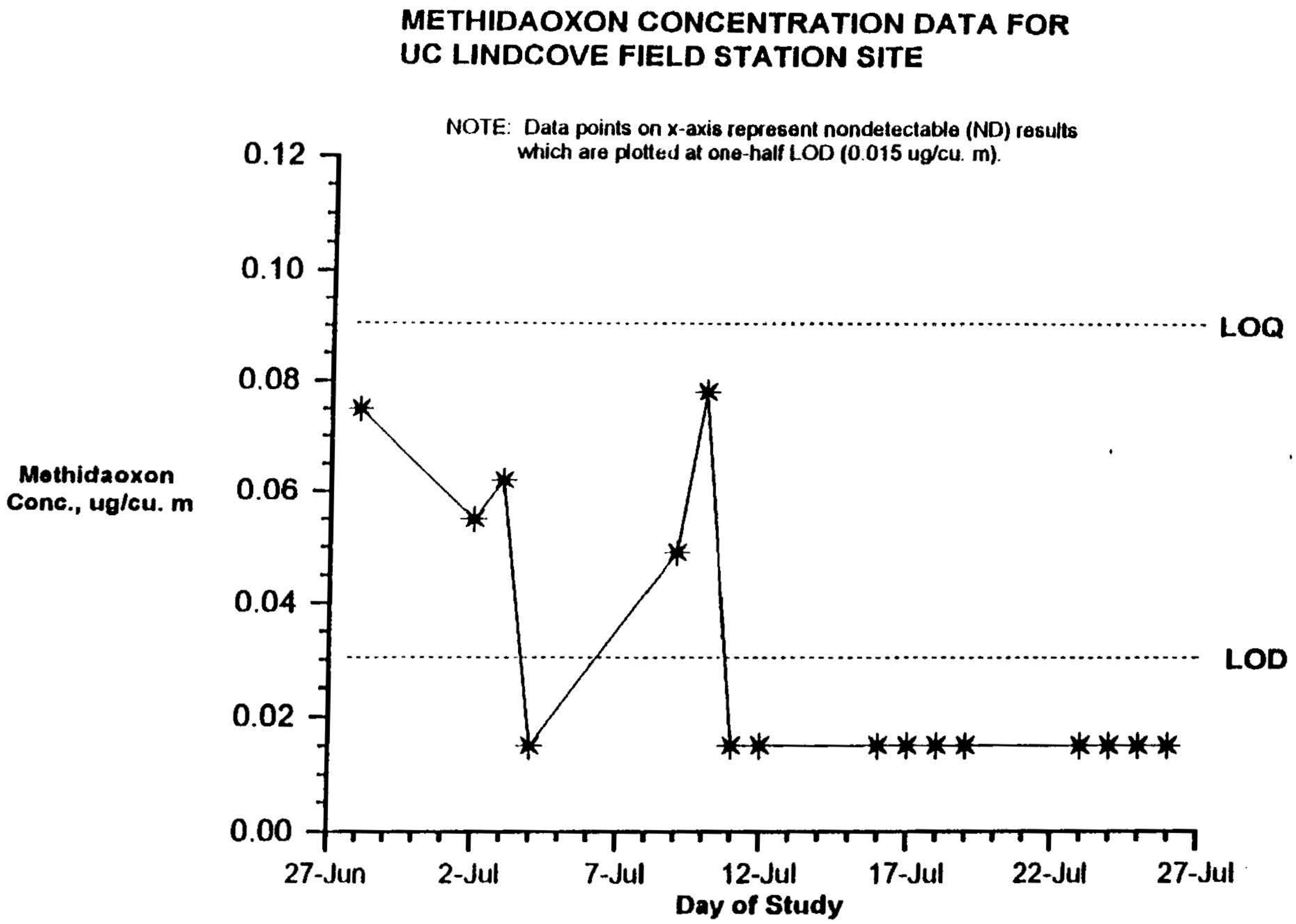
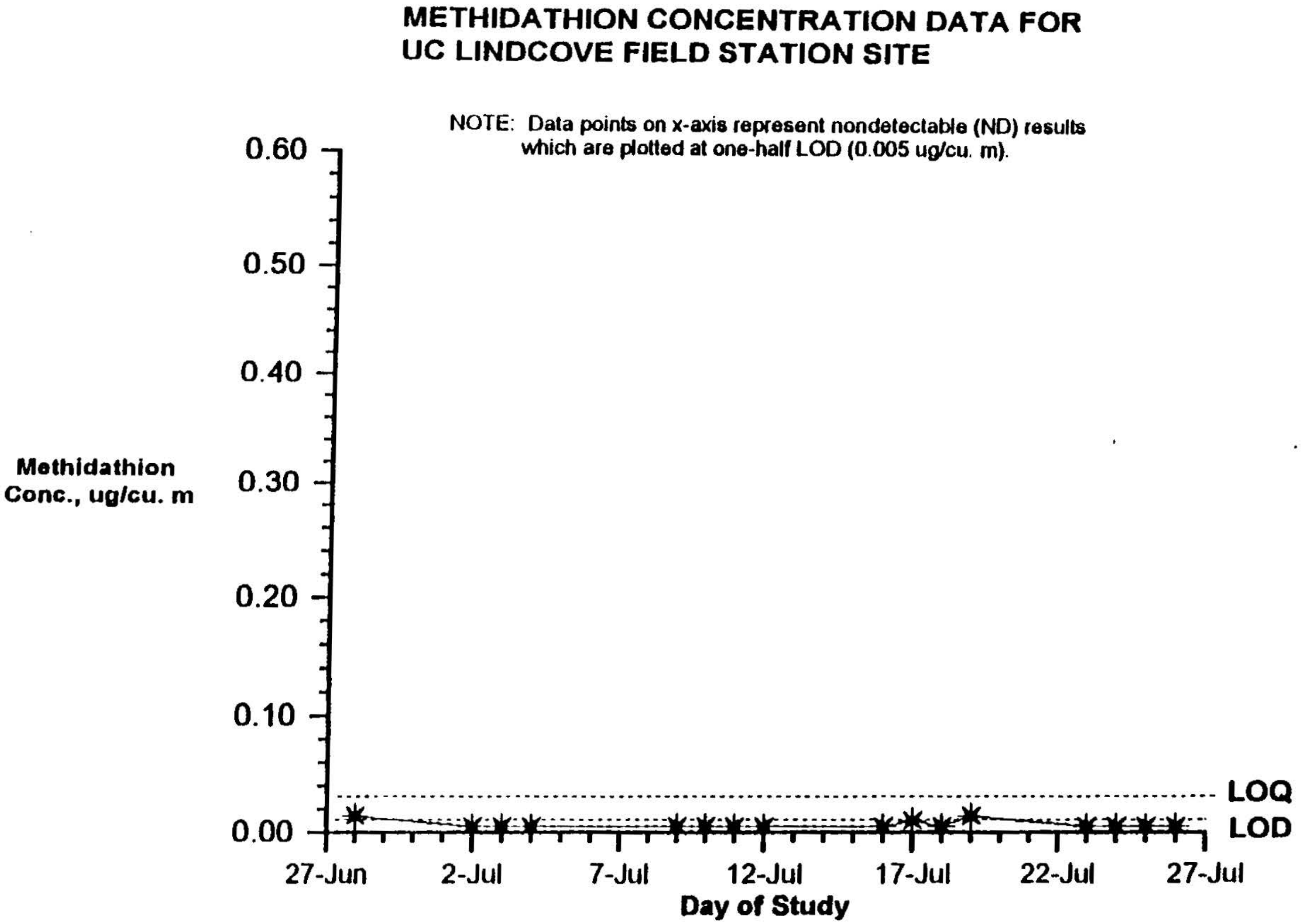


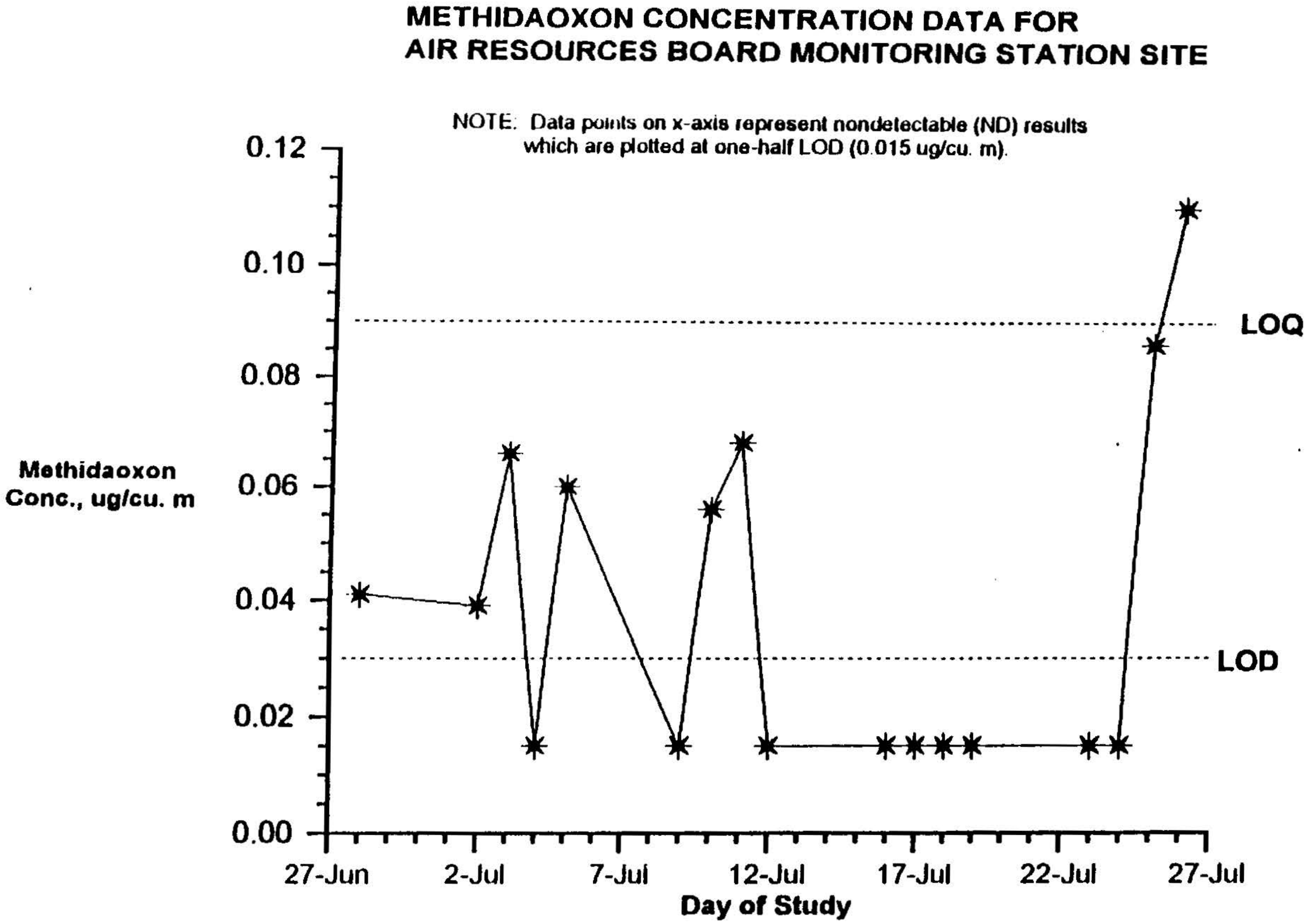
Fig. 6-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the UC Lindcove Field Station site during the June 27 - July 25, 1991 sampling period.



METHIDATHION CONCENTRATION DATA FOR UC LINDCOVE FIELD STATION SITE

NOTE: Data points on x-axis represent nondetectable (ND) results which are plotted at one-half LOD (0.005 ug/cu. m).

Fig. 6-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the UC Lindcove Field Station site during the June 27 - July 25, 1991 sampling period.


METHIDAOXON CONCENTRATION DATA FOR AIR RESOURCES BOARD MONITORING STATION SITE

NOTE: Data points on x-axis represent nondetectable (ND) results which are plotted at one-half LOD (0.015 ug/cu. m).

Fig. 7-1. Methidaoxon concentration in micrograms per cubic meter as function of the day of the study at the ARB Monitoring Station site during the June 27 - July 25, 1991 sampling period.

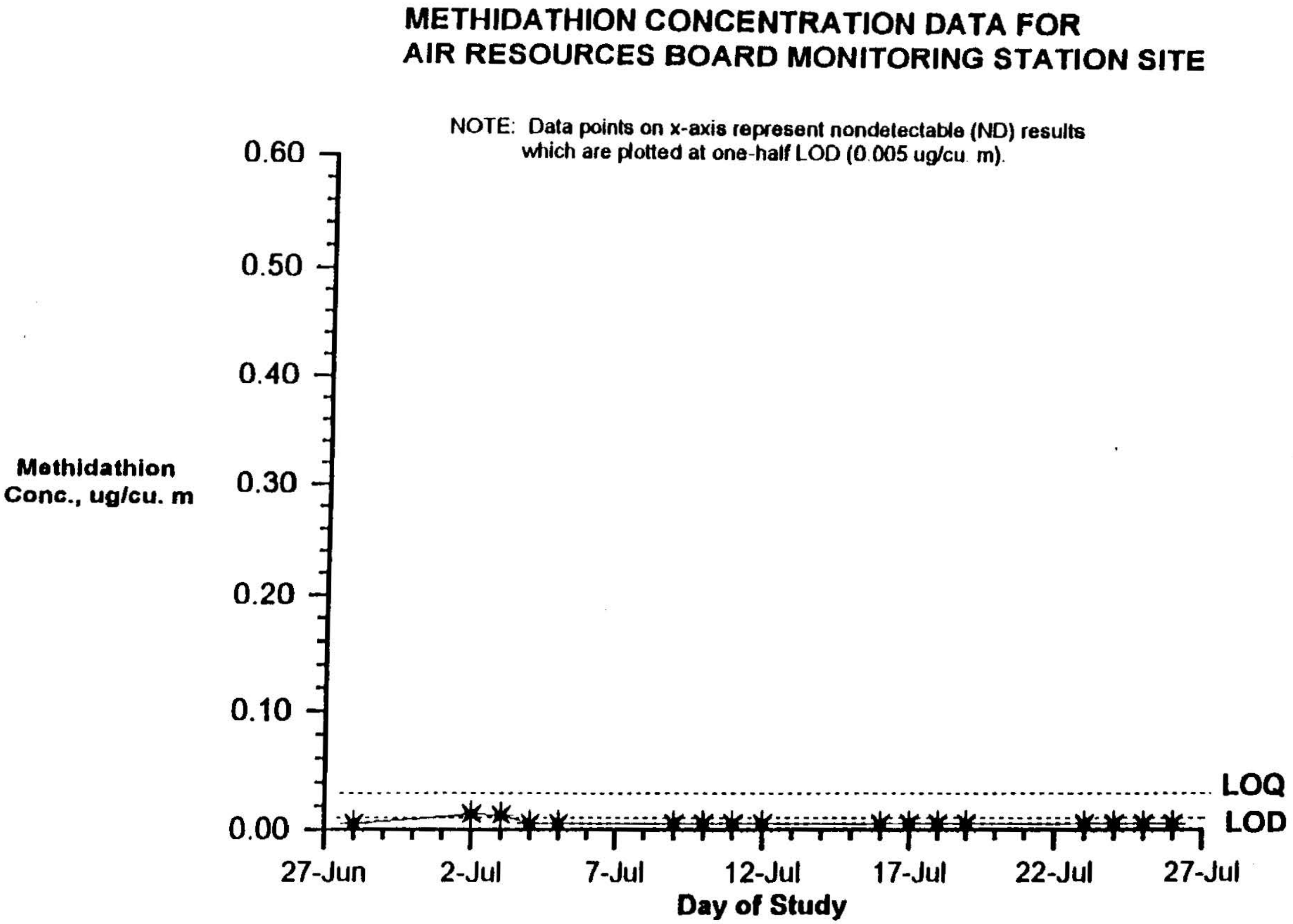


Fig. 7-2. Methidathion concentration in micrograms per cubic meter as function of the day of the study at the ARB Monitoring Station site during the June 27 - July 25, 1991 sampling period.

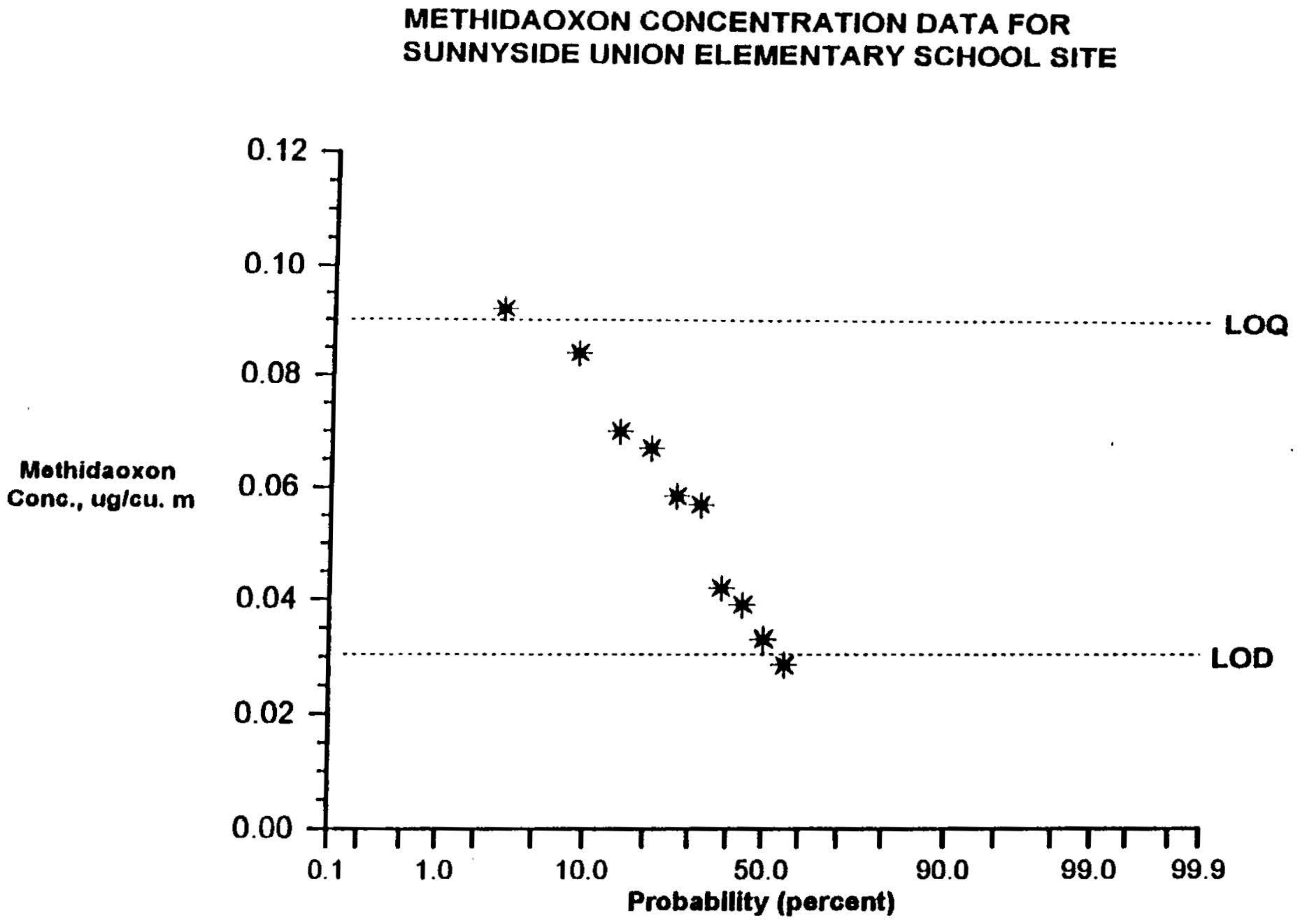


Fig. 8-1. Methidaoxon concentration in micrograms per cubic meter as function of probability (%) of methidaoxon concentration being equal to or greater than the plotted values at the Sunnyside Union Elementary School site during the June-July 1991 sampling period.

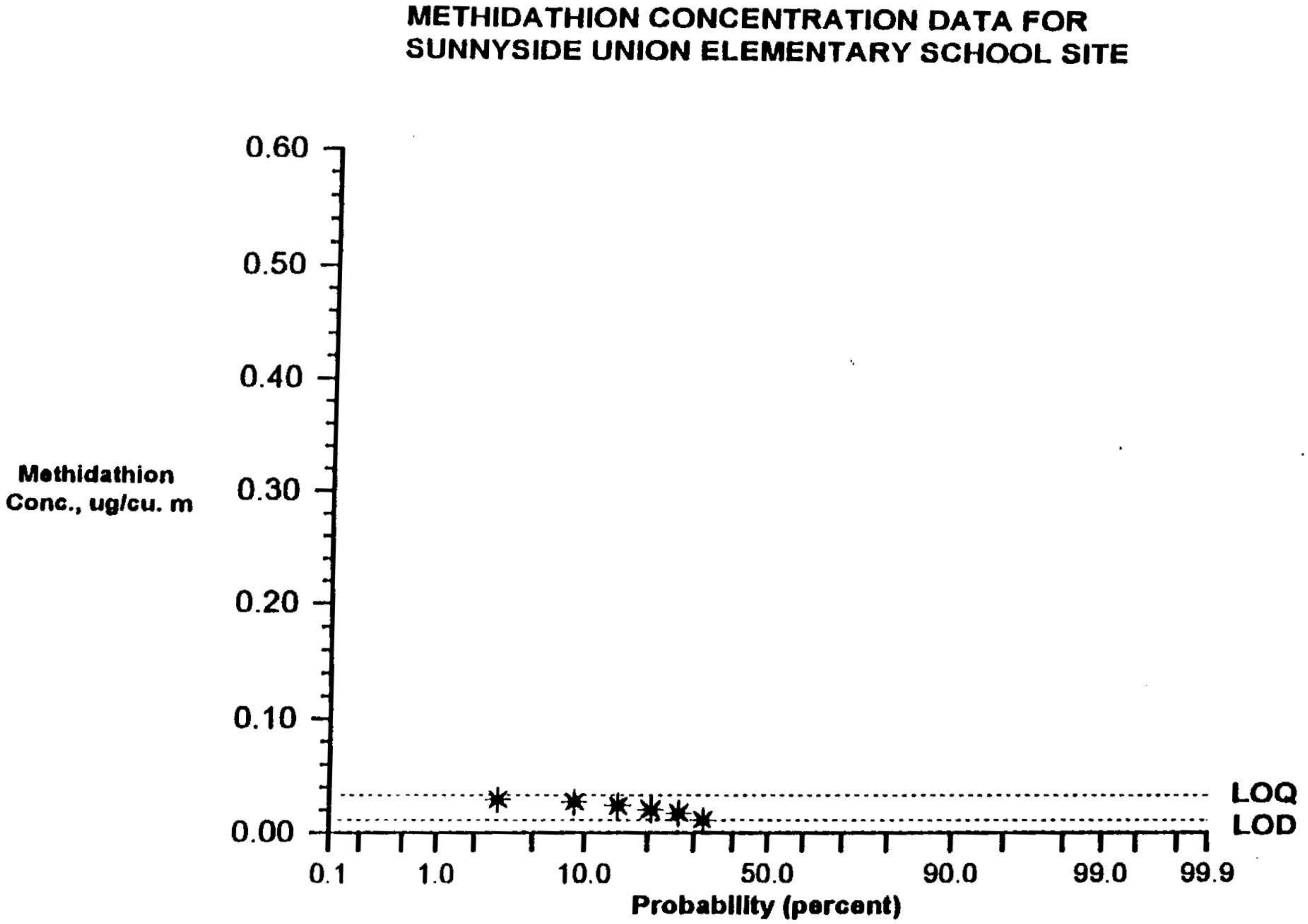


Fig. 8-2. Methidathion concentration in micrograms per cubic meter as function of probability (%) of methidathion concentration being equal to or greater than the plotted values at the Sunnyside Union Elementary School site during the June-July 1991 sampling period.

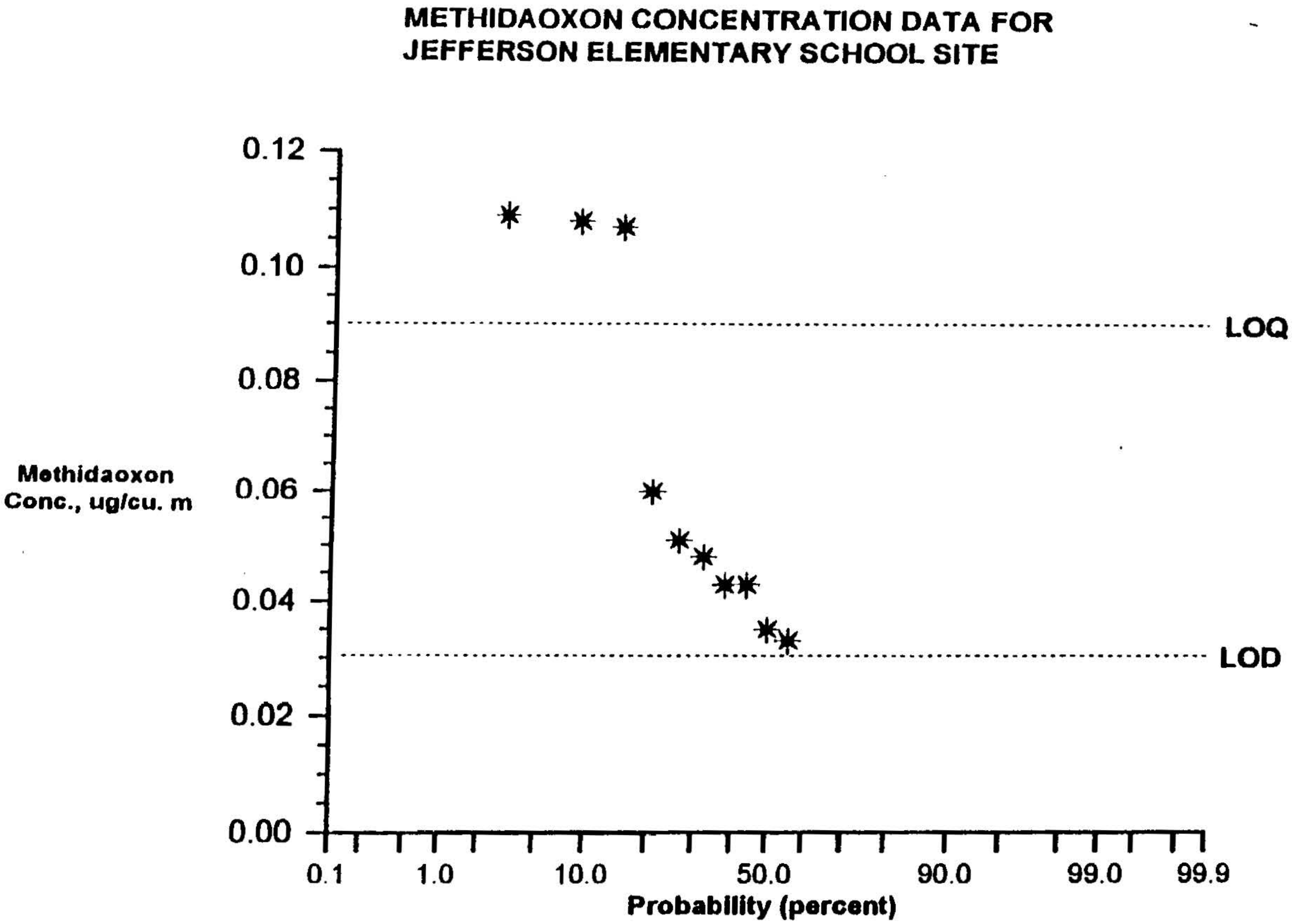


Fig. 9-1. Methidaoxon concentration in micrograms per cubic meter as function of probability (%) of methidaoxon concentration being equal to or greater than the plotted values at the Jefferson Elementary School site during the June-July 1991 sampling period.

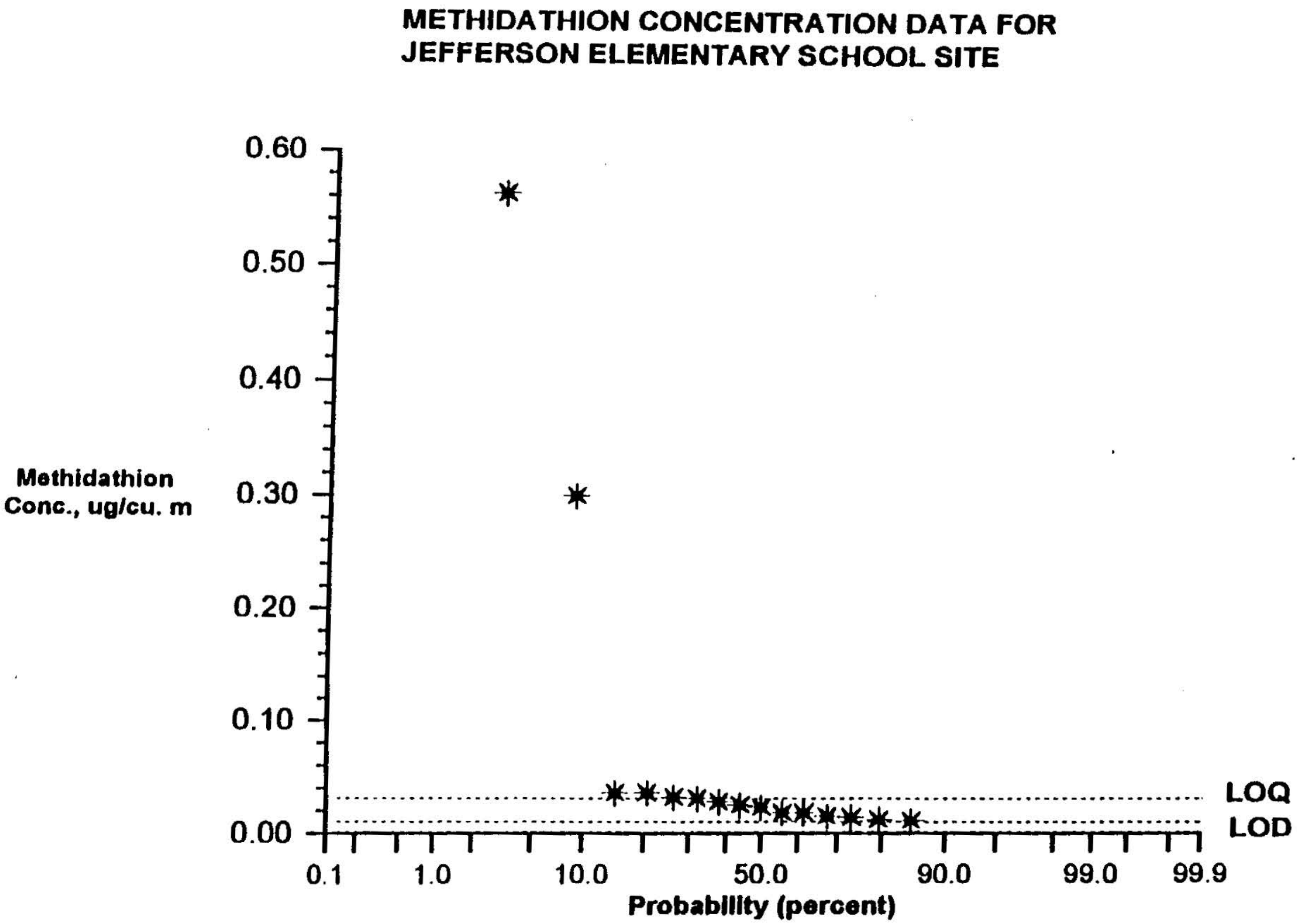


Fig. 9-2. Methidathion concentration in micrograms per cubic meter as function of probability (%) of methidathion concentration being equal to or greater than the plotted values at the Jefferson Elementary School site during the June-July 1991 sampling period.

APPENDIX A

SAMPLING DATA

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY

SAMPLE COLLECTION DATA

Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m^3)
0 S	27-Jun-91	11:25	28-Jun-91	11:00	23.6	3.9	5.519
0 J	27-Jun-91	15:25	28-Jun-91	11:30	20.1	3.9	4.700
0 E	27-Jun-91	10:45	28-Jun-91	12:05	25.3	3.9	5.928
0 UC	27-Jun-91	16:10	28-Jun-91	12:35	20.4	3.9	4.778
0 B	27-Jun-91	17:05	28-Jun-91	13:15	20.2	3.9	4.719
1 S	01-Jul-91	10:20	02-Jul-91	11:15	24.9	3.9	5.831
1 J	01-Jul-91	10:35	02-Jul-91	11:45	25.2	3.9	5.889
1 E	01-Jul-91	11:05	02-Jul-91	12:15	25.2	3.9	5.889
1 UC	01-Jul-91	11:30	02-Jul-91	12:50	25.3	3.9	5.928
1 B	01-Jul-91	12:00	02-Jul-91	13:25	25.4	3.9	5.948
2 S	02-Jul-91	11:20	03-Jul-91	11:35	24.3	3.9	5.675
2 J	02-Jul-91	11:50	03-Jul-91	12:15	24.4	3.9	5.714
2 E	02-Jul-91	12:20	03-Jul-91	12:50	24.5	3.9	5.733
2 UC	02-Jul-91	12:55	03-Jul-91	13:45	24.8	3.9	5.811
2 B	02-Jul-91	13:30	03-Jul-91	14:15	24.8	3.9	5.792
3 S	03-Jul-91	11:37	04-Jul-91	10:35	23.0	3.9	5.374
3 J	03-Jul-91	12:17	04-Jul-91	11:25	23.1	3.9	5.413
3 E	03-Jul-91	12:52	04-Jul-91	13:05	24.2	3.9	5.667
3 UC	03-Jul-91	13:47	04-Jul-91	13:32	23.8	3.9	5.558
3 B	03-Jul-91	14:17	04-Jul-91	12:55	22.6	3.9	5.296
4 S	04-Jul-91	10:50	05-Jul-91	12:15	25.4	3.9	5.948
4 J	04-Jul-91	11:30	05-Jul-91	12:37	25.1	3.9	5.877
4 E	04-Jul-91	12:00	05-Jul-91	13:00	25.0	3.9	5.850
4 UC	04-Jul-91	12:30	05-Jul-91	13:30	25.0	3.9	5.850
4 B	04-Jul-91	13:00	05-Jul-91	14:00	25.0	3.9	5.850

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School; E = Exeter Union High School; UC = University of California Lindcove Field Station; B = ARB Ambient Air Monitoring Station (background)

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY

SAMPLE COLLECTION DATA

Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m^3)
5 S	08-Jul-91	11:00	09-Jul-91	11:15	24.3	3.9	5.675
5 J	08-Jul-91	11:30	09-Jul-91	11:45	24.3	3.9	5.675
5 E	08-Jul-91	12:15	09-Jul-91	12:14	24.0	3.9	5.612
5 UC	08-Jul-91	12:50	09-Jul-91	13:15	24.4	3.9	5.714
5 B	08-Jul-91	13:30	09-Jul-91	13:45	24.3	3.9	5.675
6 S	09-Jul-91	11:17	10-Jul-91	11:20	24.1	3.9	5.628
6 J	09-Jul-91	11:48	10-Jul-91	11:50	24.0	3.9	5.624
6 E	09-Jul-91	12:35	10-Jul-91	12:40	24.1	3.9	5.636
6 UC	09-Jul-91	13:20	10-Jul-91	13:05	23.8	3.9	5.558
6 B	09-Jul-91	14:00	10-Jul-91	13:45	23.8	3.9	5.558
7 S	10-Jul-91	11:20	11-Jul-91	11:30	24.2	3.9	5.655
7 J	10-Jul-91	11:50	11-Jul-91	12:00	24.2	3.9	5.655
7 E	10-Jul-91	12:40	11-Jul-91	12:46	24.1	3.9	5.639
7 UC	10-Jul-91	13:05	11-Jul-91	13:15	24.2	3.9	5.655
7 B	10-Jul-91	13:45	11-Jul-91	13:50	24.1	3.9	5.636
8 S	11-Jul-91	11:30	12-Jul-91	10:50	23.3	3.9	5.460
8 J	11-Jul-91	12:00	12-Jul-91	11:15	23.3	3.9	5.441
8 E	11-Jul-91	12:45	12-Jul-91	11:50	23.1	3.9	5.402
8 UC	11-Jul-91	13:15	12-Jul-91	12:20	23.1	3.9	5.402
8 B	11-Jul-91	13:50	12-Jul-91	13:05	23.3	3.9	5.441
9 S	15-Jul-91	11:15	16-Jul-91	11:45	24.5	3.9	5.733
9 J	15-Jul-91	11:45	16-Jul-91	12:15	24.5	3.9	5.733
9 E	15-Jul-91	12:15	16-Jul-91	12:50	24.6	3.9	5.753
9 UC	15-Jul-91	12:45	16-Jul-91	12:30	23.8	3.9	5.558
9 B	15-Jul-91	13:15	16-Jul-91	14:00	24.8	3.9	5.792

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School; E = Exeter Union High School; UC = University of California Lindcove Field Station; B = ARB Ambient Air Monitoring Station (background)

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY

SAMPLE COLLECTION DATA

Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m^3)
10 S	16-Jul-91	11:45	17-Jul-91	11:30	23.8	3.9	5.558
10 J	16-Jul-91	13:05	17-Jul-91	12:00	22.9	3.9	5.363
10 E	16-Jul-91	12:50	17-Jul-91	12:35	23.8	3.9	5.558
10 UC	16-Jul-91	13:30	17-Jul-91	13:10	23.7	3.9	5.538
10 B	16-Jul-91	14:00	17-Jul-91	13:45	23.8	3.9	5.558
11 S	17-Jul-91	11:30	18-Jul-91	11:30	24.0	3.9	5.616
11 J	17-Jul-91	12:00	18-Jul-91	12:00	24.0	3.9	5.616
11 E	17-Jul-91	12:35	18-Jul-91	12:35	24.0	3.9	5.616
11 UC	17-Jul-91	13:10	18-Jul-91	13:10	24.0	3.9	5.616
11 B	17-Jul-91	13:45	18-Jul-91	13:45	24.0	3.9	5.616
12 S	18-Jul-91	11:30	19-Jul-91	11:20	23.8	3.9	5.577
12 J	18-Jul-91	12:00	19-Jul-91	11:50	23.8	3.9	5.577
12 E	18-Jul-91	12:35	19-Jul-91	12:25	23.8	3.9	5.577
12 UC	18-Jul-91	13:10	19-Jul-91	12:50	23.7	3.9	5.538
12 B	18-Jul-91	13:45	19-Jul-91	13:15	23.5	3.9	5.499
13 S	22-Jul-91	11:15	23-Jul-91	11:45	24.5	3.9	5.733
13 J	22-Jul-91	11:45	23-Jul-91	12:20	24.6	3.9	5.753
13 E	22-Jul-91	12:30	23-Jul-91	12:55	24.4	3.9	5.714
13 UC	22-Jul-91	13:00	23-Jul-91	13:30	24.5	3.9	5.733
13 B	22-Jul-91	13:30	23-Jul-91	14:00	24.5	3.9	5.733
14 S	23-Jul-91	11:45	24-Jul-91	11:30	23.8	3.9	5.558
14 J	23-Jul-91	12:20	24-Jul-91	12:00	23.7	3.9	5.538
14 E	23-Jul-91	12:55	24-Jul-91	12:40	23.8	3.9	5.558
14 UC	23-Jul-91	13:30	24-Jul-91	13:10	23.7	3.9	5.538
14 B	23-Jul-91	14:00	24-Jul-91	13:45	23.8	3.9	5.558

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School; E = Exeter Union High School; UC = University of California Lindcove Field Station; B = ARB Ambient Air Monitoring Station (background)

METHIDATHION AMBIENT MONITORING -- TULARE COUNTY

SAMPLE COLLECTION DATA

Field ID	Start Date	Start Time	End Date	End Time	Sampling Period (h)	Flow (Lpm)	Volume (m^3)
15 S	24-Jul-91	11:30	25-Jul-91	11:45	24.3	3.9	5.675
15 J	24-Jul-91	12:00	25-Jul-91	12:15	24.3	3.9	5.675
15 E	24-Jul-91	12:40	25-Jul-91	12:45	24.1	3.9	5.636
15 UC	24-Jul-91	13:10	25-Jul-91	13:25	24.3	3.9	5.675
15 B	24-Jul-91	13:45	25-Jul-91	13:45	24.0	3.9	5.616
16 S	25-Jul-91	11:45	26-Jul-91	11:50	24.1	3.9	5.636
16 J	25-Jul-91	12:15	26-Jul-91	12:46	24.5	3.9	5.737
16 E	25-Jul-91	12:45	26-Jul-91	13:25	24.7	3.9	5.772
16 UC	25-Jul-91	13:25	26-Jul-91	12:10	22.8	3.9	5.324
16 B	25-Jul-91	13:45	26-Jul-91	14:45	25.0	3.9	5.850

Key: S = Sunnyside Union Elementary School; J = Jefferson Elementary School; E = Exeter Union High School; UC = University of California Lindcove Field Station; B = ARB Ambient Air Monitoring Station (background)

APPENDIX B

APPLICATION MONITORING REPORT

State of California

AIR RESOURCES BOARD

METHIDATHION APPLICATION MONITORING REPORT

Ambient Air Monitoring in Tulare County for Methidathion in July, 1991, after Application to an Orange Grove

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C91-092A

Report Date: December 6, 1991

APPROVED:

________________, Project Engineer
Testing Section

Peter K. Ouchida, Manager
Testing Section

George Lew, Chief
Engineering Evaluation Branch

Methidathion Monitoring in Tulare County in July, 1991

This report presents the results of ambient monitoring for methidathion after a ground application at a selected orchard in Tulare County. The results are based on samples collected by the Air Resources Board (ARB) staff and analyzed by the staff of the Engineering Research Institute (ERI) at the California State University, Fresno (CSUF.) The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

The project engineer was Don Fitzell. The Instrument Technician was Jack Rogers of the ARB. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses was performed by the Engineering Research Institute at CSUF.

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Air Resources Board

Methidathion Monitoring in Tulare County

I. INTRODUCTION

At the request of the California Department of Pesticide Regulations (DPR), formerly the Department of Food and Agriculture, and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a two-day source impacted ambient monitoring program for methidathion and its breakdown product, methidaoxon, in Tulare County during the month of July 1991.

II. PESTICIDE DESCRIPTION

Methidathion (molecular weight 303.33 g/mole) is an organophosphorus insecticide which is colorless crystal with a melting point of 39-40°C. It is slightly volatile (vapor pressure 3.37×10^{-6} mm Hg at 25°C) and soluble in water only to the extent of 240 ppm at 20°C. It is readily soluble in acetone, benzene and methanol.

Methidathion is a restricted use pesticide under Title 3, California Code of Regulations, Section 6400. The EPA has classified it in Toxicity Category I for oral exposure, Category II for inhalation and Category III for dermal exposure.

Methdathion is used on a variety of crops. It is used on oranges to control red scale and other pests. It is typically applied with tractor-driven equipment at rates from one-quarter to one-half pound per 100 gallons of water.

III. SAMPLING LOCATIONS

An orange grove was selected (FIGURE I.) by Bob Felts of Leffingwell Ag. Sales Co., Inc. and approved by ARB staff to use for application monitoring. The prevailing wind in the area is from the northwest. Three samplers were set up: 1) approximately 25 yards north of the orchard, 2) approximately 15 yards southeast of the orchard and 3) approximately 150 yards southeast of the orchard. A meteorological station was set up near the farthest downwind sampler.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-2 tubes (see APPENDIX II.) These tubes are 8mm x 110mm, with 400 mg in the primary section and with 200 mg in the secondary (SKC catalog #226-30-06). Any methidathion present in the sampled ambient air is captured by the XAD-2 adsorbent contained in the tubes. Subsequent to sampling, the tubes were transported in an iced container to the CSUF's Engineering Research Institute in Fresno for analysis.

Sampling trains designed to operate continuously were set up at the three sampling sites identified in FIGURE II. of this report. Duplicate samples were obtained from all three sites. Sampling tubes were changed according to the schedule outlined in the QA Plan for Pesticide Monitoring (APPENDIX A.)

Each sample train consisted of an XAD-2 tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 12VDC vacuum pump. A diagram of the sampling train is shown in FIGURE III. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were wrapped around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that a flow rate of 1.85 lpm was actually achieved when the rotometers were set to 2.0 lpm.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The XAD-2 tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-2 tubes recovered from each sampler were analyzed by the CSUF Engineering Research Institute staff. The XAD-2 in the primary section of each sample tube was extracted with toluene, followed by GC separation on a DB-5 capillary column and measurement by Electron Capture Detector (APPENDIX III.) The secondary (backup) sections were saved to check for breakthrough, if necessary.

VI. RESULTS

Results for methidathion are shown in TABLE I. and a summary of the results along with meteorological data is shown in TABLE III. The results for the breakdown product, methidaoxon, is shown in TABLE II.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the S.O.P. for methidathion (APPENDIX III.)

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX A.) were followed with two exceptions: 1) monitoring was conducted for only 48-hours rather than continuing through Sunday morning, July 14 and 2) no field spike was prepared.

TABLE I. METHIDATHION MONITORING DATA

SAMPLE ID	SAMPLE TIME (HR.)	FLOW RATE (l/min.)	SAMPLE VOLUME (m^3)	MASS DETECTED (ug)	CONCENTRATION (ug/m^3)	Date Approx. Time
0N	1.00	1.85	0.11	ND	--	(background)
0SW1	1.00	1.85	0.11	ND	--	7/10
0SW2	1.00	1.85	0.11	ND	--	
						1500 - 1600
1N	7.75*	1.85	0.86	0.28	0.33	(application)
1SW1	7.83*	1.85	0.87	ND	--	7/10-11
1SW2	7.92*	1.85	0.88	ND	--	
						2330 - 0900
2N	2.00	1.85	0.22	0.19	0.86	
2SW1	2.00	1.85	0.22	ND	--	7/11
2SW2	2.00	1.85	0.22	ND	--	
						0900 - 1100
3N	3.83	1.85	0.42	0.59	1.40	
3SW1	3.83	1.85	0.42	ND	--	7/11
3SW2	3.83	1.85	0.42	ND	--	
						1100 - 1500
4N	6.83	1.85	0.76	0.62	0.82	
4SW1	6.83	1.85	0.76	0.95	1.25	7/11
4SW2	6.83	1.85	0.76	0.21	0.28	
						1500 - 2130
5N	10.08	1.85	1.12	3.54	3.16	
5SW1	10.17	1.85	1.13	0.68	0.60	7/11-12
5SW2	10.17	1.85	1.13	0.11	0.10	
5B	BLANK	--				2130 - 0730
6N	23.92	1.85	2.66	1.23	0.46	
6SW1	23.83	1.85	2.64	0.78	0.30	7/12-13
6SW2	23.75	1.85	2.64	ND	--	
						0730 - 0730

ND = Not Detected; below 0.1 ug/sample.

*Based on the application starting at 0100.

TABLE II. METHIDAOXON MONITORING DATA

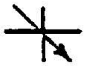
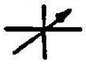
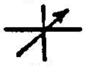
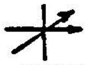
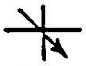
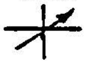
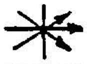
SAMPLE ID	SAMPLE TIME (HR.)	FLOW RATE (l/min.)	SAMPLE VOLUME (m^3)	MASS DETECTED (ug)	CONCENTRATION (ug/m^3)	Date Approx. Time
0N	1.00	1.85	0.11	ND	--	(background)
0SW1	1.00	1.85	0.11	ND	--	7/10
0SW2	1.00	1.85	0.11	ND	--	1500 - 1600
1N	7.75*	1.85	0.86	ND	--	(application)
1SW1	7.83*	1.85	0.87	ND	--	7/10-11
1SW2	7.92*	1.85	0.88	ND	--	2330 - 0900
2N	2.00	1.85	0.22	ND	--	
2SW1	2.00	1.85	0.22	ND	--	7/11
2SW2	2.00	1.85	0.22	ND	--	0900 - 1100
3N	3.83	1.85	0.42	ND	--	
3SW1	3.83	1.85	0.42	ND	--	7/11
3SW2	3.83	1.85	0.42	ND	--	1100 - 1500
4N	6.83	1.85	0.76	0.25	0.33	
4SW1	6.83	1.85	0.76	0.27	0.36	7/11
4SW2	6.83	1.85	0.76	ND	--	1500 - 2130
5N	10.08	1.85	1.12	0.29	0.26	
5SW1	10.17	1.85	1.13	ND	--	7/11-12
5SW2	10.17	1.85	1.13	ND	--	
5B	BLANK	--				2130 - 0730
6N	23.92	1.85	2.66	0.62	0.23	
6SW1	23.83	1.85	2.64	0.49	0.19	7/12-13
6SW2	23.75	1.85	2.64	ND	--	0730 - 0730

ND = Not Detected; below 0.25 ug/sample.

*Based on the application starting at 0100.

TABLE III. SUMMARY OF METHIDATHION DATA

Concentration ($\mu g/m^3$)

	Site "N" wind	Site "SW1"	Site "SW2"
(0)	---  NW 5 mph	---	---
(1)	0.33  SW 1 mph	---	---
(2)	0.86  SW 4 mph	---	---
(3)	1.40  W/SW 4 mph	---	---
(4)	0.82  NW 3 mph	1.25	0.28
(5)	3.16  SW 1 mph	0.60	0.10
(6)	0.46  SW/NW/E/S 3 mph	0.30	---

--- indicates not detected.
( ) indicates sampling period.
Arrowhead indicates direction wind is blowing toward.

FIGURE I. PESTICIDE MONITORING AREA

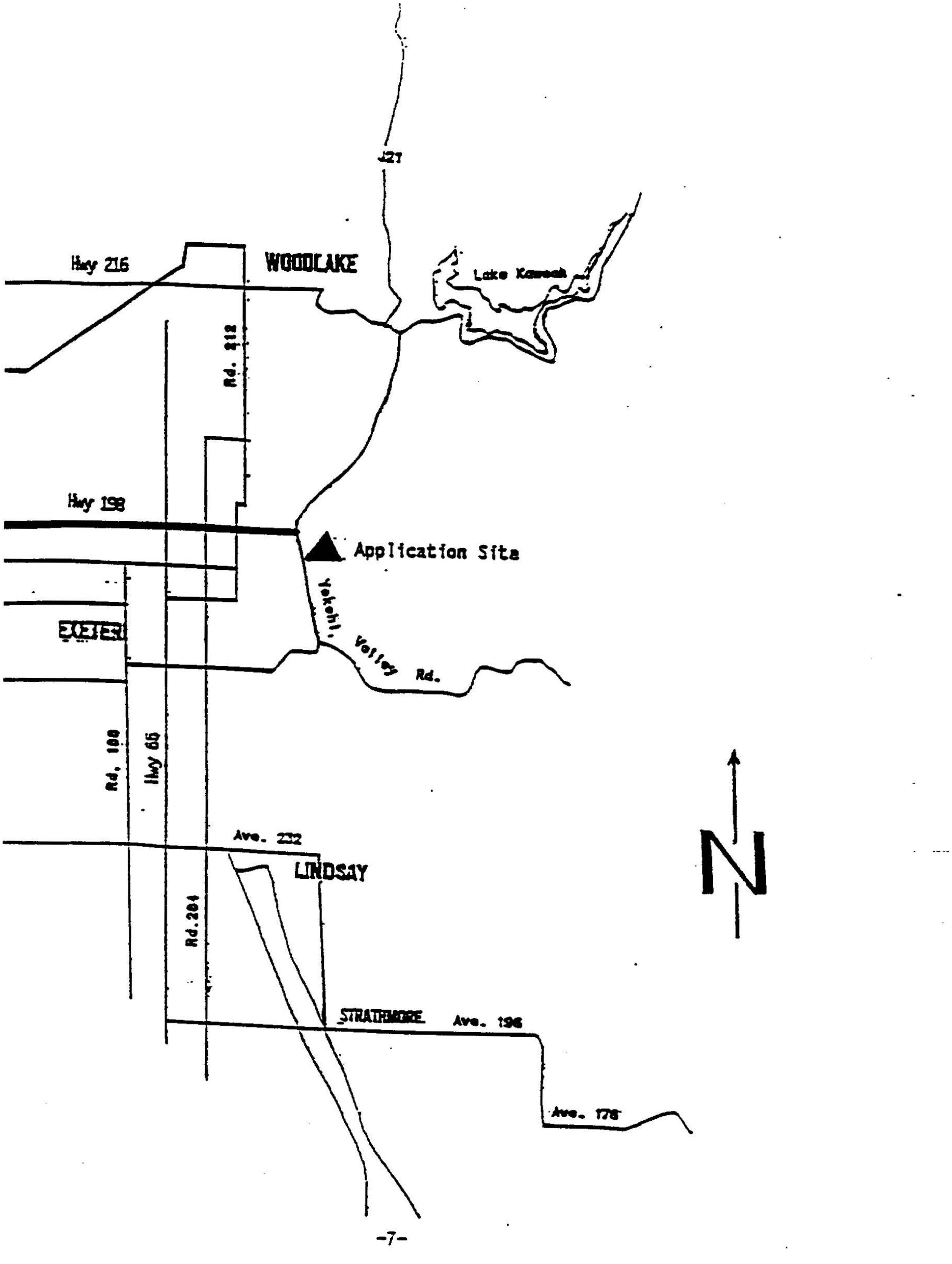
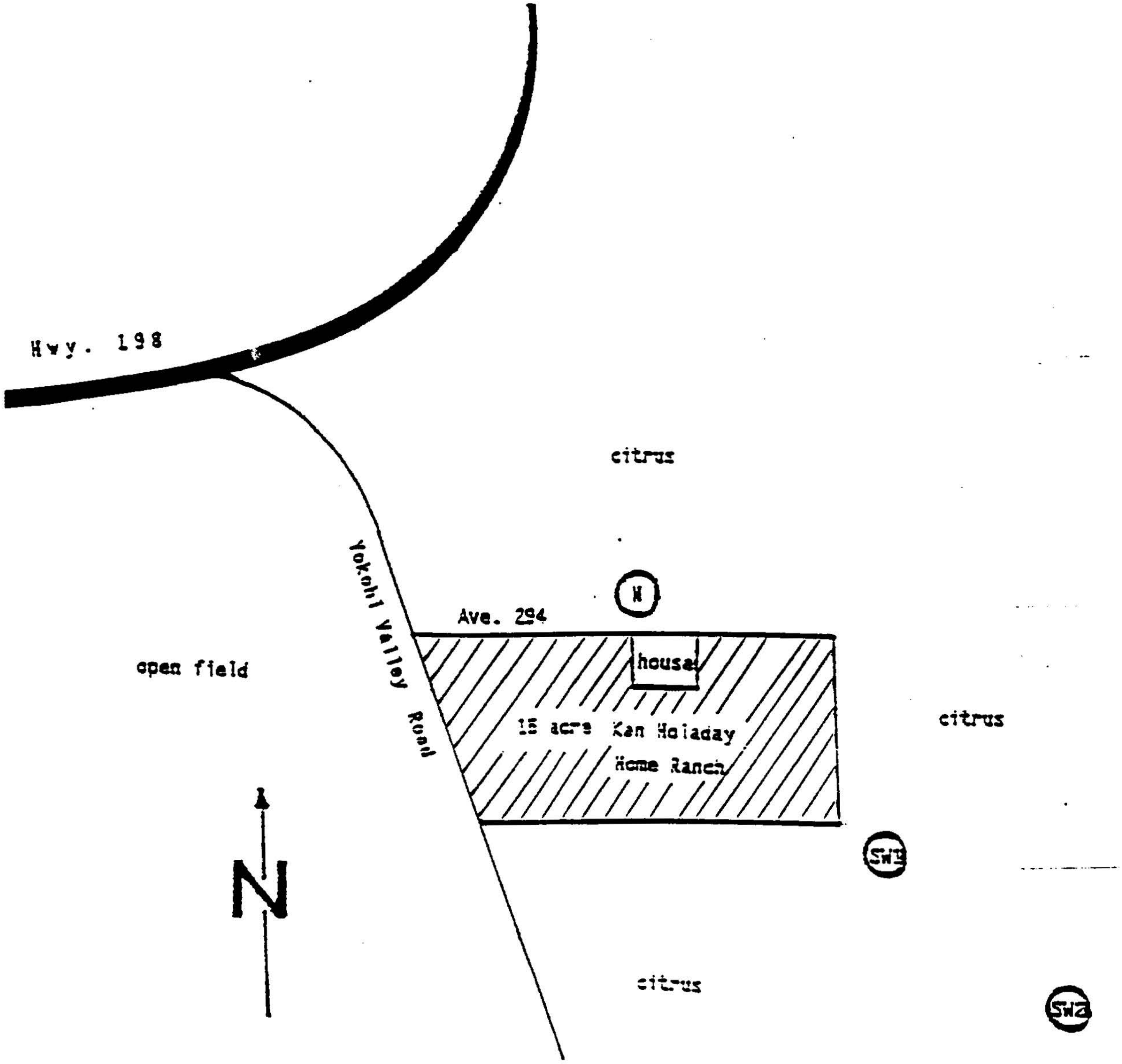


FIGURE II. PESTICIDE MONITORING SITES

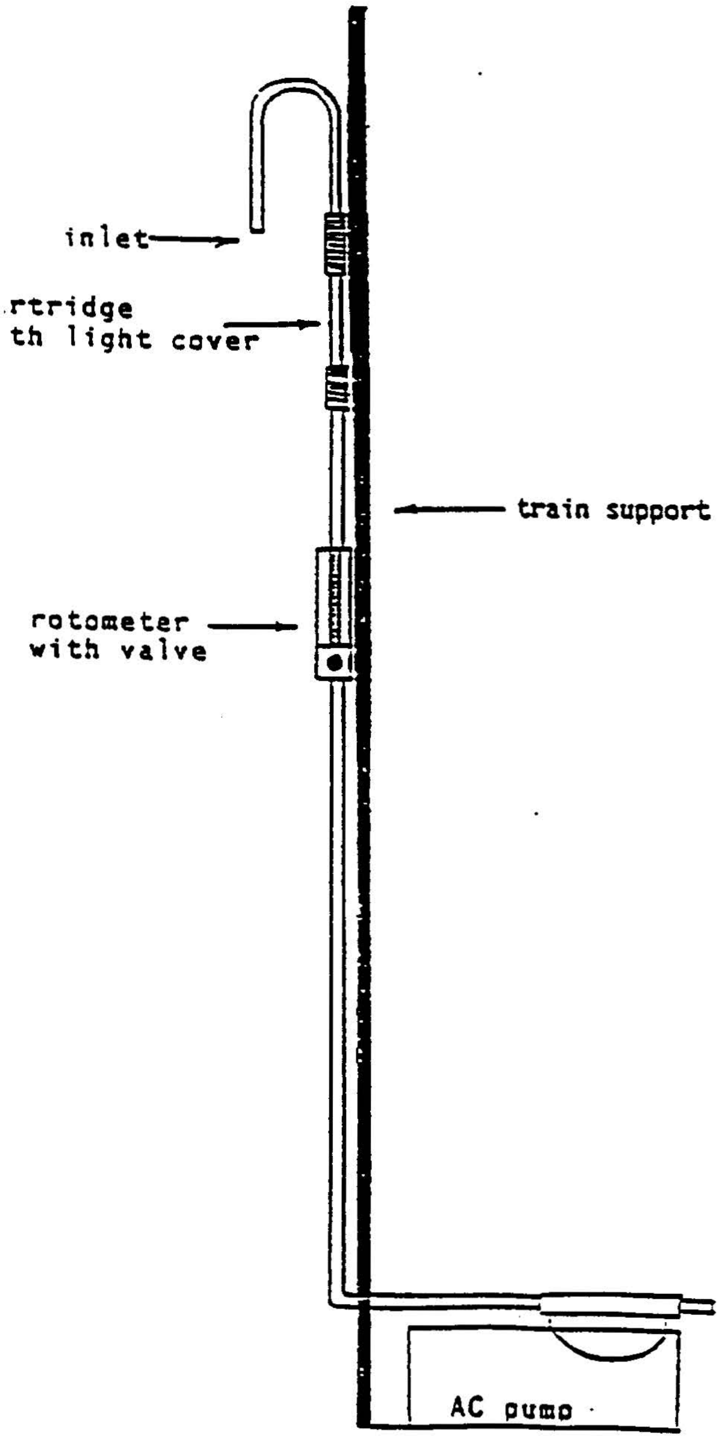


N = "upwind" sampler

SW1 = closest "downwind" sampler

SW2 = farthest "downwind" sampler

FIGURE III. PESTICIDE SAMPLING APPARATUS



APPENDIX I.

MONITORING OF PESTICIDES IN AIR -- 1991
METHIDATHION AND METHIDAOXON
APPLICATION MONITORING

SAMPLE RESULTS -- SUMMARY

Field Log #	Field ID	Lab Number	Methidaoxon ug	Methidathion ug
1	0 N	91-46A. 1	ND	ND
2	0 SW1	91-46A. 3	ND	ND
3	0 SW2	91-46A. 5	ND	ND
4	1 N	91-46A. 7	ND	0.28
5	1 SW1 *	91-46A. 9	ND	ND
5	1 SW1 *	91-46A. 10	ND	ND
6	1 SW2	91-46A. 11	ND	ND
7	2 N	91-46A. 13	ND	0.19
8	2 SW1	91-46A. 15	ND	ND
9	2 SW2	91-46A. 17	ND	ND
10	3 N	91-46A. 19	ND	0.59
11	3 SW1	91-46A. 21	ND	ND
12	3 SW2	91-46A. 23	ND	ND
13	4 N	91-46A. 25	0.25	0.62
14	4 SW1	91-46A. 27	0.27	0.95
15	4 SW2 *	91-46A. 29	ND	0.21
15	4 SW2 *	91-46A. 30	ND	0.21
16	5 N	91-46A. 31	0.29	3.54
17	5 SW1 **	91-46A. 33	ND	0.70
17	5 SW1 **	91-46A. 33	ND	0.66
18	5 SW2	91-46A. 35	ND	0.11
19	5 B	91-46A. 37	ND	ND
20	6 N	91-50A. 1	0.62	1.23
21	6 SW1	91-50A. 3	0.49	0.78
22	6 SW2	91-50A. 5	ND	ND
	MDL		0.25	0.10

* Duplicate extraction
** Duplicate injection

APPENDIX C

ANALYTICAL RESULTS

Methidathion in Air -- Tulare County ($\mu g/m^3$)

	Sunnyside Union Elementary				Jefferson Elementary			
	Methidaoxon		Methidathion		Methidaoxon		Methidathion	
Date	1	2	1	2	1	2	1	2
27-Jun-91	0.042		0.027		0.035		0.032	
01-Jul-91	0.061	0.058	0.023	0.024	0.051		0.018	
02-Jul-91	0.073	0.067	ND	ND	0.11		0.018	
03-Jul-91	0.051	ND	ND	ND	ND		0.012	
04-Jul-91	0.036	ND	ND	ND	0.033		0.011	
08-Jul-91	0.067		ND		0.048	0.077	ND	ND
09-Jul-91	0.084		ND		0.043	0.077	ND	ND
10-Jul-91	0.057		ND		0.11	0.097	0.56	0.56
11-Jul-91	0.033		ND		0.060	0.089	0.29	0.32
15-Jul-91	ND		0.017		ND		0.036	
16-Jul-91	ND		0.020		ND		0.023	
17-Jul-91	ND		ND		0.043		0.036	
18-Jul-91	ND		0.011		ND		0.031	
22-Jul-91	ND		ND		ND		0.028	
23-Jul-91	ND		ND		ND		0.025	
24-Jul-91	ND		0.029		ND		0.015	
25-Jul-91	0.092		ND		0.11		0.014	

LOD:		LOQ:	
Methidathion -- 0.01 $\mu g/m^3$		Methidathion -- 0.03 $\mu g/m^3$	
Methidaoxon -- 0.03 $\mu g/m^3$		Methidaoxon -- 0.09 $\mu g/m^3$	

KEY:
1 = Primary sampling tube
2 = Replicate sampling tube

Methidathion in Air -- Tulare County ($\mu g/m^3$)

	Exeter Union High School				UC Lindcove Field Station			
	Methidaoxon		Methidathion		Methidaoxon		Methidathion	
Date	1	2	1	2	1	2	1	2
27-Jun-91	0.043		0.019		0.075		0.014	
01-Jul-91	0.037		ND		0.055		ND	
02-Jul-91	0.12		0.028		0.062		ND	
03-Jul-91*	ND		0.012		ND		ND	
04-Jul-91*	—		—		—		—	
08-Jul-91	0.046		ND		0.049		ND	
09-Jul-91	0.039		ND		0.078		ND	
10-Jul-91	ND		ND		ND		ND	
11-Jul-91	0.057		ND		NR**		NR**	
15-Jul-91	ND	ND	0.015	0.011	ND		ND	
16-Jul-91	ND	ND	ND	ND	ND		0.010	
17-Jul-91	ND	ND	ND	ND	ND		ND	
18-Jul-91	ND	ND	0.098	0.042	ND		0.014	
22-Jul-91	ND		0.017		ND	ND	ND	ND
23-Jul-91	ND		ND		ND	ND	ND	ND
24-Jul-91	0.066		ND		ND	ND	ND	ND
25-Jul-91	0.12		ND		ND	ND	ND	0.011

LOD: Methidathion -- 0.01 $\mu g/m^3$
Methidaoxon -- 0.03 $\mu g/m^3$

LOQ: Methidathion -- 0.03 $\mu g/m^3$
Methidaoxon -- 0.09 $\mu g/m^3$

KEY: 1 = Primary sampling tube
2 = Repilcate sampling tube

* These two sites were not accesible on July 4. As a result, the July 3 sample represents a two day sampling period from July 3 to July 5.

** Sample not run; sample tubes broken.

Methidathion in Air -- Tulare County ($\mu g/m^3$)

	ARB Monitoring Station (Background)			
	Methidaoxon		Methidathion	
Date	1	2	1	2
27-Jun-91	0.041		ND	
01-Jul-91	0.039		0.013	
02-Jul-91	0.066		0.012	
03-Jul-91	ND		ND	
04-Jul-91	0.060		ND	
08-Jul-91	ND		ND	
09-Jul-91	0.056		ND	
10-Jul-91	0.068		ND	
11-Jul-91	ND		ND	
15-Jul-91	ND		ND	
16-Jul-91	ND		ND	
17-Jul-91	ND		ND	
18-Jul-91	ND		ND	
22-Jul-91	ND		ND	
23-Jul-91	ND		ND	
24-Jul-91	0.086		ND	
25-Jul-91	0.11		ND	

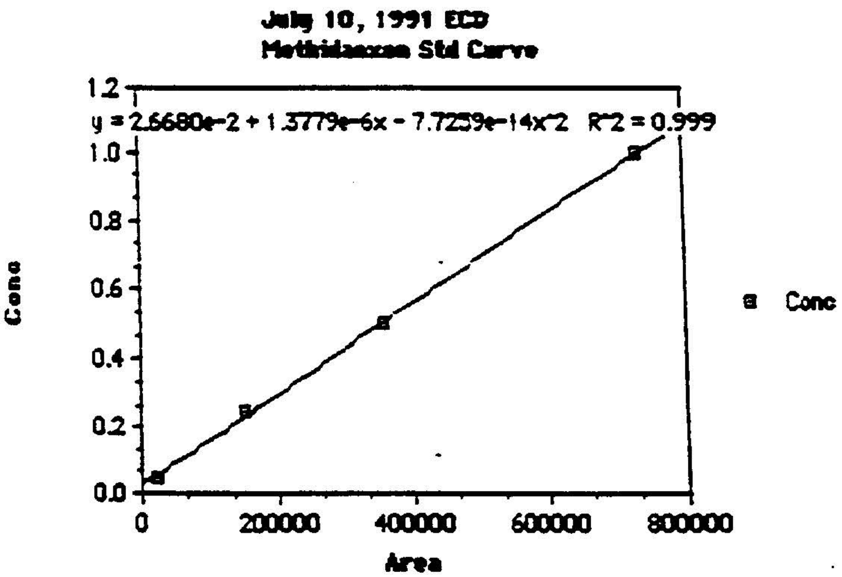
LOD: Methidathion -- 0.01 $\mu g/m^3$
Methidaoxon -- 0.03 $\mu g/m^3$

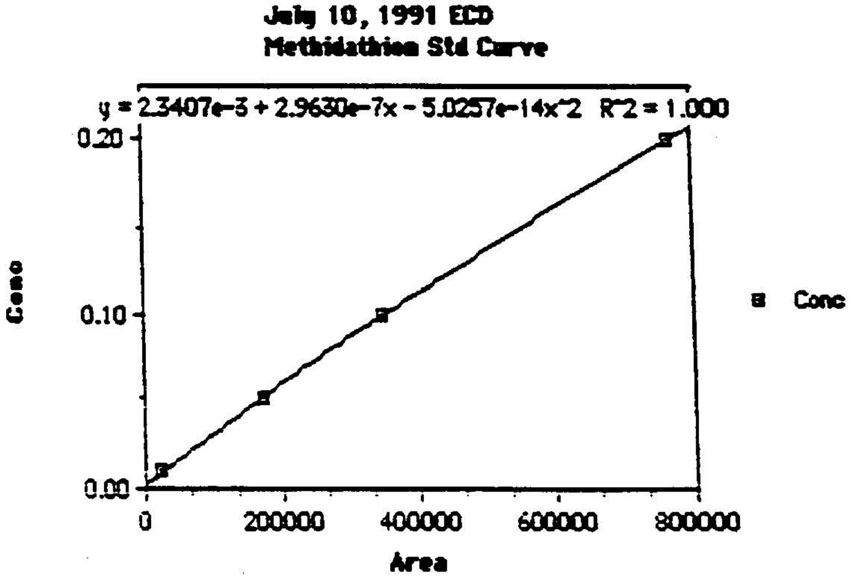
LOQ: Methidathion -- 0.03 $\mu g/m^3$
Methidaoxon -- 0.09 $\mu g/m^3$

KEY: 1 = Primary sampling tube
2 = Repilcate sampling tube

APPENDIX D

STANDARD CURVE EXAMPLE



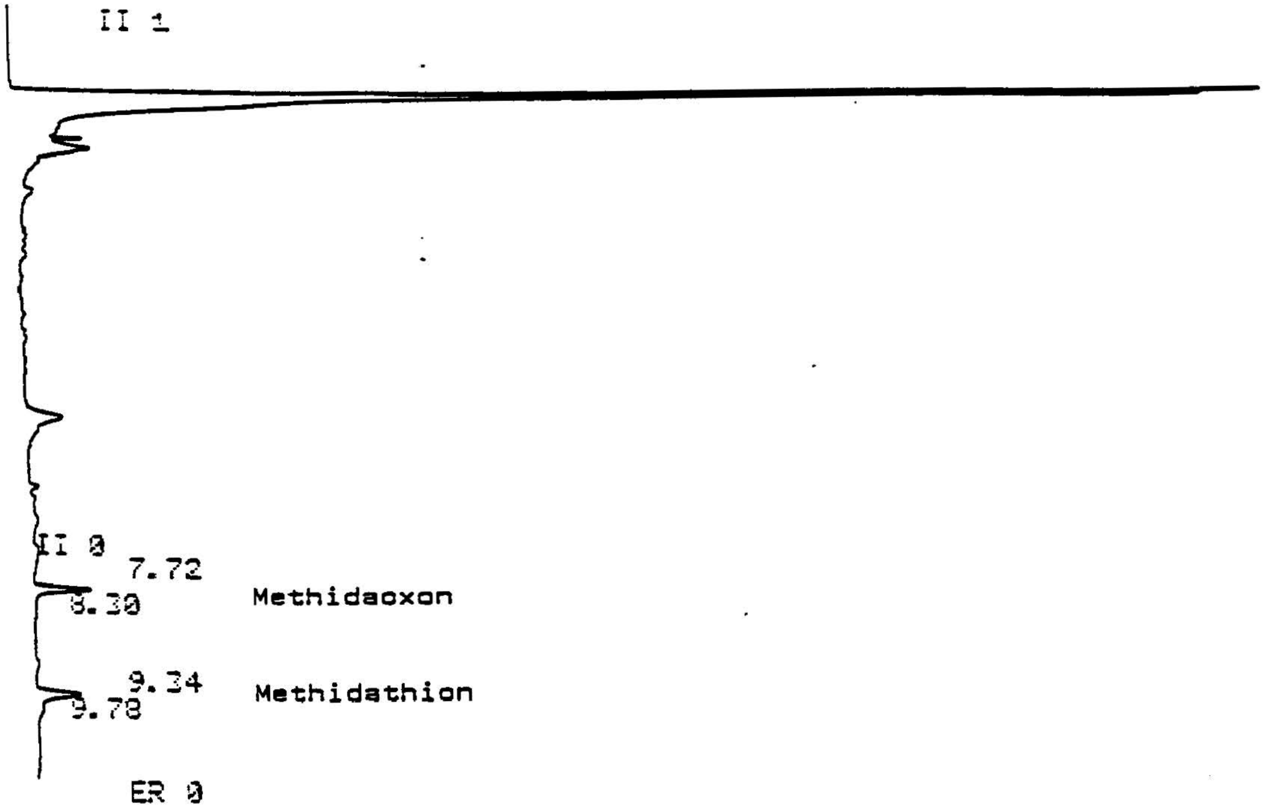


Untitled Data #1 Thu, Jul 11, 1991 12:39 PM

onc	Area	Conc	Area
1.000	735392.000	0.200	767236.000
0.500	358440.000	0.100	347711.000
0.250	150144.000	0.050	169449.000
0.050	23705.000	0.010	24294.000

Standard Curve Equations for Methidaoxon and Methidathion

```
WS 156  .01/.05 ME/MEOX

CHANNEL A       INJECT  07/10/91 10:10:02
```

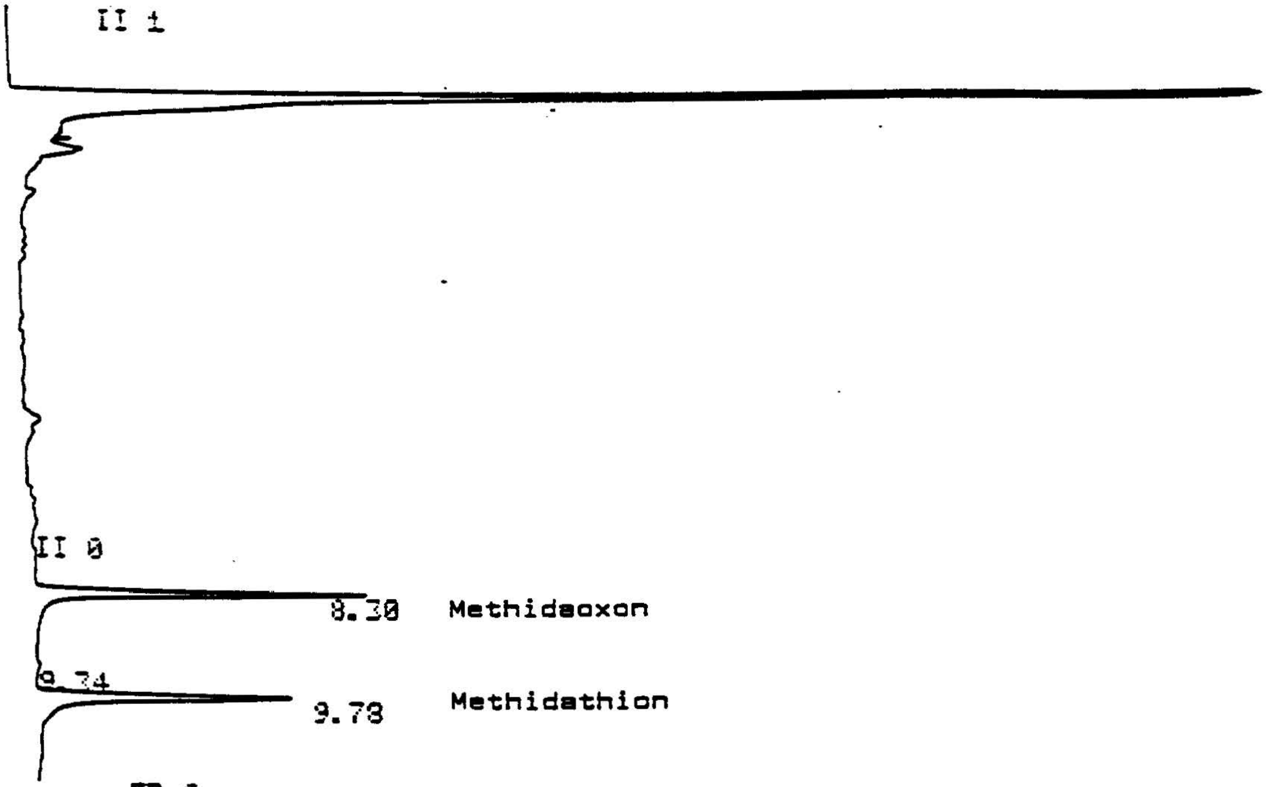


```
METHIDATHION/METHIDAOXON        07/10/91 10:10:02      CH= "A"   PS=  1.

FILE  1.      METHOD  0.      RUN 100      INDEX 100

PEAK#      AREA%          RT        AREA BC

    1        8.801      7.72       4882 01
    2       42.734      8.3       23705 01
    3        4.669      9.34       2590 01
    4       43.796      9.78      24294 01

TOTAL      100.                   55471
```

Working Standard Chromatogram

0.05 ug/mL Methidaoxon; 0.01 ug/mL Methidathion

```
WS 155  .05/.250  ME/MEOX

CHANNEL A      INJECT  07/10/91 09:55:50
```

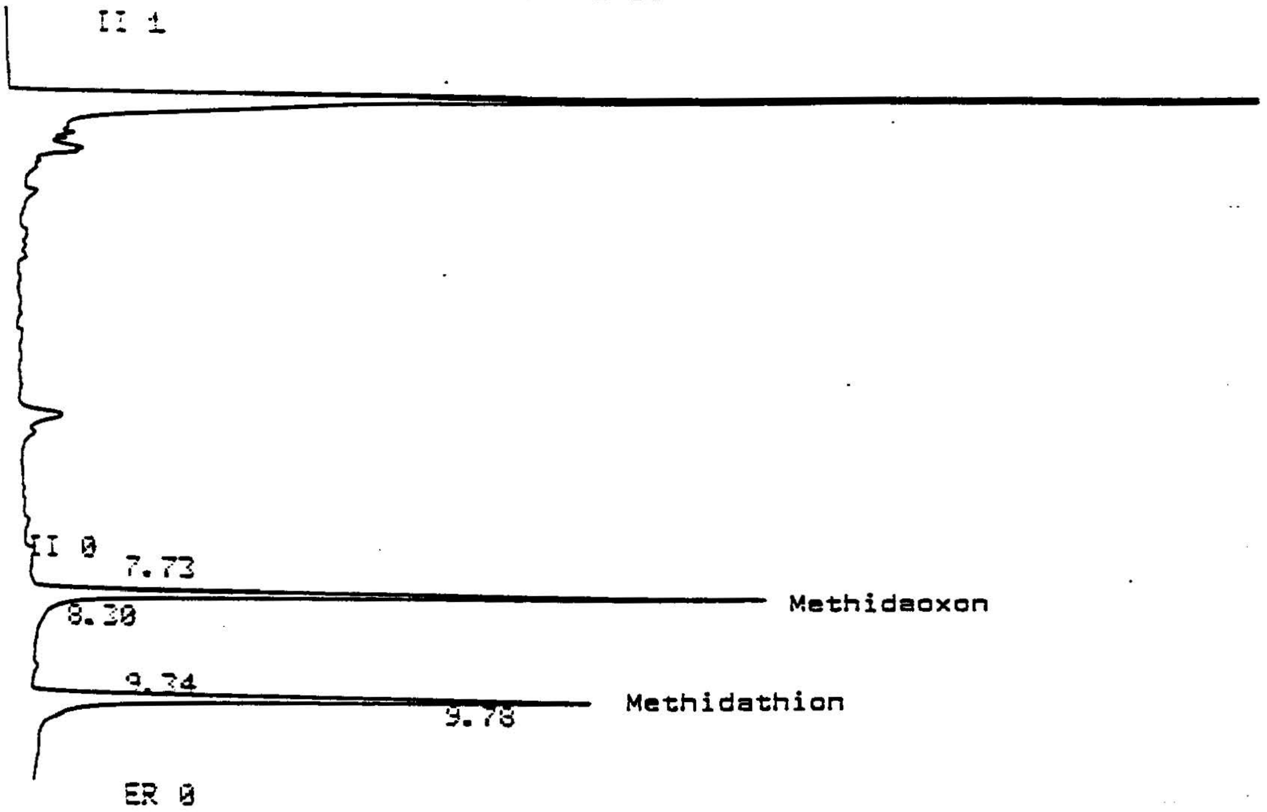


```
METHIDATHION/METHIDAOXON       07/10/91 09:55:50      CH= "A"  PS=  1.

FILE  1.      METHOD  0.      RUN  99      INDEX  99

PEAK#       AREA%        RT       AREA BC

    1       46.658      8.3     150144 01
    2        0.685      9.34      2205 01
    3       52.657      9.78    169449 01

TOTAL      100.                 321798
```

Working Standard Chromatogram

0.25 ug/mL Methidaoxon; 0.05 ug/mL Methidathion

```
WS 154  .10/.50  ME/MEOX
CHANNEL A      INJECT  07/10/91 09:41:36
```

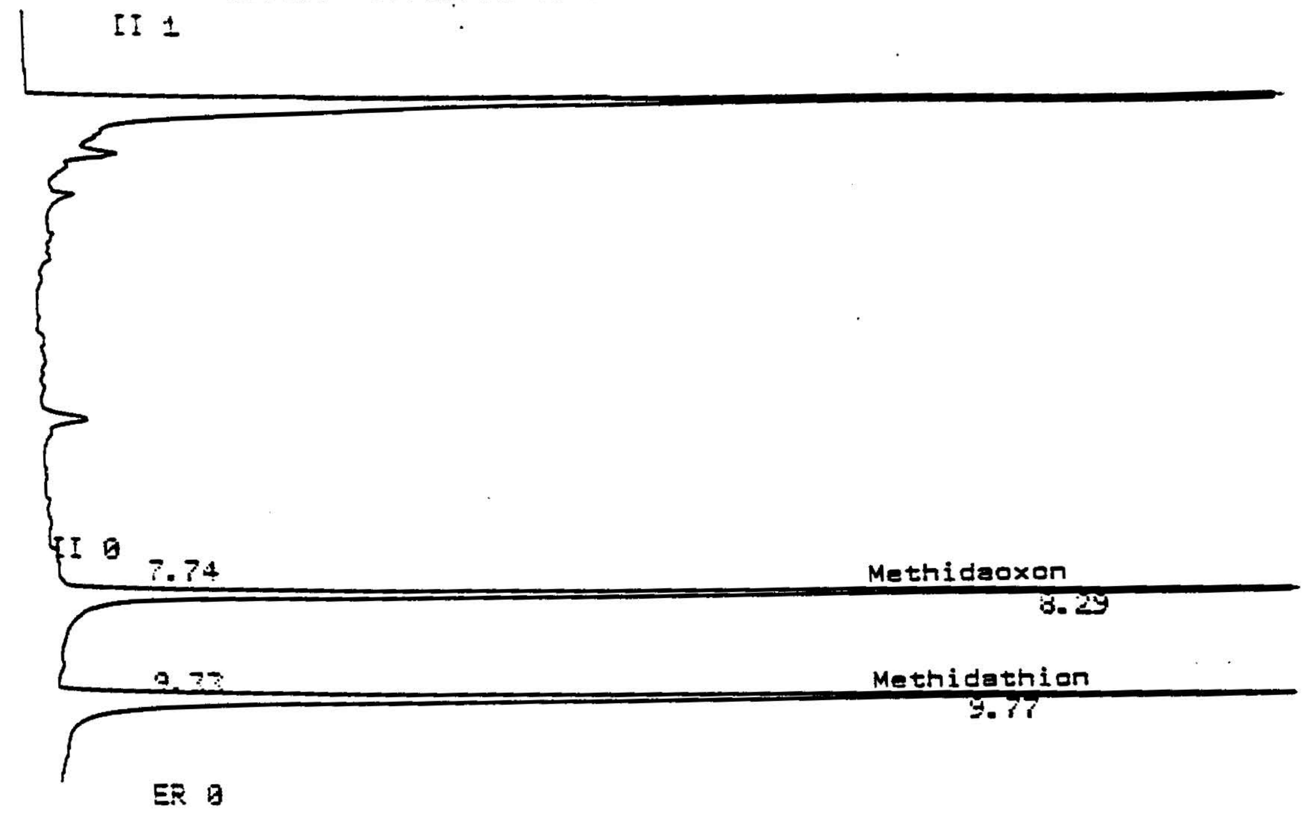


```
METHIDATHION/METHIDAOXON       07/10/91 09:41:36      CH= "A"   PS=  1.
FILE  1.       METHOD  0.      RUN  98       INDEX  98
PEAK#      AREA%        RT       AREA BC

   1         1.165     7.73      8352 01
   2        49.981     8.3     358440 01
   3         0.37      9.34      2652 01
   4        48.485     9.78    347711 01

TOTAL      100.                717155
```

Working Standard Chromatogram

0.5 ug/mL Methidaoxon; 0.1 ug/mL Methidathion

```
WS 153  .20/1.0  ME/MEOX

CHANNEL A      INJECT  07/10/91 09:27:10
```



```
METHIDATHION/METHIDAOXON       07/10/91 09:27:10      CH= "A"   PS=  1.

FILE  1.      METHOD  0.      RUN  97      INDEX  97

PEAK#       AREA%          RT        AREA BC

    1        1.117       7.74      16999 02
    2       48.324       8.29     735392 03
    3        0.143       9.33       2174 01
    4       50.416       9.77     767236 01

TOTAL       100.                 1521801
```

Working Standard Chromatogram

1.0 ug/mL Methidaoxon; 0.2 ug/mL Methidathion

APPENDIX E

QUALITY ASSURANCE REPORT

March 31, 1993

Audit Report
Methidathion and Methidaoxon Monitoring in Tulare County

SUMMARY

Field Audit

On June 27, 1991, staff of the Quality Assurance Section of the California Air Resources Board conducted a field audit of the five samplers used in the ambient air monitoring of Methidathion and Methidaoxon by the Engineering Research Institute of the California State University, Fresno. The audit consisted of an assessment of each sampler's conformance with the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring, and an evaluation of the flow rate accuracy of each sampler with a mass flow meter traceable to the National Institute of Standards and Technology.

The siting criteria were met in most cases with the following exceptions: all the samplers were located within 20 meters of a tree dripline, but in every case the distance between the sampler and the tree was more than twice the height that the tree protruded above the sampler; the probe of the sampler at the University of California field station in Lindcove was only 1.8 meters above the ground; and the sampler at the Exeter High School was located within 3.5 meters of a pair of smokestacks which protruded about 2 meters above the sampler's inlets, and whose operational status was unknown.

The flow rate audits resulted in an average percent difference of 1.4%, with individual differences ranging from -0.9% to 4.2%. The records for field operations were appropriate and consistent with good practice.

In addition, the samplers used by the Air Resources Board's Engineering Evaluation Branch staff in the monitoring of a Methidathion application were audited before and after the sampling period. The difference between the reported and the true flow rates averaged 1.7% with a range of 0% to 3.4% in the pre-application audit, and 1.7% with a range of 0.5% to 2.7% after the application.

Laboratory Audit

An audit of the laboratory operations in support of the Methidathion and Methidaoxon monitoring project was conducted between July 10, 1991 and June 8, 1992. The laboratory audit was composed of both a system and an analytical performance audit. The system audit consisted of a review of the laboratory instrumentation used for the project and the quality control measures pertaining to sample handling, analysis and documentation. For the analytical performance audit, XAD-2 resin tubes were spiked with Methidathion and Methidaoxon by QA staff and submitted to the laboratory for analysis.

In general, good quality control practices were followed in the study. The sampling, sample handling and storage, method validation, and documentation were adequate.

The results of the analytical audit for Methidathion showed a positive bias averaging 16.7% and ranging from 11.5% to 23.1%. The results for the Methidaoxon audit showed an average difference of 16.5% with a range of -1.2% to 42.9%. It is speculated that the positive biases were causes by interferences in the method, and further studies may be necessary to characterize the magnitude and possible source of the interference.

Audit Report
Methidathion and Methidaoxon Monitoring in Tulare County

FIELD AUDIT

On June 27, 1991, Gabriel Ruiz of the Quality Assurance (QA) Section of the California Air Resources Board (ARB) conducted a field audit of the five samplers used in the Methidathion and Methidaoxon air monitoring project by the Engineering Research Institute (ERI) of the California State University, Fresno. The audit consisted of an evaluation of the flow rate accuracy of each sampler, and an assessment of each sampler's conformance with the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring prepared by the Monitoring and Laboratory Division (MLD) and the Stationary Source Division (SSD).

Sampler Siting

The five monitoring sites were located at the ARB air monitoring station in Visalia, the Exeter High School in Exeter, the University of California field station in Lindcove, the Jefferson Elementary School in Lindsay, and the Sunnyside Union Elementary School in Strathmore. The sites were selected by the MLD's Engineering Evaluation Branch (EEB) staff, following the guidelines specified in the Quality Assurance Plan for Pesticide Monitoring.

Three deviations from the siting criteria were observed (see Table 1). First, all the samplers were located within 20 meters of a tree dripline; however, in all cases the distance between the tree and the sampler was more than twice the height that the tree protruded above the sampler's probe. Second, the sampler's probe at the University of California field station in Lindcove was only 1.8 meters above the ground. While it is not likely that the probe's height had an effect on the integrity of the samples, an effort should be made to conform with the established siting criteria, so that uniformity can be maintained. And third, the sampler at the Exeter High School was located within 3.5 meters of a pair of smokestacks which protruded about 2 meters above the sampler's inlets. The operational status of the stacks was unknown at the time of the audit.

Table 1. Summary of the samplers' conformance with the siting criteria during the ambient monitoring of Methidathion.

Site Location	Height from ground 2-15 meters	Distance from supporting structure Vertical 1 meter	Distance from supporting structure Horizontal 1 meter	20 meters from tree dripline	Distance from obstacles larger than two times the height the obstacle protrudes above the sampler	Unrestricted airflow 270 degrees around the sampler	10 meters from incineration flues
Visalia-ARB Monitoring Station 310 N. Church Street Visalia, CA	Yes	Yes	Yes	No[1]	Yes	Yes	Yes
Exter High School Exeter, CA	Yes	Yes	Yes	No[2]	Yes	Yes	No[3]
U.C. Field Sation - Lindcove 22963 Carson Avenue Exeter, CA	No[4]	Yes	Yes	No[5]	Yes	Yes	Yes
Jefferson Elementary School 333 Westwood Avenue Lindsay, CA	Yes	Yes	Yes	No[6]	Yes	Yes	Yes
Sunnyside Union Elementary School 21644 Avenue 196 Strathmore, CA	Yes	Yes	Yes	No[7]	Yes	Yes	Yes

NOTES:

1. Sampler was 7.5 m from tree dripline. The tree protruded about 3 m above the sampler's probe.
2. Sampler was 10.0 m from tree dripline. The tree protruded about 0.6 m above the sampler's probe.
3. Sampler was 3.4 m from smokestacks.
4. Sampler probe was about 1.0 m from ground.
5. Sampler was 10.5 m from tree dripline. The tree protruded about 0.5 m above the sampler's probe.
6. Sampler was 15.5 m from tree dripline. The tree protruded about 6 m above the sampler's probe.
7. Sampler was 16.0 m from tree dripline. The tree protruded about 3 m above the sampler's probe.

Field Operations

Sample collection and other field operations were carried out by Barthelemy Konan of the ERI. The sampling apparatus consisted of two XAD-2 resin tubes, each connected with latex tubing to a rotameter. The rotameters were then connected with latex tubing to a single pump. The assembly was supported with a 2 meter section of aluminum tubing (see Figure 1). The adsorbant tubes were covered with aluminum foil to protect them from sunlight.

Before deploying the samplers in the field, a single-point calibration of the rotameters was performed by setting the flow rate at 4.0 liters per minute (lpm) and measuring the actual flow with a bubble meter. The measured flow rate was then reported as the sample collection flow rate.

The audit was conducted on the same day that the samplers were set up and background sampling was initiated, thus the sampling records available at the time were limited to sampler location, date start time, and initial flow rate. Information to be collected later included stop time, final flow rate, and comments about unusual conditions. The records for field operations were appropriate and consistent with good practice.

Flow Rate Audits

A flow rate audit of the samplers used by the ERI was conducted in the field with a 0-10 lpm mass flow meter certified against a primary standard gas flow calibration system traceable to the National Institute of Standards and Technology (NIST). The audit was conducted following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged 1.4% and ranged from -0.9% to 4.2% (Table 2).

Also, three samplers used by the EEB in the monitoring of a Methidathion application were audited at the EEB's shop prior to the application on July 3, 1991, and after the application on July 15, 1991.

A single-point calibration of the rotameters was performed by the EEB staff by setting the flow rate at 2.0 lpm and measuring the actual flow with a bubble meter. The average of the measured flows was then assigned as the sample collection flow rate. The flow rates were audited with a NIST traceable 0-3 lpm mass flow meter (see Attachment I). The difference between the reported and the true flow rates in the pre-application audit averaged 1.7% and ranged from 0% to 3.4% (Table 3). The post-application audit results confirmed the rotameters' stability with an average difference of 1.7% and a range of 0.5% to 2.7% (Table 4).

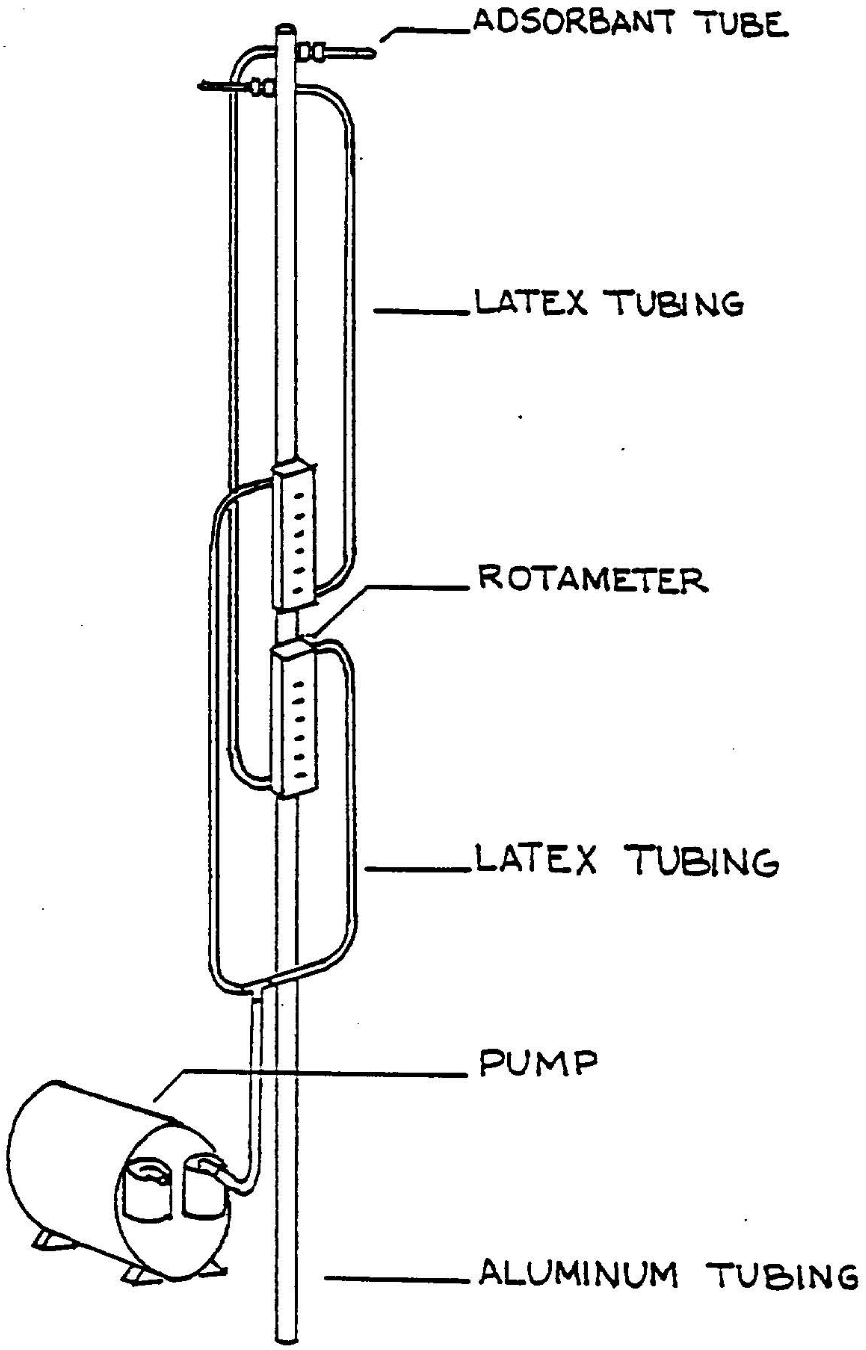


Figure 1. Air Sampler used in the monitoring of Methidathion and Methidaoxon

Table 2. Results of the flow rate audit of the ERI samplers.

Site	Rotameter Number	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
Visalia - ARB	9	3.45	3.47	-0.6
	10	3.47	3.42	1.5
Exeter High School	5	3.45	3.48	-0.9
	6	3.43	3.42	0.3
U.C. Field Station	7	3.44	3.47	-0.9
	8	3.45	3.44	0.3
Jefferson Elementary School	11	3.44	3.33	3.3
	12	3.49	3.37	3.6
Sunnyside Union Elementary School	1	3.49	3.35	4.2
	2	3.47	3.38	2.7

Table 3. Results of the pre-application flow rate audit of the EEB samplers.

Sampler Number	Rotameter Number	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
5	10	1.85	1.82	1.6
	11	1.86	1.86	0.0
7	13	1.87	1.86	0.5
	14	1.88	1.82	3.3
9	3B	1.85	1.82	1.6
	17	1.85	1.79	3.4

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

Table 4. Results of the post-application flow rate audit of the EEB samplers.

Sampler Number	Rotameter Number	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
5	10	1.85	1.82	1.6
	11	1.86	1.82	2.2
7	13	1.87	1.83	2.2
	14	1.88	1.83	2.7
9	38	1.85	1.83	1.1
	17	1.85	1.84	0.5

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

LABORATORY AUDIT

A system audit of the Engineering Research Institute's laboratory operations in support of the Methidathion and Methidaoxon monitoring project was conducted between July 10, 1991 and June 8, 1992, by Gabriel Ruiz. The audit was conducted primarily through electronic mail and telephone conversations with Brenda Royce of the ERI, and it consisted of a review of the instrumentation, a review of the quality control measures used to monitor data quality, and an analytical performance audit. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected every 24-hours, stored inside individual screw cap glass culture tubes in an ice chest, and delivered to the laboratory on a daily basis. The samples were stored in a freezer at -10 to -15°C and extracted within one week. The extracts were then stored in the freezer, and analyses were performed within one month. The unused part of the extracts was retained until the end of the study.

Laboratory Instrumentation

Analysis of the samples was performed with a Varian 3400 Gas Chromatograph equipped with an electron capture detector. The chromatograph was interfaced to a Varian 4290 integrator. The integrator was used for area counts only, and the concentrations were determined by separate calculations.

Sample Analysis

The analytical procedure was developed by the ERI's laboratory staff and documented in a preliminary draft entitled "Standard Operating Procedure for the Determination of Methidathion and Methidaoxon in Ambient Air". The method entails extraction with toluene followed by GC analysis. (Refer to the draft of the SOP available in the QA office for further details.)

The detection limit of the method was determined as 0.05 ug total mass for Methidathion and 0.13 ug for Methidaoxon, using three standard deviations at the lowest calibration point plus the absolute value of the intercept. Since the detector had a non-linear calibration curve, a second-order best fit curve of area count vs. concentration was used to determine the concentrations.

The method recovery rates averaged 106% for Methidathion samples ranging in size from 0.06 to 1.6 ug, and 126% for Methidaoxon samples ranging in size from 0.3 ug to 3.0 ug. A retention efficiency study was conducted for triplicate samples containing 0.3 ug Methidathion and 1.5 ug Methidaoxon. After drawing ambient air through the tubes at 4 lpm for 24-hours, the average recoveries were 89% for Methidathion and 108% for Methidaoxon. Sample stability data was not reported to the Quality Assurance Section.

Quality control activities performed routinely to monitor and document the data quality included the following: daily four-point calibration, a calibration update every 10 samples, analysis of one control sample per batch of field samples, plotting of control charts with control limits defined at ±3 standard deviations, analysis of a field duplicate per sampling day, replicate analyses of 5% of the samples, analysis of a lab and field spike every 10 samples, and analysis of a lab blank for every batch of samples. In addition, field blanks were analyzed occasionally, and qualitative confirmations were made with a Hall electrolytic conductivity detector.

Documentation

The ERI's laboratory staff followed adequate chain-of-custody procedures. All samples were accompanied by field data sheets and chain-of-custody records. A unique laboratory sample number independent of the field sample number was assigned to each sample when it was logged in. In addition, the extracts were given a separate laboratory number, and all the numbers were cross-referenced.

Sample logs, laboratory records, and instrument run and maintenance logs were kept in bound notebooks with numbered pages. The entries included sample number, sample type, date sample was received, date of analysis, raw analytical data, results of the analysis, and receptor of the analytical data.

The chromatograms, integrator printouts, and summary sheets for the analysis sequence were saved in an accessible form. Data reduction and calculations were performed on an electronic spreadsheet and the finalized data were stored on electronic media.

Analytical Performance Audit

The performance of the ERI's analytical method was evaluated by submitting for analysis a set of six audit samples spiked with measured amounts of Methidathion and Methidaoxon. The samples were prepared by Gabriel Ruiz on July 30, 1991, following the procedures outlined in Attachment II. The samples were analyzed on August 2, following the laboratory's standard operating procedures.

The analytical results for Methidathion showed a positive bias averaging 16.7% and ranging from 11.5% to 23.1% (Table 5). The results for duplicate samples M2 and M3 indicate a high degree of precision, but it also must be noted that sample M6 was reported as nondetectable, even though it was spiked with more than twice the detection limit value for Methidathion.

The Methidaoxon results showed more variability (Table 6). The difference between the assigned and the reported values averaged 16.5% and ranged from -1.2% to 42.9%. The results for duplicate samples M2 and M6 also indicate a high degree of precision for the method. Samples M4 and M5 were not spiked with Methidaoxon, but the laboratory reported masses of 0.28 and 0.18 ug per sample, respectively.

CONCLUSIONS

The ERI followed good quality control procedures overall. The sampling was conducted following good practices, sample handling and storage were appropriate, the analytical method was validated, and the documentation was adequate. The analytical audit results showed a fair agreement between the assigned and the reported mass of both compounds and were consistent with the method's recovery rates.

The only area that we feel needs further attention is the possibility of interference. The reported method recovery rates were greater than 100% for both compounds in most studies, and the audit results confirmed them. Moreover, the laboratory reported positive results for two Methidaoxon blanks (although breakdown of Methidathion could have accounted for the positive reading in one of the samples, the other was a blank for both compounds). Further analyses of the method validation and quality control data may be necessary to characterize the magnitude and possible source of the interference.

Table 5. Results of ERI's analyses of Methidathion audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
M1	0	ND	N/A
M2	0.26	0.32	23.1
M3	0.26	0.30	15.4
M4	0	ND	N/A
M5	0.52	0.58	11.5
M6	0.13	ND	N/A

Table 6. Results of ERI's analyses of Methidaoxon audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
M1	1.68	1.97	17.3
M2	0.84	0.83	- 1.2
M3	0.42	0.60	42.9
M4	0	0.28	N/A
M5	0	0.18	N/A
M6	0.84	0.90	7.1

ND = Not Detected

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

ATTACHMENT I

Flow Audit Procedure for Pesticide Samplers

Introduction

The pesticide sampler is audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable primary standard gas flow calibration system.

The audit device is placed in series with the sample probe 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 reported flow rate is then compared to the true flow rate, and a percent difference is determined.

Equipment

The basic equipment required for the pesticide 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.
6. 1/4" I.D. Tygon tubing.

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 probe inlet with a small section of Tygon tubing.
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 reported flow rate.

ATTACHMENT II

Performance Audit Procedure For The Laboratory Analysis Of Methidathion

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 Methidathion and its breakdown product Methidaoxon. The audit is conducted by submitting audit samples prepared by spiking XAD-2 resin tubes with measured amounts of Methidathion and Methidaoxon. 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. Methidathion, neat compound
2. Methidaoxon, neat compound
3. Toluene, high purity
4. XAD-2 Resin Tubes
5. 50 ul Microsyringe

Safety Precautions

Methidathion and Methidaoxon may be fatal if inhaled, swallowed, or absorbed through the skin. Avoid direct physical contact. Vapors or direct eye contact can cause severe eye burns. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

3 mg/ml Methidathion Stock Solution: Weigh about 30 mg of Methidathion into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

4 mg/ml Methidaoxon Stock Solution: Weigh about 40 mg of Methidaoxon into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

12 ug/ml Methidathion Spiking Standard: Transfer 100 ul of the 3 mg/ml Methidathion stock solution to a clean 25 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

40 ug/ml Methidaoxon Spiking Standard: Transfer 100 ul of the 4 mg/ml Methidaoxon stock solution to a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

Sample Preparation

Prepare six audit samples from the Methidathion and Methidaoxon spiking standards according to the following table:

Sample	Methidathion 12 ug/ml Std	Methidaoxon 40 ug/ml Std
1	10 ul	20 ul
2	20	20
3	20	10
4	40	0
5	0	40
6	0	0

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 spiking 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. Assign a random number to each sample, keeping track of the concentrations. Label each tube with its assigned number and store at or below 4°C until ready for analysis.

APPENDIX F

METHOD VALIDATION RESULTS

METHIDATHION METHOD VALIDATION RESULTS

		METHIDAOXON			METHIDATHION	
DESCRIPTION	FORTIF ug	RESULTS ug	RECOV. %	FORTIF. ug	RESULTS ug	RECOV. %
EXTRACTION EFFICIENCY						
Level 1	0.30	0.435	144.9%	0.06	0.061	102.0%
		0.511	170.2%		0.082	136.0%
		0.391	130.2%		0.055	91.0%
Average:			148.4%			109.7%
Std Dev:			20.2%			23.5%
Level 2	1.5	1.882	125.5%	0.3	0.316	105.2%
		1.464	97.6%		0.245	81.8%
		2.013	134.2%		0.284	94.6%
		1.574	104.9%		0.331	110.4%
		1.737	115.8%		0.330	110.2%
Average:			115.6%			100.4%
Std Dev:			14.8%			12.2%
Level 3	3.0	2.832	94.4%	0.6	0.774	129.0%
		3.327	110.9%		0.748	124.7%
		2.805	93.5%		7.684	114.0%
Average:			99.6%			122.6%
Std Dev:			9.8%			7.7%
Level 4	10.9	13.52	124.0%	9.8	10.26	104.8%
INJECTION REPRODUCIBILITY						
Level 1	0.3	0.391		0.06	0.052	
		0.396			0.055	
		0.380			0.070	
Average:		0.389			0.059	
Std Dev:		0.0078			0.0098	
Rel SD:		2.00%			16.57%	
Level 2	1.5	2.013		0.3	0.284	
		1.670			0.300	
		2.324			0.311	
Average:		2.002			0.298	
Std Dev:		0.327			0.0135	
Rel SD:		16.4%			4.51%	

METHIDATHION METHOD VALIDATION RESULTS

			METHIDAOXON			METHIDATHION	
DESCRIPTION		FORTIF. ug	RESULTS ug	RECOV. %	FORTIF. ug	RESULTS ug	RECOV. %
INJECTION REPRODUCIBILITY (cont'd)							
Level 3		3.0	2.805		0.6	0.834	
			2.484			0.744	
			2.670			0.816	
	Average:		2.653			0.798	
	Std Dev:		0.161			0.0476	
	Rel SD:		6.08%			5.97%	
RETENTION EFFICIENCY							
Blank		0.0	0.150	—	0.0	0.012	—
			0.142	—		0.007	—
Level 1		0.3	0.353	117.6%	0.06	0.078	130.5%
			0.279	93.0%		0.090	150.5%
			0.326	108.8%		0.110	183.5%
	Average:			106.5%			154.8%
	Std Dev:			11.8%			25.2%
Level 2		1.5	1.639	109.3%	0.3	0.399	133.0%
			1.558	103.9%		0.369	123.0%
			1.444	96.3%		0.253	84.2%
			1.723	114.9%		0.269	89.7%
	Average:			106.1%			107.8%
	Std Dev:			7.9%			24.2%
Level 3		3.0	3.125	104.2%	0.6	0.589	98.2%
			3.005	100.2%		0.645	107.5%
			3.204	106.8%		0.619	103.2%
	Average:			103.7%			102.9%
	Std Dev:			3.2%			4.4%
Level 4		54.5	61.38	112.6%	49.0	62.69	128.1%

METHIDATHION METHOD VALIDATION RESULTS

		METHIDAOXON			METHIDATHION	
DESCRIPTION	FORTIF. ug	RESULTS ug	RECOV. %	FORTIF. ug	RESULTS ug	RECOV. %
RETENTION BREAKTHROUGH – BACK UP SECTION						
Level 1	10.9	0.126	1.2%	9.8	ND	—
		0.150	1.4%		ND	—
Level 2	27.3	0.097	0.4%	24.5	ND	—
Level 3	54.5	0.126	0.2%	49.0	ND	—
		0.148	0.3%		ND	—
Level 4	109.0	0.140	0.1%	97.9	ND	—
STORAGE STABILITY Freezer Stability						
03 Day	1.5	1.193	79.5%	0.3	0.431	143.8%
		1.370	91.3%		0.486	161.9%
		1.514	100.9%		0.485	161.5%
Average:			90.6%			155.7%
Std Dev:			10.7%			10.3%
07 Day	1.5	1.968	131.2%	0.3	0.427	142.4%
		1.768	117.9%		0.305	101.6%
		1.936	129.1%		1.384	128.0%
Average:			126.1%			124.0%
Std Dev:			7.2%			12.8%
14 Day	1.5	1.728	115.2%	0.3	0.369	123.0%
		1.540	102.6%		0.350	116.8%
		1.534	102.3%		0.295	98.4%
Average:			106.7%			112.7%
Std Dev:			7.4%			12.8%

METHIDATHION METHOD VALIDATION RESULTS

		METHIDAOXON			METHIDATHION	
DESCRIPTION	FORTIF. ug	RESULTS ug	RECOV. %	FORTIF. ug	RESULTS ug	RECOV. %
STORAGE STABILITY						
Freezer Stability (cont'd)						
21 Day	1.5	1.848	123.2%	0.3	0.376	125.2%
		2.130	142.0%		0.367	122.4%
		2.157	143.8%		0.353	117.7%
Average:			136.3%			121.8%
Std Dev:			11.4%			3.8%
28 Day	1.5	2.075	138.4%	0.3	0.332	110.7%
		1.663	110.9%		0.317	105.6%
		1.694	112.9%		0.285	95.1%
Average:			120.7%			103.8%
Std Dev:			15.3%			8.0%
80 Day	1.5	1.3353	89.0%	0.3	0.274	91.2%
Ice Chest Stability						
01 Day	1.5	1.603	106.9%	0.3	0.259	86.2%
		1.967	131.1%		0.310	103.3%
		1.740	116.0%		0.375	125.1%
Average:			118.0%			104.9%
Std Dev:			12.2%			19.5%
03 Day	1.5	2.353	156.8%	0.3	0.370	123.2%
		2.345	156.3%		0.393	131.1%
		1.196	79.7%		0.392	130.9%
Average:			131.0%			128.4%
Std Dev:			44.4%			4.5%
07 Day	1.5	1.853	123.5%	0.3	0.371	123.6%
		1.781	118.8%		0.368	122.6%
		1.983	132.2%		0.329	109.8%
Average:			124.8%			118.7%
Std Dev:			6.8%			7.7%

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION		FORTIF. ug	METHIDAOXON RESULTS ug	RECOV. %	FORTIF. ug	METHIDATHION RESULTS ug	RECOV. %
STORAGE STABILITY Room Temperature Stability							
01 Day		1.5	2.336	155.7%	0.3	0.259	862%
			1.868	124.5%		0.310	1033%
	Average:			140.1%			948%
	Std Dev:			22.1%			120%
03 Day		1.5	1.600	106.6%	0.3	0.323	1077%
			1.513	100.9%		0.348	1160%
	Average:			103.8%			1119%
	Std Dev:			7.1%			59%
07 Day		1.5	1.139	75.9%	0.3	0.230	767%
			1.855	123.7%		0.336	1120%
	Average:			99.8%			944%
	Std Dev:			33.7%			250%
FIELD CONTROLS							
Blank		0.0	0.161	—	0.0	0.008	—
			0.107	—		0.010	—
			0.114	—		0.007	—
Spike		1.5	1.759	117.3%	0.3	0.324	1080%
			1.642	109.5%		0.361	1203%
			1.811	120.7%		0.335	1117%
	Average:			115.8%			1133%
	Std Dev:			5.7%			63%

METHIDATHION METHOD VALIDATION RESULTS

DESCRIPTION	FORTIF. ug	METHIDAOXON RESULTS ug	RECOV. %	FORTIF. ug	METHIDATHION RESULTS ug	RECOV. %
EXTRACTION CONTROLS						
	1.5	2.222	148.1%	0.3	0.392	130.6%
	1.5	1.400	93.3%	0.3	0.457	152.2%
	1.5	1.861	124.1%	0.3	0.325	108.3%
	1.5	1.785	119.0%	0.3	0.359	119.6%
	1.5	2.510	167.3%	0.3	0.311	103.5%
	1.5	1.986	132.4%	0.3	0.419	139.6%
	1.5	2.348	156.5%	0.3	0.445	148.4%

Control Limits:

	METHIDAOXON	METHIDATHION
UCL	3.064	0.589
UWL	2.652	0.523
LWL	1.004	0.259
LCL	0.592	0.194

Airborne Concentrations of Oxydemeton-Methyl and Dioxydemeton-Methyl in Salinas Valley from Sampling Conducted August 31 to October 9, 1992

Prepared for California Air Resources Board
Contract No: A032-094

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JUNE 24, 1993

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DISCLAIMER

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TABLE OF CONTENTS

SUMMARY

The monitoring conducted in this study has been carried out at the request of the Department of Pesticide Regulation in support of their Toxic air Contaminant Program. Both ambient and application monitoring for oxydemeton-methyl and its oxidation product, diozydemetion-methyl and its oxidation product, dioxydemeton-methyl, were performed in the Salinas Valley during August of October of 1992. Neither oxydemeton-methyl or dioxydemeton-methyl were detected at any of the five ambient monitoring sites. They also were not detected during the two application monitoring periods. Appendices B and C contain a more detailed presentation of the monitoring data.

INTRODUCTION

Ambient air samples were collected at the low flow rate of 4 *lpm* at five sites in Monterey County for analysis of an organophosphate insecticide, oxydemeton-methyl, and its oxidization product, dioxydemeton-methyl. This compound, a restricted use pesticide, is a liquid at room temperature (melting point, -10C; boiling point, 365C; vapor presure data not available), and dioxydemeton-methyl is a crystalline solid (melting point, boiling point, and vapor pressure data not available). Samples collected for the analyses for these compounds were collected at two application sites at the very low flow rate of 2 *lpm*.

Oxydemeton-methyl (*S-(2-ethylsulfinyl)ethyl)O, O-dimethyl phosphorothioate*) is the active ingredient in a product formulated as an emulsifiable concentrate. The location and time period for sampling were based on reported applications of oxydemeton-methyl in recent years. The Salinas Valley in Monterey County was selected as the study area. Oxydemeton-methyl is applied in Monterey County throughout the year to various truck crops. Examples of these truck crops are beans, broccoli, Brussels sprouts, cabbage, cauliflower, lettuce, peppers, and sugar beets. In 1986, most of the reported use of oxydemeton-methyl in California was on broccoli (45,702 pounds of active ingredient), cauliflower (34,822 pounds of active ingredient), and sugar beets (14,645 pounds of active ingredient).

SITE DESCRIPTION

Five sampling sites for ambient monitoring were chosen by California Air Resources Board (ARB) personnel from an area of Monterey County where the use of oxydemeton-methyl on various crops is predominant. Sites were selected for their proximity to the fields where oxydemeton-methyl application were being made with considerations for both accessibility and security of the sampling equipment. The five sites are described below and they are shown on Figure 1. Individual site maps for application monitoring are in Appendix A.

- the La Joya Elementary School located at 55 Rogge Road in Salinas;
- the ARB District Ambient Station located at the Monterey County Public Health Department building located in Salinas;
- the Salinas Rural Fire Department Station No. 2 in Chualar;
- the California Division of Forestry (CDF) fire station at Soledad located on the east side of state highway 101 next to the Soledad Correctional Facility; and,
- the City of Greenfield water tank located near Oak and 13th Streets.

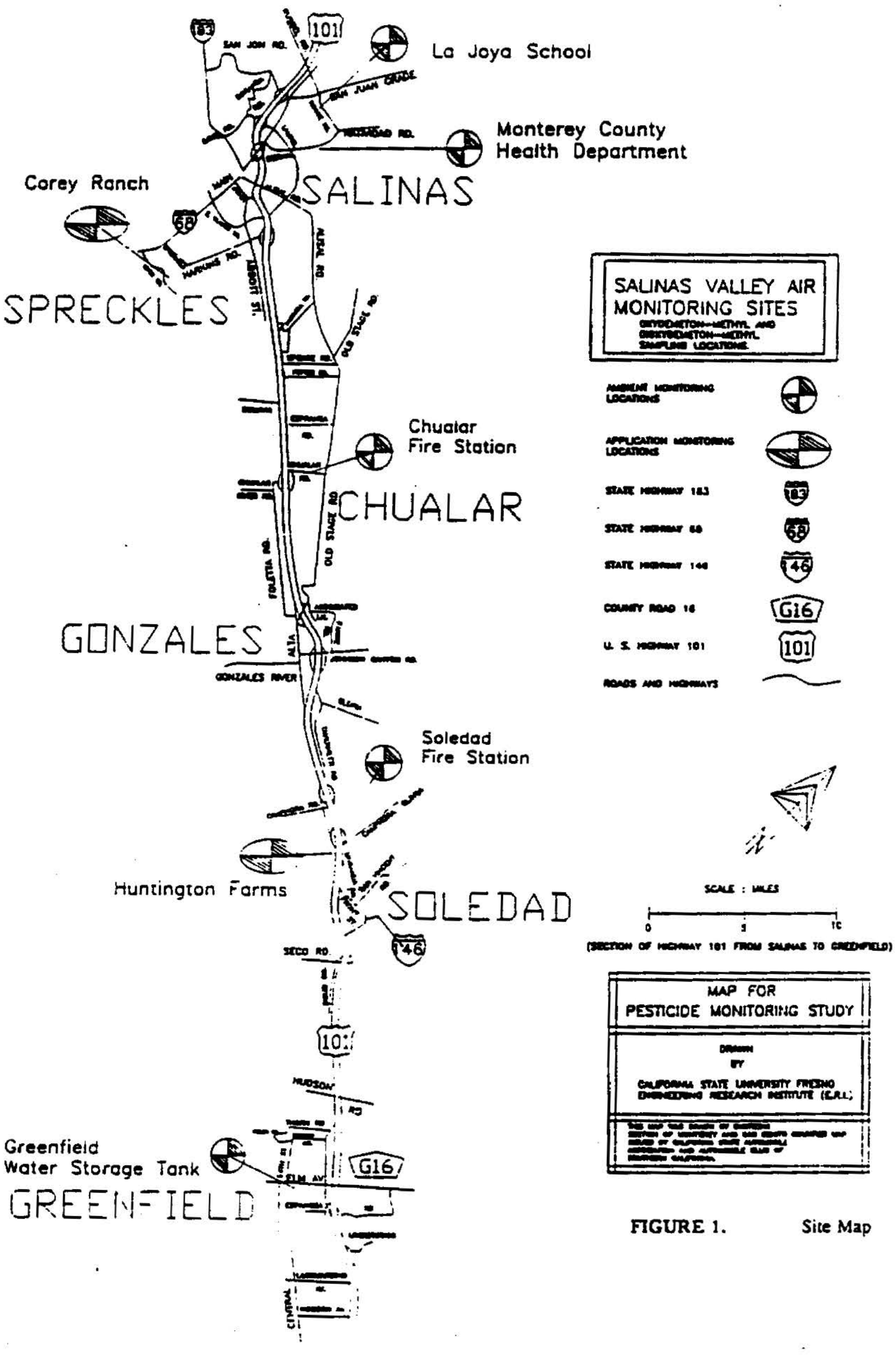


FIGURE 1. Site Map

Samplers were located on the roof of buildings at the La Joya Elementary School and ARB sites in the City of Salinas, on the roof of the Fire Station building in Chualar, on the ground in an open area southwest of the CDF Soledad fire station, and on top of the City of Greenfield water tank.

Various truck crops are grown directly adjacent to the sampler sites at the elementary school and the City of Greenfield water tank. Truck crops are also grown within one-half mile of the Chualar fire station site and the Soledad CDF fire station site. The Monterey County Health Department site is in an urbanized area but truck crops are grown within about one mile of the site.

The first and primary application monitoring took place at the Huntington Farms near Soledad on Highway 101 during the period of September 14-17, 1992. ARB personnel set up and maintained the equipment at the site and collected samples, and CSUF personnel observed. The second application monitoring was conducted at the Corey Ranch outside of Spreckels on River Road during the period of October 7-9, 1992. Both applications were made by ground sprayer rigs operating during the night. The application of Meta Systox R 2.5 GA, in a mixture of dimethoate and other materials, was made at a rate of 0.25 gallons per acre at both sites. The Corey Ranch and Huntington Farms sites receiving application of the insectide had areas of 16.6 and 23.5 acres, respectively. Meteorological data for the Huntington Farms site is in Appendix B. CSUF personnel set up and maintained the samplers and collected samples at the Corey Ranch site, and ARB personnel observed and critiqued set-up and collection procedures.

The ambient monitoring samples were collected by California State University, Fresno (CSUF) personnel over a five week period from August 31, to October 1, 1992. All ambient and application monitoring samples were transported to CSUF for analysis.

SAMPLING

Ambient and application samplers consisted of a glass tube (8*mm* x 110*mm*) containing one section of XAD-7 resin connected by teflon tubing to a flowmeter and a sampling pump. Each sampling pump had two resin tubes attached to it with the air flow through each tube being monitored by an independent flowmeter. A diagram of the sampling apparatus is presented in Figure 2. Flow rates for each sampling tube were measured at the beginning and at the end of each sampling period. The flow rates were 4 *lpm* and 2 *lpm* for ambient monitoring samples and application monitoring samples, respectively. Sampling periods for ambient monitoring were nominally 24 hours and varied from approximately 23 to 25 hours. Sampling periods for application monitoring ranged from about 1.5 to 24 hours. The sampling data are presented in Appendix B. At the end of the sampling period, each resin tube was removed from the sampling apparatus and capped, labeled, and placed in a screw cap glass culture tube. The culture tubes with their contents were then placed in an ice chest containing ice. The samples were stored in the ice chests until delivery at the end of each sampling day to CSUF for analysis. At CSUF samples were stored in a freezer at $-15^{\circ}C$ until extracted for analysis.

PESTICIDE SAMPLING APPARATUS

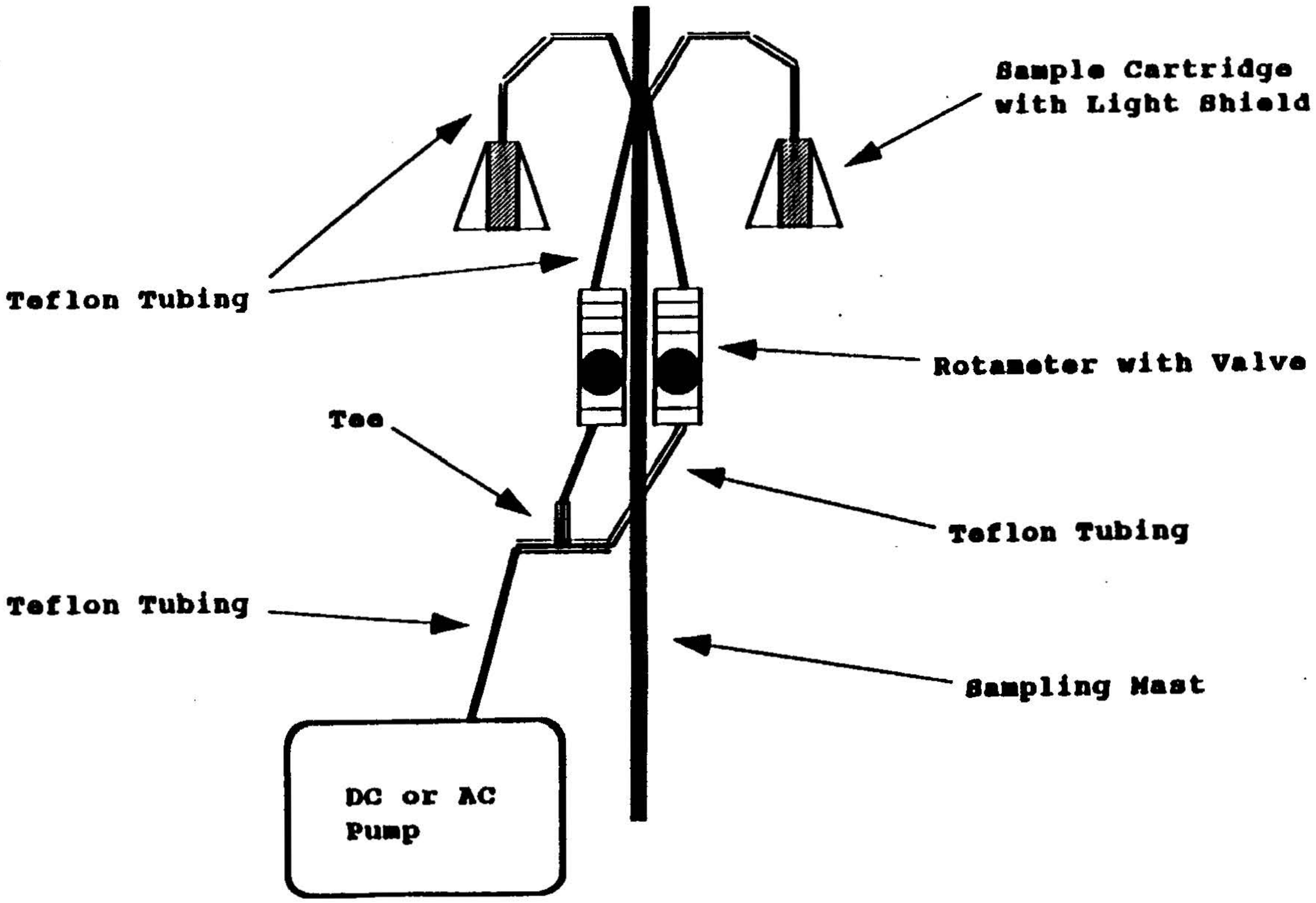


Figure 2 SAMPLING APPARATUS

LABORATORY ANALYSIS

All samples were warmed to room temperature before extraction. The resin was extracted with 3.0 *mL* of acetonitrile by sonicating for 30 minutes. The extract was allowed to settle, filtered through a plug of glass wool, and transferred to a 4 *mL* screw cap vial. All extracts were stored in the freezer.

A portion of each sample extract was oxidized with potassium permanganate to convert any oxydemeton-methyl to dioxydemeton-methyl for analysis. A 1.0 *mL* aliquot of each sample was added to a 250 *mL* separatory funnel containing 5 *mL* of 20% magnesium sulfate. Five milliliters of 0.1 *M* potassium permanganate were added to the funnel and the contents swirled to mix. The samples were allowed to oxidize for 45 minutes with occasional mixing. The oxidized samples were then extracted with three 10 *mL* aliquots of chloroform. Each successive portion was drained through anhydrous sodium sulfate into a 125 *mL* boiling flask. The combined chloroform extracts were evaporated to less than one milliliter on a rotor evaporator. The final portion of solvent was removed under a stream of dry air and the residue was redissolved in 1.0 *mL* of toluene. The toluene was transferred to a small screw cap vial with a Teflon-lined septum and stored in the freezer until analyzed.

The samples were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with an OI model 4420 electrolytic conductivity detector operating in the sulfur mode and a Hewlett-Packard model 3396A integrator. A J&W Scientific DB-5 megabore column (30*m* x 0.53*mm* ID) provided the separation. Table 1 contains the instrument conditions.

Table 1. Instrument Conditions

Temperatures		
Injector °C	Detector °C	Reactor °C
200	250	850

Column Program				
Initial °C	Hold *min*	Ramp °C/min	Final °C	Hold *min*
210	3	10	240	6.5

Gas Flows (*mL/min*)		
Carrier He	Make Up He	Reactor Air
7	30	63

A four point calibration curve was prepared by injecting 5 *µL* of each of the working standards (5-50 *µg/mL* range) into the gas chromatograph. A second-order equation for the standard curve was generated from the resulting peak area data using Cricket Graph™. Five microliters of each oxidized sample was injected into the gas chromatograph for comparison to the standards to determine total dioxydemeton-methyl (oxydemeton-methyl and dioxydemeton-methyl). The unoxidized portion of any sample having a peak matching the dioxydemeton-methyl standard was analyzed to determine dioxydemeton-methyl alone. The oxydemeton-methyl was determined by difference.

The analytical results for oxydemeton-methyl and dioxydemeton-methyl are found in Appendix C at the end of this report. An example using the chromatograms and equations for one set of standard curves can be found in Appendix D.

QUALITY CONTROL/QUALITY ASSURANCE

Sampling and analysis were conducted according to the project quality assurance plan. Collocated replicate samples were collected at each sampling site for each sampling period. Replicate samples from one site each week (20% of the samples) were analyzed as part of the quality control requirements. Control spikes were analyzed with each extraction set to monitor extraction efficiencies. Additionally, an oxidation control was prepared and analyzed with each set of oxidized samples. When detectable levels of the study compound were identified in any field sample, the replicate sample was also extracted and analyzed.

The limit of detection (LOD) was determined to be three times the standard deviation of low concentration control samples. The limit of quantitation (LOQ) is three time the LOD. The limit of detection (LOD) for oxydemeton-methyl and its oxidation product, dioxydemeton-methyl, in air are 2.0 and 1.5 *µg/m³*, respectively. The LOQ is 6.0 and 4.5 *µg/m³* for oxydemeton-methyl and dioxydemeton-methyl, respectively. LOD's and LOQ's were determined based upon the standard deviation of replicate injections of the lowest working standard, a sample collection period of 24 hours and a flowrate of 4 *lpm*.

The results for application monitoring are reported in total micrograms (µg) for each sample. The LOD is 11.2 µg and 8.4 µg for oxydemeton-methyl and dioxydemeton-methyl, respectively. The LOQ is 33.6 µg and 25.2 µg for oxydemeton-methyl and dioxydemeton-methyl, respectively.

A set of control samples was prepared and submitted to CSUF by Gabriel Ruiz (ARB) during the monitoring period. These were analyzed and the data returned to ARB.

During the method validation, a number of parameters were evaluated. The parameters studied include extraction efficiency, sampling recovery, and storage stability. The data for these parameters are presented in Appendix E.

RESULTS AND DISCUSSION

Retention efficiencies for oxydemeton-methyl and dioxydemeton-methyl were generally in the range of 70-103% and 81-109%, respectively. Stability of the study compounds was studied under three separate conditions: freezer storage for up to thirty days, ice chest storage for up to ten days, and ambient room temperature for up to seven days. The resulting data demonstrated no pattern of degradation under any of the three storage conditions. Recoveries from extraction and oxidation controls were all within the control limits of plus or minus three standard deviations of the main value. Other quality control data were also satisfactory.

All analyses from both ambient and application monitoring yielded nondetectable (ND) results. These data cannot be explained as being caused by quality control or quality assurance problems. These data are particularly unusual considering that the study compounds, oxydemeton-methyl and dioxydemeton-methyl, were not detected during either of two application monitoring trials where the samplers were in close proximity to actual applications of oxydemeton-methyl.

One explanation for all monitoring analyses yielding nondetectable results might be that the oxydemeton-methyl's volatilization rate is sufficiently low that an amount of the compound sufficient for detection was not captured. Another explanation might be that the method of validating the sampling process requires application of the study compound directly onto sampling tube resin. This procedure does not validate the efficiency of the resin for trapping the study compound in the vapor phase.

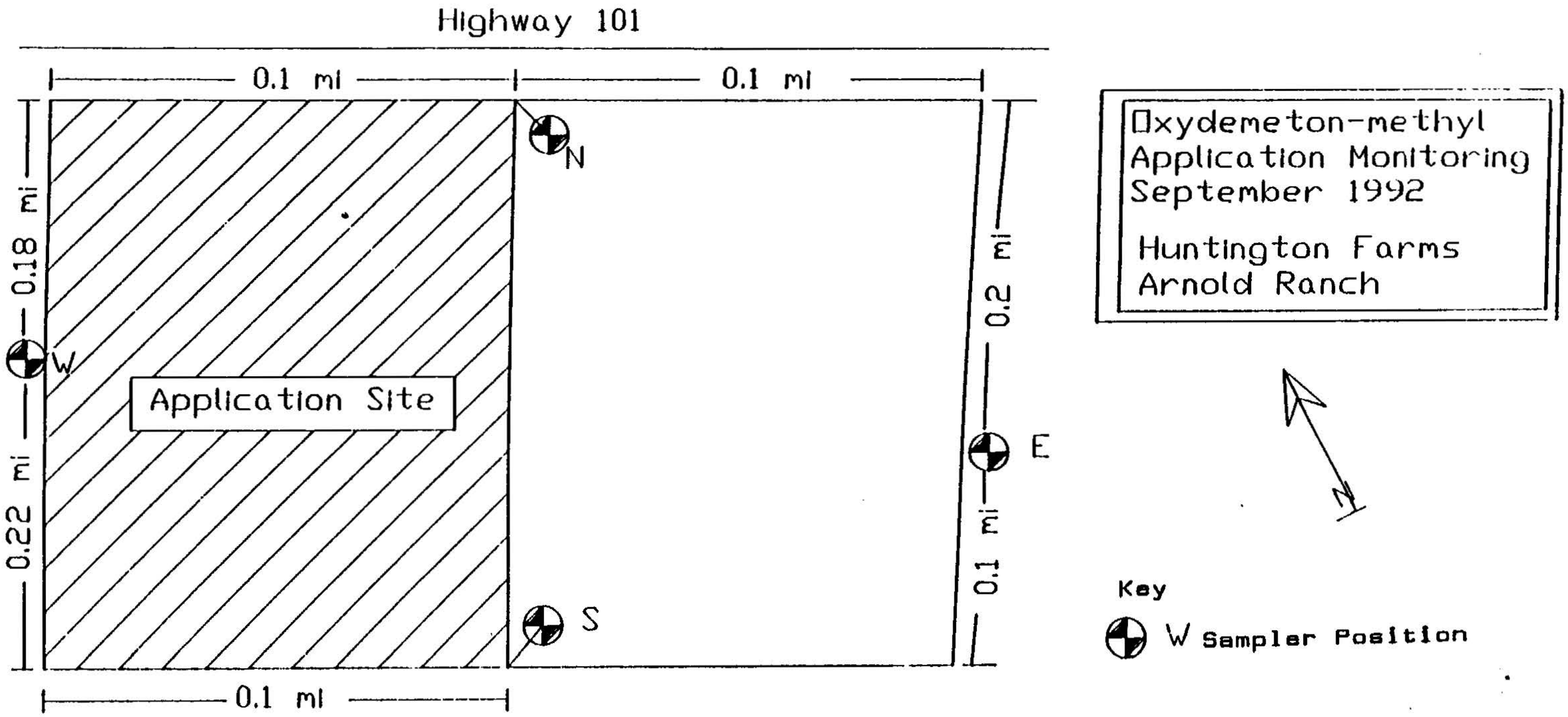
CONCLUSIONS

All data presented in this report for oxydemeton-methyl and dioxydemeton-methyl have been determined and accepted subject to a rigorous quality assurance program. All data for both the ambient and application monitoring events are below the LOD's for both oxydemeton-methyl and dioxydemeton-methyl.

Oxydemeton-methyl and dioxydemeton-methyl do not appear to persist sufficiently long to be routinely detected at the sampling sites chosen for this study and under the environmental conditions prevailing during the period that sampling was conducted, or the resin was unable to capture these compounds in the vapor phase.

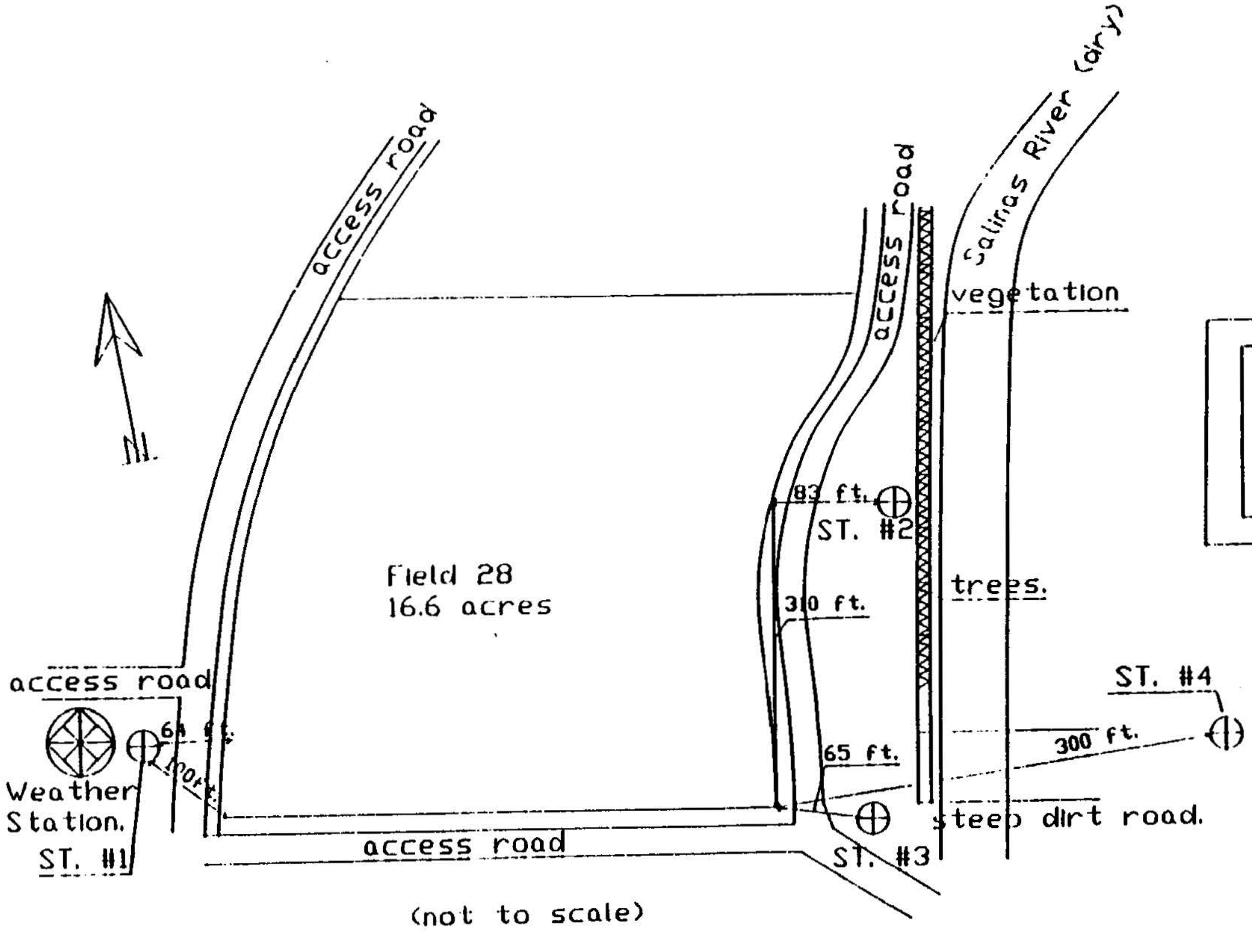
APPENDIX A

SITE MAPS



(not to scale)

NOTE: Actual distances from the application site for samplers N, S, and W, along with the field acreage were not documented. However, these were selected at the time of the study to fulfill the requirements of the quality assurance plan.



Oxydemeton-methyl
Application Monitoring
October 1992
Corey Ranch

Key

⦶	**Sampler Position**

APPENDIX B

SAMPLING DATA

OXYDEMETON-METHYL AMBIENT MONTORING -- MONTEREY COUNTY

SAMPLE COLLECTION DATA

Field	Start		End		Period	Flow	Vol
ID	Date	Time	Date	Time	h	Lpm	m^3
1 LJ	31-Aug-92	9:45	01-Sep-92	8:50	23.1	3.9	5.402
1 HD	31-Aug-92	10:30	01-Sep-92	9:10	22.7	3.9	5.304
1 CH	31-Aug-92	11:20	01-Sep-92	9:50	22.5	3.9	5.265
1 SL	31-Aug-92	12:00	01-Sep-92	10:05	22.1	3.9	5.168
1 GR	31-Aug-92	14:20	01-Sep-92	10:35	20.3	3.9	4.739
2 LJ	01-Sep-92	8:50	02-Sep-92	10:15	25.4	3.9	5.948
2 HD	01-Sep-92	9:10	02-Sep-92	10:40	25.5	3.9	5.967
2 CH	01-Sep-92	9:50	02-Sep-92	11:10	25.3	3.9	5.928
2 SL	01-Sep-92	10:05	02-Sep-92	11:30	25.4	3.9	5.948
2 GR	01-Sep-92	10:35	02-Sep-92	12:10	25.6	3.9	5.987
3 LJ	02-Sep-92	10:15	03-Sep-92	9:55	23.7	3.9	5.538
3 HD	02-Sep-92	10:40	03-Sep-92	10:10	23.5	3.9	5.499
3 CH	02-Sep-92	11:10	03-Sep-92	10:35	23.4	3.9	5.480
3 SL	02-Sep-92	11:30	03-Sep-92	10:55	23.4	3.9	5.480
3 GR	02-Sep-92	12:10	03-Sep-92	11:25	23.3	3.9	5.441
4 LJ	03-Sep-92	9:55	04-Sep-92	10:25	24.5	3.9	5.733
4 HD	03-Sep-92	10:10	04-Sep-92	10:45	24.6	3.9	5.753
4 CH	03-Sep-92	10:35	04-Sep-92	11:10	24.6	3.9	5.753
4 SL	03-Sep-92	10:55	04-Sep-92	11:30	24.6	3.9	5.753
4 GR	03-Sep-92	11:25	04-Sep-92	12:00	24.6	3.9	5.753
5 LJ	08-Sep-92	10:20	09-Sep-92	10:05	23.8	3.9	5.558
5 HD	08-Sep-92	10:40	09-Sep-92	10:25	23.8	3.9	5.558
5 CH	08-Sep-92	11:10	09-Sep-92	10:55	23.8	3.9	5.558
5 SL	08-Sep-92	11:30	09-Sep-92	11:20	23.8	3.9	5.577
5 GR	08-Sep-92	12:00	09-Sep-92	11:50	23.8	3.9	5.577

KEY: LJ= La Joya Elementrary School, HD= Monterey Bay Unified Air District, at the Monterey County Public Health Department, CH= Salinas Rural Fire Department Station No. 2, Chualar, SL= California Division of Foresty (CDF), GR= City of Greenfield Water Tank

OXYDEMETON-METHYL AMBIENT MONTORING -- MONTEREY COUNTY							
SAMPLE COLLECTION DATA							
Field	Start		End		Period	Flow	Vol
ID	Date	Time	Date	Time	h	Lpm	m^3
6 LJ	09-Sep-92	10:05	10-Sep-92	10:30	24.4	3.9	5.714
6 HD	09-Sep-92	10:25	10-Sep-92	10:55	24.5	3.9	5.733
6 CH	09-Sep-92	10:55	10-Sep-92	11:25	24.5	3.9	5.733
6 SL	09-Sep-92	11:20	10-Sep-92	11:45	24.4	3.9	5.714
6 GR	09-Sep-92	11:50	10-Sep-92	12:10	24.3	3.9	5.694
7 LJ	10-Sep-92	10:30	11-Sep-92	10:15	23.8	3.9	5.558
7 HD	10-Sep-92	10:55	11-Sep-92	10:35	23.7	3.9	5.538
7 CH	10-Sep-92	11:25	11-Sep-92	11:05	23.7	3.9	5.538
7 SL	10-Sep-92	11:45	11-Sep-92	11:20	23.6	3.9	5.519
7 GR	10-Sep-92	12:10	11-Sep-92	11:45	23.6	3.9	5.519
8 LJ	14-Sep-92	10:55	15-Sep-92	10:40	23.8	3.9	5.558
8 HD	14-Sep-92	10:35	15-Sep-92	11:00	24.4	3.9	5.714
8 CH	14-Sep-92	11:30	15-Sep-92	11:45	24.3	3.9	5.675
8 SL	14-Sep-92	11:50	15-Sep-92	12:05	24.3	3.9	5.675
8 GR	14-Sep-92	12:15	15-Sep-92	12:45	24.5	3.9	5.733
9 LJ	15-Sep-92	10:40	16-Sep-92	10:25	23.8	3.9	5.558
9 HD	15-Sep-92	11:00	16-Sep-92	10:45	23.8	3.9	5.558
9 CH	15-Sep-92	11:45	16-Sep-92	11:10	23.4	3.9	5.480
9 SL	15-Sep-92	12:05	16-Sep-92	11:40	23.6	3.9	5.519
9 GR	15-Sep-92	12:45	16-Sep-92	12:00	23.3	3.9	5.441
10 LJ	16-Sep-92	10:25	17-Sep-92	10:40	24.3	3.9	5.675
10 HD	16-Sep-92	10:45	17-Sep-92	10:55	24.2	3.9	5.655
10 CH	16-Sep-92	11:10	17-Sep-92	11:25	24.3	3.9	5.675
10 SL	16-Sep-92	11:40	17-Sep-92	11:50	24.2	3.9	5.655
10 GR	16-Sep-92	12:00	17-Sep-92	12:15	24.3	3.9	5.675

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OXYDEMETON-METHYL AMBIENT MONTORING -- MONTEREY COUNTY

SAMPLE COLLECTION DATA

Field	Start		End		Period	Flow	Vol
ID	Date	Time	Date	Time	h	Lpm	m^3
11 LJ	17-Sep-92	10:40	18-Sep-92	9:35	22.9	3.9	5.363
11 HD	17-Sep-92	10:55	18-Sep-92	9:55	23.0	3.9	5.382
11 CH	17-Sep-92	11:25	18-Sep-92	10:15	22.8	3.9	5.343
11 SL	17-Sep-92	11:50	18-Sep-92	10:30	22.7	3.9	5.304
11 GR	17-Sep-92	12:15	18-Sep-92	10:55	22.7	3.9	5.304
12 LJ	21-Sep-92	8:30	22-Sep-92	9:05	24.6	3.9	5.753
12 HD	21-Sep-92	8:45	22-Sep-92	10:00	25.3	3.9	5.909
12 CH	21-Sep-92	9:05	22-Sep-92	10:30	25.4	3.9	5.948
12 SL	21-Sep-92	9:25	22-Sep-92	10:50	25.4	3.9	5.948
12 GR	21-Sep-92	9:50	22-Sep-92	11:30	25.7	3.9	6.006
13 LJ	22-Sep-92	9:05	23-Sep-92	10:45	25.7	3.9	6.006
13 HD	22-Sep-92	10:00	23-Sep-92	10:55	24.9	3.9	5.831
13 CH	22-Sep-92	10:30	23-Sep-92	11:20	24.8	3.9	5.811
13 SL	22-Sep-92	10:50	23-Sep-92	11:40	24.8	3.9	5.811
13 GR	22-Sep-92	11:30	23-Sep-92	12:00	24.5	3.9	5.733
14 LJ	23-Sep-92	10:45	24-Sep-92	11:30	24.8	3.9	5.792
14 HD	23-Sep-92	10:55	24-Sep-92	11:45	24.8	3.9	5.811
14 CH	23-Sep-92	11:20	24-Sep-92	12:15	24.9	3.9	5.831
14 SL	23-Sep-92	11:40	24-Sep-92	12:30	24.8	3.9	5.811
14 GR	23-Sep-92	12:00	24-Sep-92	13:00	25.0	3.9	5.850
15 LJ	24-Sep-92	11:30	25-Sep-92	10:35	23.1	3.9	5.402
15 HD	24-Sep-92	11:45	25-Sep-92	10:50	23.1	3.9	5.402
15 CH	24-Sep-92	12:15	25-Sep-92	11:15	23.0	3.9	5.382
15 SL	24-Sep-92	12:30	25-Sep-92	11:35	23.1	3.9	5.402
15 GR	24-Sep-92	13:00	25-Sep-92	12:00	23.0	3.9	5.382

KEY: LJ= La Joya Elementrary School, HD= Monterey Bay Unified Air District, at the Monterey County Public Health Department, CH= Salinas Rural Fire Department Station No. 2, Chualar, SL= California Division of Foresty (CDF), GR= City of Greenfield Water Tank

OXYDEMETON-METHYL AMBIENT MONTORING -- MONTEREY COUNTY

SAMPLE COLLECTION DATA

Field	Start		End		Period	Flow	Vol
ID	Date	Time	Date	Time	h	Lpm	m^3
16 LJ	25-Sep-92	10:35	26-Sep-92	11:30	24.9	3.9	5.831
16 HD	25-Sep-92	10:50	26-Sep-92	11:50	25.0	3.9	5.850
16 CH	25-Sep-92	11:15	26-Sep-92	12:20	25.1	3.9	5.870
16 SL	25-Sep-92	11:35	26-Sep-92	12:35	25.0	3.9	5.850
16 GR	25-Sep-92	12:00	26-Sep-92	13:00	25.0	3.9	5.850
17 LJ	28-Sep-92	08:25	29-Sep-92	08:25	24.0	3.9	5.616
17 HD	28-Sep-92	08:40	29-Sep-92	08:40	24.0	3.9	5.616
17 CH	28-Sep-92	09:00	29-Sep-92	09:00	24.0	3.9	5.616
17 SL	28-Sep-92	09:20	29-Sep-92	09:20	24.0	3.9	5.616
17 GR	28-Sep-92	09:50	29-Sep-92	09:50	24.0	3.9	5.616
18 LJ	29-Sep-92	08:25	30-Sep-92	08:00	23.6	3.9	5.519
18 HD	29-Sep-92	08:40	30-Sep-92	08:20	23.7	3.9	5.538
18 CH	29-Sep-92	09:00	30-Sep-92	08:45	23.8	3.9	5.558
18 SL	29-Sep-92	09:20	30-Sep-92	09:05	23.8	3.9	5.558
18 GR	29-Sep-92	09:50	30-Sep-92	09:30	23.7	3.9	5.538
19 LJ	30-Sep-92	08:00	01-Oct-92	09:40	25.7	3.9	6.006
19 HD	30-Sep-92	08:20	01-Oct-92	09:55	25.6	3.9	5.987
19 CH	30-Sep-92	08:45	01-Oct-92	10:15	25.5	3.9	5.967
19 SL	30-Sep-92	09:05	01-Oct-92	10:45	25.7	3.9	6.006
19 GR	30-Sep-92	09:30	01-Oct-92	11:10	25.7	3.9	6.006
20 LJ	01-Oct-92	09:40	02-Oct-92	08:40	23.0	3.9	5.382
20 HD	01-Oct-92	09:55	02-Oct-92	09:45	23.8	3.9	5.577
20 CH	01-Oct-92	10:15	02-Oct-92	10:35	24.3	3.9	5.694
20 SL	01-Oct-92	10:45	02-Oct-92	11:30	24.8	3.9	5.792
20 GR	01-Oct-92	11:10	02-Oct-92	12:15	25.1	3.9	5.870

KEY: LJ= La Joya Elementrary School, HD= Monterey Bay Unified Air District, at the Monterey County Public Health Department, CH= Salinas Rural Fire Department Station No. 2, Chualar, SL= California Division of Foresty (CDF), GR= City of Greenfield Water Tank

OXYDEMETON-METHYL APPLICATION MONTORING -- MONTEREY COUNTY
HUNTINGTON FARMS (September 14-17, 1992)
SAMPLE COLLECTION DATA

Field	Start		End		Sampling		
ID	Date	Time	Date	Time	Period	Flow	Volume
					(h)	(lpm)	(m^3)
0 S	14-Sep-92	19:30	14-Sep-92	21:15	1.8	1.9	0.200
0 N	14-Sep-92	20:00	14-Sep-92	21:00	1.0	1.9	0.114
0 E	14-Sep-92	19:20	14-Sep-92	21:10	1.8	1.9	0.209
0 W	14-Sep-92	19:40	14-Sep-92	21:25	1.8	1.9	0.200
1 S	14-Sep-92	21:25	15-Sep-92	00:00	2.6	1.9	0.295
1 N	14-Sep-92	21:10	14-Sep-92	23:45	2.6	1.9	0.295
1 E	14-Sep-92	21:15	14-Sep-92	23:55	2.7	1.9	0.304
1 W	14-Sep-92	21:00	15-Sep-92	00:05	3.1	1.9	0.352
2 S	15-Sep-92	00:00	15-Sep-92	04:10	4.2	1.9	0.475
2 N	14-Sep-92	23:45	15-Sep-92	03:55	4.2	1.9	0.475
2 E	14-Sep-92	23:55	15-Sep-92	04:05	4.2	1.9	0.475
2 W	15-Sep-92	00:05	15-Sep-92	04:15	4.2	1.9	0.475
3 S	15-Sep-92	04:10	15-Sep-92	08:10	4.0	1.9	0.456
3 N	15-Sep-92	03:55	15-Sep-92	08:00	4.1	1.9	0.466
3 E	15-Sep-92	04:05	15-Sep-92	08:05	4.0	1.9	0.456
3 W	15-Sep-92	04:15	15-Sep-92	08:15	4.0	1.9	0.456
4 S	15-Sep-92	08:10	15-Sep-92	12:30	4.3	1.9	0.494
4 N	15-Sep-92	08:00	15-Sep-92	12:15	4.3	1.9	0.485
4 E	15-Sep-92	08:05	15-Sep-92	12:25	4.3	1.9	0.494
4 W	15-Sep-92	08:15	15-Sep-92	12:35	4.3	1.9	0.494
4 B*	15-Sep-92	---	15-Sep-92	---	---	---	---
5 S	15-Sep-92	12:30	15-Sep-92	19:30	7.0	1.9	0.798
5 N	15-Sep-92	12:15	15-Sep-92	19:15	7.0	1.9	0.798
5 E	15-Sep-92	12:25	15-Sep-92	19:25	7.0	1.9	0.798

* Field Blank

OXYDEMETON-METHYL APPLICATION MONTORING – MONTEREY COUNTY
HUNTINGTON FARMS (September 14-17, 1992)
SAMPLE COLLECTION DATA

Field	Start		End		Sampling		
ID	Date	Time	Date	Time	Period	Flow	Volume
					(h)	(lpm)	(m^3)
5 W	15-Sep-92	12:35	15-Sep-92	19:35	7.0	1.9	0.798
6 S	15-Sep-92	19:30	15-Sep-92	18:45	23.3	1.9	2.651
6 N	15-Sep-92	19:15	16-Sep-92	18:35	23.3	1.9	2.660
6 E	15-Sep-92	19:25	16-Sep-92	18:40	23.3	1.9	2.651
6 W	15-Sep-92	19:35	16-Sep-92	18:55	23.3	1.9	2.660
7 S	16-Sep-92	18:45	16-Sep-92	15:25	20.7	1.9	2.356
7 N	16-Sep-92	18:35	17-Sep-92	15:15	20.7	1.9	2.356
7 E	17-Sep-92	18:40	17-Sep-92	15:20	20.7	1.9	2.356
7 W	17-Sep-92	18:55	17-Sep-92	15:30	20.6	1.9	2.347

OXYDEMETON-METHYL METEOROLOGICAL DATA Application Monitoring September 14-17, 1992		
Sampling Period	Wind Direction	Wind Speed (mph)
0	(Meteorological data lost)	
1	W (NW)	4
2	E (NE/SE)	2
3	E(NE)	5
4	W (S/E)	2
5	W	16
6	W	7
7	W (S/E)	6

OXYDEMETON-METHYL APPLICATION MONTORING -- MONTEREY COUNTY
COREY RANCH (October 7-9, 1992)
SAMPLE COLLECTION DATA

Field	Start		End		Sampling		
ID	Date	Time	Date	Time	Period	Flow	Volume
					(h)	(lpm)	(m^3)
0 W	07-Oct-92	18:05	07-Oct-92	19:50	1.8	1.9	0.200
0 N	07-Oct-92	18:20	07-Oct-92	19:55	1.6	1.9	0.181
0 S	07-Oct-92	18:30	07-Oct-92	20:00	1.5	1.9	0.171
0 E	07-Oct-92	18:35	07-Oct-92	20:05	1.5	1.9	0.171
1 W	07-Oct-92	19:50	07-Oct-92	23:05	3.3	1.9	0.371
1 N	07-Oct-92	19:55	07-Oct-92	23:15	3.3	1.9	0.380
1 S	07-Oct-92	20:00	07-Oct-92	23:20	3.3	1.9	0.380
1 E	07-Oct-92	20:05	07-Oct-92	23:25	3.3	1.9	0.380
2 W	07-Oct-92	23:05	08-Oct-92	2:10	3.1	1.9	0.352
2 N	07-Oct-92	23:15	08-Oct-92	2:15	3.0	1.9	0.342
2 S	07-Oct-92	23:20	08-Oct-92	2:20	3.0	1.9	0.342
2 E	07-Oct-92	23:25	08-Oct-92	2:25	3.0	1.9	0.342
3 W	08-Oct-92	2:10	08-Oct-92	8:10	6.0	1.9	0.684
3 N	08-Oct-92	2:15	08-Oct-92	8:25	6.2	1.9	0.703
3 S	08-Oct-92	2:20	08-Oct-92	8:35	6.3	1.9	0.713
3 E	08-Oct-92	2:25	08-Oct-92	8:40	6.3	1.9	0.713
4 W	08-Oct-92	8:10	08-Oct-92	14:00	5.8	1.9	0.665
4 N	08-Oct-92	8:25	08-Oct-92	14:05	5.7	1.9	0.646
4 S	08-Oct-92	8:35	08-Oct-92	14:10	5.6	1.9	0.637
4 E	08-Oct-92	8:40	08-Oct-92	14:15	5.6	1.9	0.637
5 W	08-Oct-92	14:00	08-Oct-92	20:30	6.5	1.9	0.741
5 N	08-Oct-92	14:05	08-Oct-92	20:35	6.5	1.9	0.741
5 S	08-Oct-92	14:10	08-Oct-92	20:37	6.5	1.9	0.735
5 E	08-Oct-92	14:15	08-Oct-92	20:40	6.4	1.9	0.732
6 W	08-Oct-92	20:30	09-Oct-92	20:20	23.8	1.9	2.717
6 N	08-Oct-92	20:35	09-Oct-92	20:30	23.9	1.9	2.727
6 S	08-Oct-92	20:45	09-Oct-92	20:40	23.9	1.9	2.727
6 E	08-Oct-92	20:40	09-Oct-92	20:50	24.2	1.9	2.755

APPENDIX C

ANALYTICAL RESULTS

OXYDEMETON-METHYL AMBIENT MONITORING -- MONTEREY COUNTY
SAMPLE RESULTS

	La Joya Elementary School				Monterey Bay Unified Air District Station			
	ODM (ug/m³)		DODM (ug/m³)		ODM (ug/m³)		DODM (ug/m³)	
Date	A	B	A	B	A	B	A	B
31-Aug-92	ND	ND	ND	ND	ND		ND	
01-Sep-92	ND	ND	ND	ND	ND		ND	
02-Sep-92	ND	ND	ND	ND	ND		ND	
03-Sep-92	ND	ND	ND	ND	ND		ND	
08-Sep-92	ND		ND		ND		ND	
09-Sep-92	ND		ND		ND		ND	
10-Sep-92	ND		ND		ND		ND	
14-Sep-92	ND		ND		ND		ND	
15-Sep-92	ND		ND		ND		ND	
16-Sep-92	ND		ND		ND		ND	
17-Sep-92	ND		ND		ND		ND	
21-Sep-92	ND		ND		ND		ND	
22-Sep-92	ND		ND		ND		ND	
23-Sep-92	ND		ND		ND		ND	
24-Sep-92	ND		ND		ND		ND	
25-Sep-92	ND		ND		ND		ND	
28-Sep-92	ND		ND		ND		ND	
29-Sep-92	ND		ND		ND		ND	
30-Sep-92	ND		ND		ND	ND	ND	ND
01-Oct-92	ND		ND		ND	ND	ND	ND

LOD:	Oxydemeton-methyl ---- 2.0 μg/m³
	Dioxydemeton-methyl -- 1.5 μg/m³
LOQ:	Oxydemeton-methyl ---- 6.0 μg/m³
	Dioxydemeton-methyl -- 4.5 μg/m³

KEY:
ODM = Oxydemeton-methyl
DODM = Dioxydemeton-methyl
A = Primary sampling tube
B = Replicate sampling tube

OXYDEMETON-METHYL AMBIENT MONITORING -- MONTEREY COUNTY
SAMPLE RESULTS

	SRFD Station, Chualar				CDF Station, Soledad			
	ODM (ug/m^3)		DODM (ug/m^3)		ODM (ug/m^3)		DODM (ug/m^3)	
Date	A	B	A	B	A	B	A	B
31-Aug-92	ND		ND		ND		ND	
01-Sep-92	ND		ND		ND		ND	
02-Sep-92	ND		ND		ND		ND	
03-Sep-92	ND		ND		ND		ND	
08-Sep-92	ND	ND	ND	ND	ND		ND	
09-Sep-92	ND	ND	ND	ND	ND		ND	
10-Sep-92	ND	ND	ND	ND	ND		ND	
14-Sep-92	ND		ND		ND	ND	ND	ND
15-Sep-92	ND		ND		ND	ND	ND	ND
16-Sep-92	ND		ND		ND	ND	ND	ND
17-Sep-92	ND		ND		ND	ND	ND	ND
21-Sep-92	ND		ND		ND		ND	
22-Sep-92	ND		ND		ND		ND	
23-Sep-92	ND		ND		ND		ND	
24-Sep-92	ND		ND		ND		ND	
25-Sep-92	ND		ND		ND		ND	
28-Sep-92	ND		ND		ND		ND	
29-Sep-92	ND		ND		ND		ND	
30-Sep-92	ND		ND		ND		ND	
01-Oct-92	ND		ND		ND		ND	

LOD: Oxydemeton-methyl ---- 2.0 $\mu g/m^3$
Dioxydemeton-methyl -- 1.5 $\mu g/m^3$

LOQ: Oxydemeton-methyl ---- 6.0 $\mu g/m^3$
Dioxydemeton-methyl -- 4.5 $\mu g/m^3$

KEY: ODM = Oxydemeton-methyl DODM = Dioxydemeton-methyl
A = Primary sampling tube B = Replicate sampling tube

OXYDEMETON-METHYL AMBIENT MONITORING -- MONTEREY COUNTY
SAMPLE RESULTS

	Greenfield Water Tank			
	ODM (ug/m^3)		DODM (ug/m^3)	
Date	A	B	A	B
31-Aug-92	ND		ND	
01-Sep-92	ND		ND	
02-Sep-92	ND		ND	
03-Sep-92	ND		ND	
08-Sep-92	ND		ND	
09-Sep-92	ND		ND	
10-Sep-92	ND		ND	
14-Sep-92	ND		ND	
15-Sep-92	ND		ND	
16-Sep-92	ND		ND	
17-Sep-92	ND		ND	
21-Sep-92	ND	ND	ND	ND
22-Sep-92	ND	ND	ND	ND
23-Sep-92	ND	ND	ND	ND
24-Sep-92	ND	ND	ND	ND
25-Sep-92	ND	ND	ND	ND
28-Sep-92	ND	ND	ND	ND
29-Sep-92	ND	ND	ND	ND
30-Sep-92	ND		ND	
01-Oct-92	ND	ND	ND	ND

LOD: Oxydemeton-methyl ---- 2.0 μg/m^3
Dioxydemeton-methyl -- 1.5 μg/m^3

LOQ: Oxydemeton-methyl ---- 6.0 μg/m^3
Dioxydemeton-methyl -- 4.5 μg/m^3

KEY: ODM = Oxydemeton-methyl   DODM = Dioxydemeton-methyl
A = Primary sampling tube   B. = Replicate sampling tube

OXYDEMETON-METHYL APPLICATION MONTORING – MONTEREY COUNTY
HUNTINGTON FARMS (September 14-17, 1992)
SAMPLE RESULTS DATA

Start		Field	ODM (µg)		DODM (µg)	
Date	Time	ID	A	B	A	B
14-Sep-92	19:30	0 S	ND		ND	
14-Sep-92	20:00	0 N	ND		ND	
14-Sep-92	19:20	0 E	ND	ND	ND	ND
14-Sep-92	19:40	0 W	ND		ND	
14-Sep-92	21:25	1 S	ND	ND	ND	ND
14-Sep-92	21:10	1 N	ND		ND	
14-Sep-92	21:15	1 E	ND		ND	
14-Sep-92	21:00	1 W	ND		ND	
15-Sep-92	00:00	2 S	ND	ND	ND	ND
14-Sep-92	23:45	2 N	ND		ND	
14-Sep-92	23:55	2 E	ND		ND	
15-Sep-92	00:05	2 W	ND		ND	
15-Sep-92	04:10	3 S	ND		ND	
15-Sep-92	03:55	3 N	ND		ND	
15-Sep-92	04:05	3 E	ND		ND	
15-Sep-92	04:15	3 W	ND	ND	ND	ND
15-Sep-92	08:10	4 S	ND		ND	
15-Sep-92	08:00	4 N	ND	ND	ND	ND
15-Sep-92	08:05	4 E	ND		ND	
15-Sep-92	08:15	4 W	ND		ND	
15-Sep-92	—	4 B*	ND		ND	
15-Sep-92	12:30	5 S	ND		ND	
15-Sep-92	12:15	5 N	ND		ND	
15-Sep-92	12:25	5 E	ND	ND	ND	ND
15-Sep-92	12:35	5 W	ND		ND	

* Field Blank

OXYDEMETON-METHYL APPLICATION MONTORING -- MONTEREY COUNTY HUNTINGTON FARMS (September 14-17, 1992) SAMPLE RESULTS DATA						
Start		Field	ODM (µg)		DODM (µg)	
Date	Time	ID	A	B	A	B
15-Sep-92	19:30	6 S	ND	ND	ND	ND
15-Sep-92	19:15	6 N	ND		ND	
15-Sep-92	19:25	6 E	ND		ND	
15-Sep-92	19:35	6 W	ND		ND	
16-Sep-92	18:45	7 S	ND		ND	
16-Sep-92	18:35	7 N	ND		ND	
17-Sep-92	18:40	7 E	ND		ND	
17-Sep-92	18:55	7 W	ND	ND	ND	ND

NOTE: LOQ = 33.6 µg for oxydemeton-methyl;
LOQ = 25.2 µg for dioxydemeton0methyl

OXYDEMETON-METHYL APPLICATION MONTORING -- MONTEREY COUNTY
COREY RANCH (October 7-9, 1992)
SAMPLE RESULTS DATA

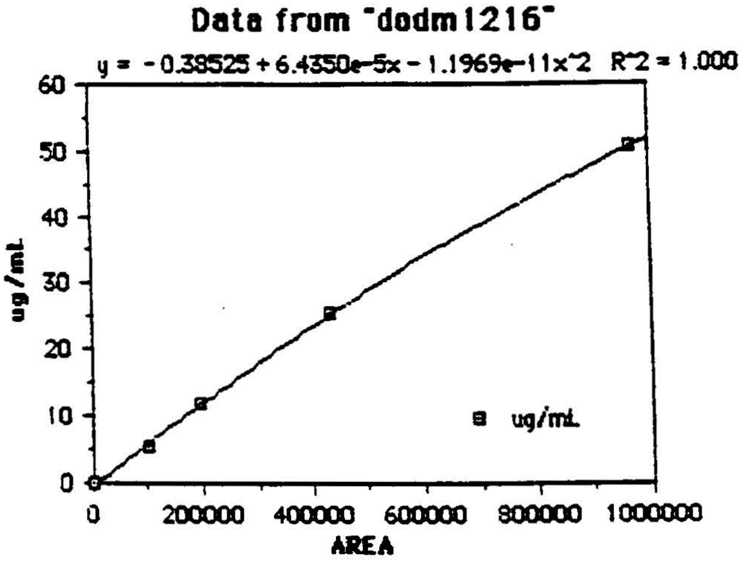
Start		Field	ODM (μg)		DODM (μg)	
Date	Time	ID	A	B	A	B
07-Oct-92	18:05	0 W	ND		ND	
07-Oct-92	18:20	0 N	ND		ND	
07-Oct-92	18:30	0 S	ND		ND	
07-Oct-92	18:35	0 E	ND	ND	ND	ND
07-Oct-92	19:50	1 W	ND		ND	
07-Oct-92	19:55	1 N	ND		ND	
07-Oct-92	20:00	1 S	ND		ND	
07-Oct-92	20:05	1 E	ND	ND	ND	ND
07-Oct-92	23:05	2 W	ND		ND	
07-Oct-92	23:15	2 N	ND		ND	
07-Oct-92	23:20	2 S	ND		ND	
07-Oct-92	23:25	2 E	ND	ND	ND	ND
08-Oct-92	2:10	3 W	ND		ND	
08-Oct-92	2:15	3 N	ND		ND	
08-Oct-92	2:20	3 S	ND		ND	
08-Oct-92	2:25	3 E	ND	ND	ND	ND
08-Oct-92	8:10	4 W	ND		ND	
08-Oct-92	8:25	4 N	ND		ND	
08-Oct-92	8:35	4 S	ND		ND	
08-Oct-92	8:40	4 E	ND	ND	ND	ND
08-Oct-92	14:00	5 W	ND		ND	
08-Oct-92	14:05	5 N	ND		ND	
08-Oct-92	14:10	5 S	ND		ND	
08-Oct-92	14:15	5 E	ND	ND	ND	ND
08-Oct-92	20:30	6 W	ND		ND	
08-Oct-92	20:35	6 N	ND		ND	
08-Oct-92	20:45	6 S	ND		ND	
08-Oct-92	20:40	6 E	ND	ND	ND	ND

NOTE: LOQ = 33.6 μg for oxydemeton-methyl;
LOQ = 25.2 μg for dioxydemeton-methyl

APPENDIX D

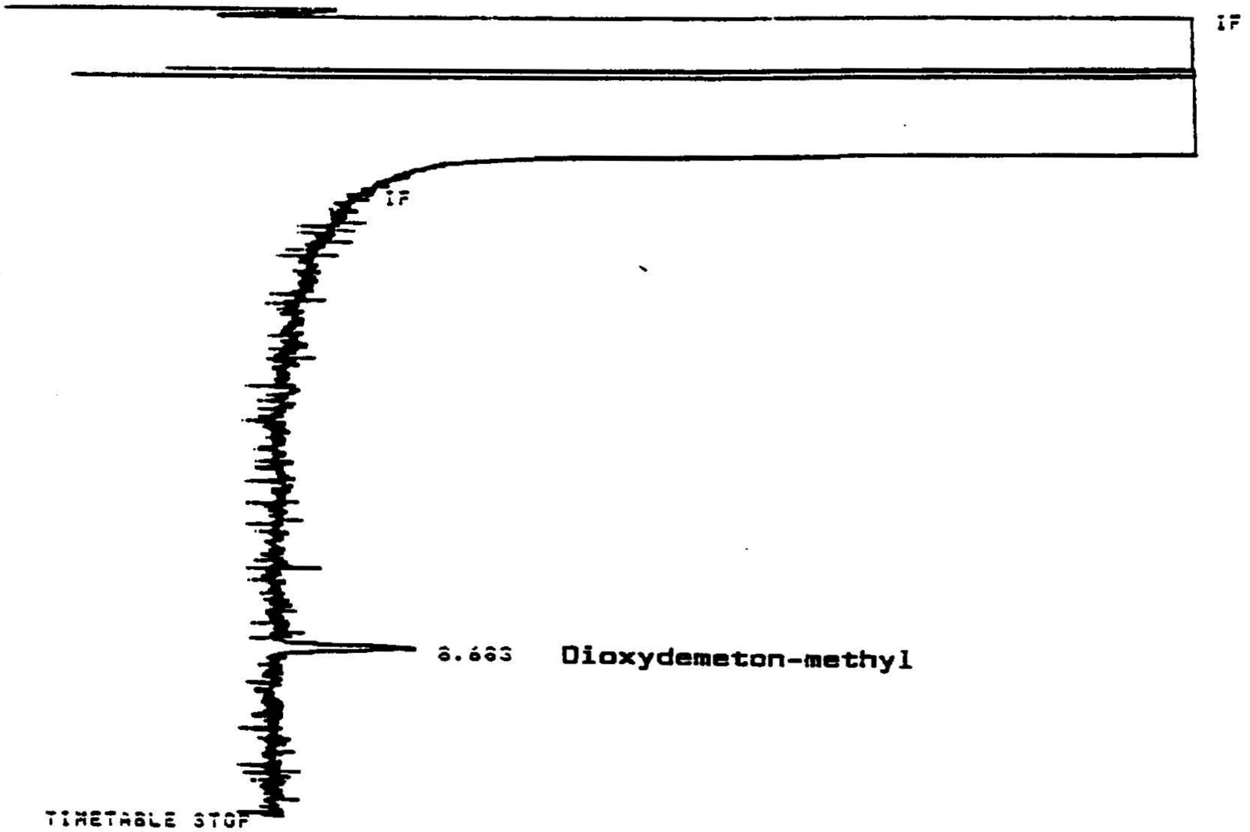
STANDARD CURVE EXAMPLE

Dioxydemeton-methyl Standard Curve



	ug/mL	AREA	
1	0.0	0	
2	5.5	103872	8.683
3	11.9	195579	8.674
4	25.3	431313	8.668
5	50.7	968951	8.687

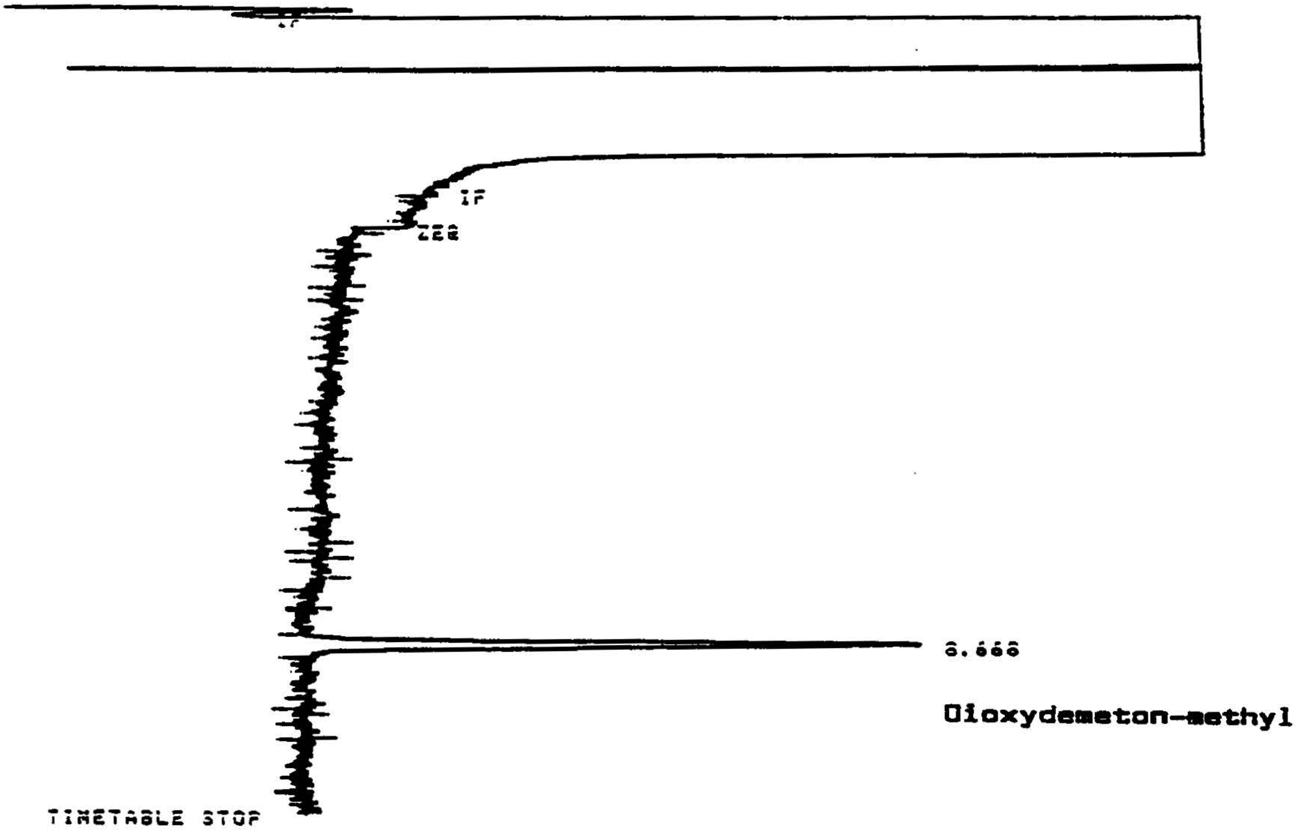
```
*WS 234 5.5 UG/ML  BREAK

*  RUN #  661       DEC 16, 1992  13:03:07
START
```



```
TIMETABLE STOP


RUN#   661             DEC 16, 1992  13:03:07

AREA%
      RT        AREA TYPE  WIDTH       AREA%
   6.663    103672    BP    .099  100.00000

TOTAL AREA= 103672
MUL FACTOR=1.0000E+00
```

Dioxydemeton Standard 5.5 ug/mL

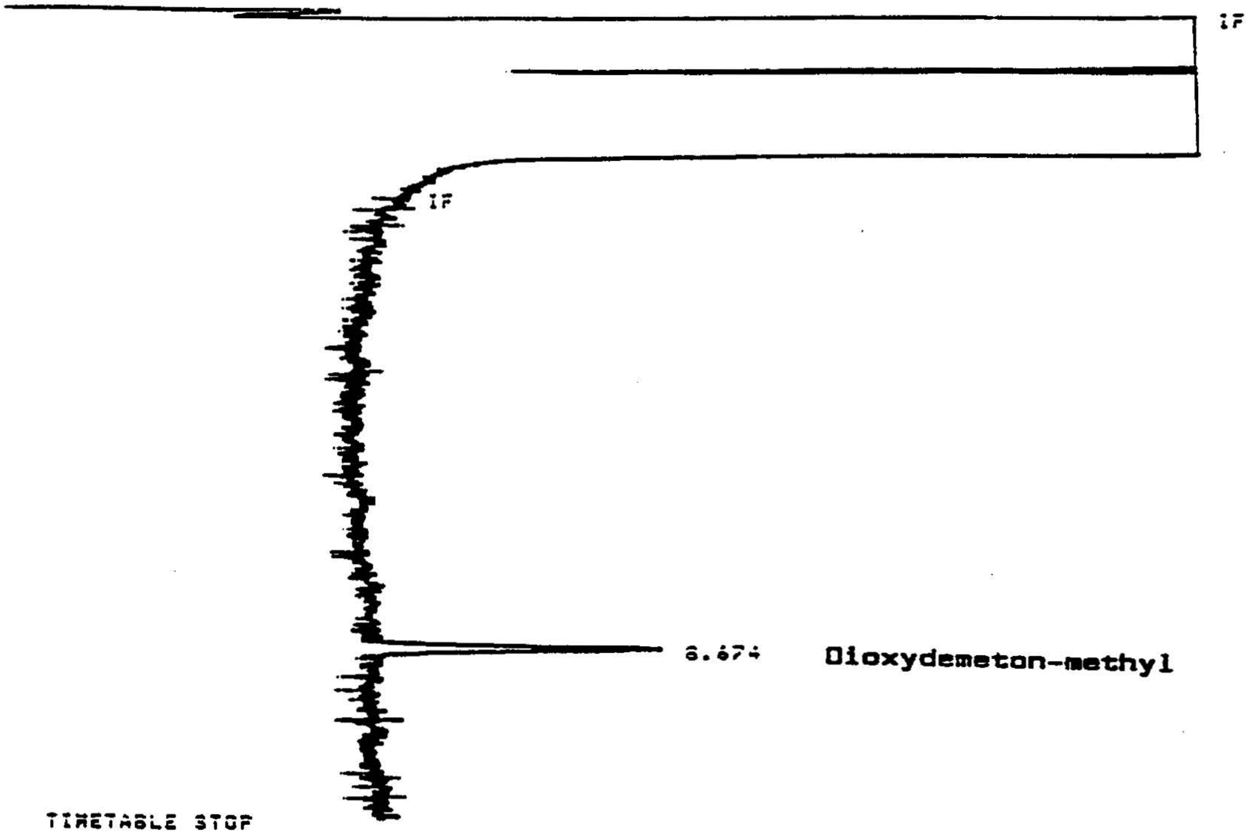
```
+WS 256 25.3 UG/ML  BREAK

+  RUN #  663       DEC 16, 1992  13:30:40
START
```



```
TIMETABLE STOP


RUN#   663            DEC 16, 1992  13:30:40

AREA%
      RT        AREA TYPE  WIDTH       AREA%
   0.666    431313   BP    .096  100.00000

TOTAL AREA= 431313
MUL FACTOR=1.0000E+00
```

Dioxydemeton Standard 25.3 ug/mL

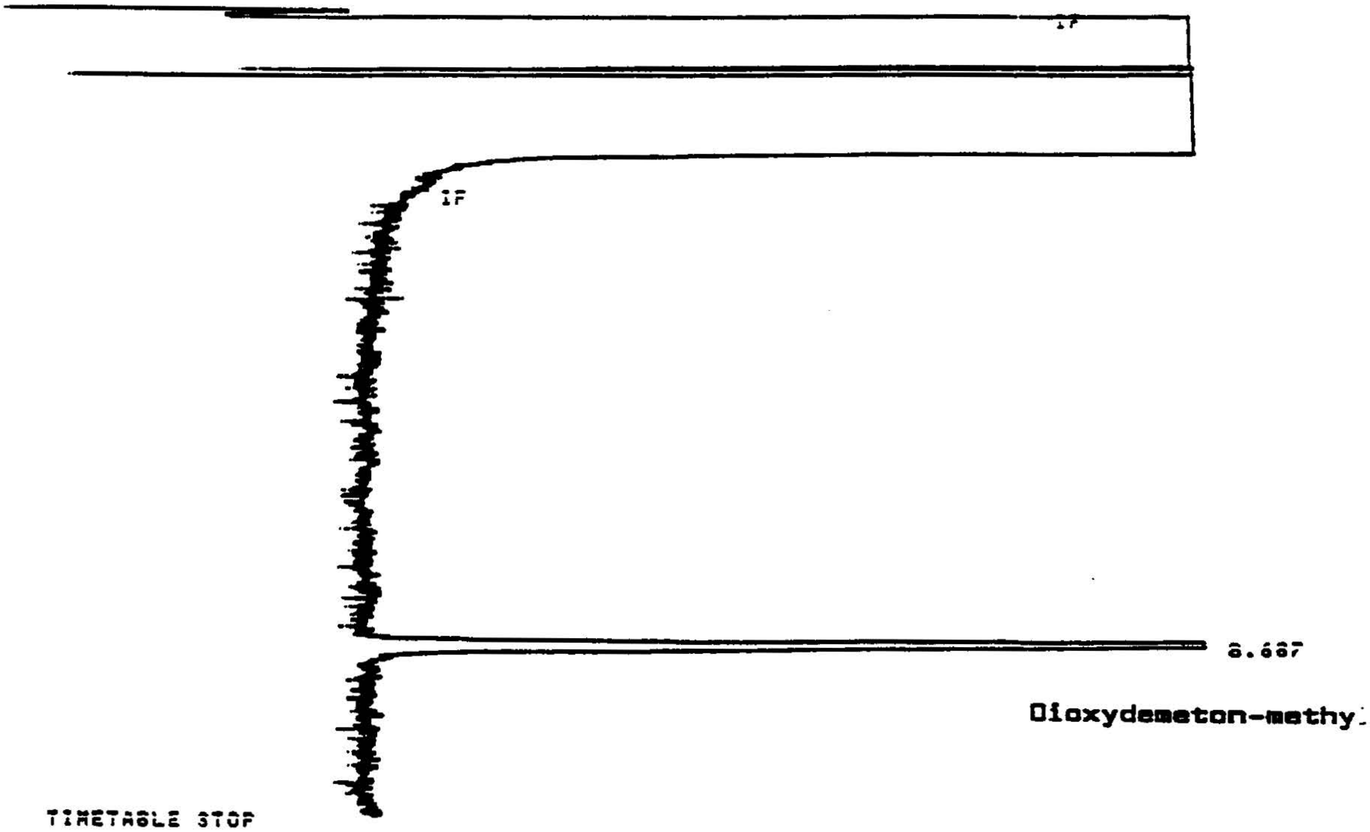
```
*WS 233 11.9 UG/ML  BREAK

*  RUN #  662       DEC 16, 1992  13:18:03
START
```



```
TIMETABLE STOP


RUN#   662            DEC 16, 1992  13:18:03

AREA%
      RT       AREA TYPE  WIDTH      AREA%
   6.674    193379   PV    .069  100.00000

TOTAL AREA- 193379
MUL FACTOR-1.0000E+00
```

Dioxydemeton Standard 11.9 ug/mL

```
+WS257 50.7 UG/ML  BREAK

+  RUN #  664       DEC 16, 1992  15:43:35
START
```



```
TIMETABLE STOP


RUN#   664            DEC 16, 1992  15:43:35

AREA%
      RT       AREA TYPE  WIDTH      AREA%
   0.687    968931    FF   .098  100.00000

TOTAL AREA- 968931
MUL FACTOR-1.0000E+00
```

Dioxydemeton Standard 50.7 ug/mL

APPENDIX E

QUALITY ASSURANCE REPORT

STATE OF CALIFORNIA PETE WILSON, Governor

AIR RESOURCES BOARD
2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

April 29, 1993

Brenda Royce, Laboratory Manager
Engineering Research Institute
California State University, Fresno
2368 E. San Ramon Avenue
Fresno, CA 93740-0094

RE: Oxydemeton-methyl Monitoring Audit Report

Dear Ms. Royce:

Please find attached a final audit report on the ambient monitoring of Oxydemeton-methyl and Dioxydemeton-methyl conducted in Monterey County by the Engineering Research Institute and the ARB's Engineering Evaluation Branch in September of 1992. The report consists of the results of a field audit conducted on August 31, 1992, and the results of a system and analytical audit conducted between August 26, 1992 and February 11, 1993.

If you have any questions, please contact Gabriel Ruiz of my staff at (916) 327-0885.

Sincerely,

for Alice Westerinen, Manager
Quality Assurance Section
Monitoring and Laboratory Division

Attachment

cc: Gabriel Ruiz

April 29, 1993

Audit Report
Oxydemeton-methyl and Dioxydemeton-methyl Monitoring in Monterey County

SUMMARY

Field Audit

On August 31, 1992, staff of the Quality Assurance Section of the California Air Resources Board conducted a field audit of the five samplers used in the ambient air monitoring of Oxydemeton-methyl and Dioxydemeton-methyl by the Engineering Research Institute of the California State University, Fresno. The audit consisted of an assessment of each sampler's conformance with the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring, and an evaluation of the flow rate accuracy of each sampler with a mass flow meter traceable to the National Institute of Standards and Technology.

The siting criteria were met in most cases, with two exceptions: two samplers were located within 20 meters of a tree dripline, but in both cases the distance between the sampler and the tree was more than twice the height that the tree protruded above the sampler.

The flow rate audits resulted in an average percent difference of 0.8%, with individual differences ranging from 0% to 2.6%. The records for field operations were appropriate and consistent with good practice.

In addition, the samplers used by the Air Resources Board's Engineering Evaluation Branch staff in the monitoring of an Oxydemeton-methyl application were audited. The difference between the reported and the true flow rates averaged 0.9% with a range of -1.0% to 3.8%.

Laboratory Audit

An audit of the laboratory operations in support of the Oxydemeton-methyl and Dioxydemeton-methyl monitoring project was conducted between August 26, 1992 and February 11, 1993. The laboratory audit was composed of both a system and an analytical performance audit. The system audit consisted of a review of the laboratory instrumentation used for the project and the quality control measures pertaining to sample handling, analysis and documentation. For the analytical performance audit, XAD-7 resin tubes were spiked with Oxydemeton-methyl and Dioxydemeton-methyl by QA staff and submitted to the laboratory for analysis.

In general, good quality control practices were followed in the study. The sampling, sample handling and storage, method validation, and documentation were adequate. The only deficiencies noticed were the exclusion of field blanks and field spikes.

The results of the analytical audit for Oxydemeton-methyl showed a positive bias averaging 88.9% and ranging from -2.9% to 188.9%. The results for the Dioxydemeton-methyl audit showed an average difference of -12.5% with a range of -30.0% to 2.5%. The results show that the accuracy and precision of the method improve as the concentration increases.

FIELD AUDIT

On August 31, 1992, Gabriel Ruiz of the Quality Assurance (QA) Section of the California Air Resources Board (ARB) conducted a field audit of the five samplers used in the Oxydemeton-methyl and Dioxydemeton-methyl air monitoring project by the Engineering Research Institute (ERI) of the California State University, Fresno. The audit consisted of an evaluation of the flow rate accuracy of each sampler, and an assessment of each sampler's conformance with the siting criteria outlined in the Quality Assurance Plan for Pesticide Monitoring prepared by the Monitoring and Laboratory Division (MLD) and the Stationary Source Division (SSD).

Sampler Siting

The locations of the five monitoring sites were: the La Jolla Elementary School in Salinas, the Monterey County Health Department in Salinas, the Fire Department in Chualar, the Gonzales Forest Fire Station in Soledad, and a water storage tank on Oak Avenue and 13th Street in Greenfield.

Two deviations from the siting criteria were observed (see Table 1): the samplers at La Jolla Elementary School and the Gonzales Forest Fire Station were located within 20 meters of a tree dripline; however, in both cases the distance between the tree and the sampler was more than twice the height that the tree protruded above the sampler's probe.

Table 1. Summary of the samplers' conformance with the siting criteria during the ambient monitoring of Oxydemeton-methyl.

Site location	2-15 meters above ground	1 meter from supporting structure		20 meters from tree dripline	Distance from obstacles larger than twice the height the obstacle protrudes above the sampler	Unrestricted airflow 270 degrees around the sampler	10 meters from incineration flues
		Vertical	Horizontal				
Salinas La Jolla Elementary School	Yes	Yes	Yes	No[1]	Yes	Yes	Yes
Salinas Monterey Co. Health Dept.	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Chualar Fire Department	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Soledad Gonzales Forest Fire Station	Yes	Yes	Yes	No[2]	Yes	Yes	Yes
Greenfield Oak Ave. at 13th St.	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Notes: 1. Sampler was 13.5 m from tree dripline. The tree protruded about 4.5 m above the sampler.
2. Sampler was 17.5 m from a line of small trees. The tallest tree protruded about 1.2 m above the sampler.

Field Operations

Sample collection and other field operations were carried out by ERI personnel. The sampling apparatus consisted of two XAD-7 resin tubes, each connected with Teflon tubing to a rotameter. The rotameters were then connected with Teflon tubing to a single pump. The assembly was supported with a 2 meter section of aluminum tubing (see Figure 1). The adsorbant tubes were covered with a plastic hood to protect them from sunlight.

Before deploying the samplers in the field, a single-point calibration of the rotameters was performed by setting the flow rate at 4.2 liters per minute (lpm) and measuring the actual flow with a bubble meter. The measured flow rate was then reported as the sample collection flow rate.

The records for field operations were appropriate and consistent with good practice. The information recorded included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Flow Rate Audits

A flow rate audit of the samplers used by the ERI was conducted in the field with a 0-10 lpm mass flow meter certified against a primary standard gas flow calibration system traceable to the National Institute of Standards and Technology (NIST). The audit was conducted following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged 0.8% and ranged from 0% to 2.6% (Table 2).

Also, four samplers used by the EEB in the monitoring of an Oxydemeton-methyl application were audited at the EEB's shop on October 1, 1992. A single-point calibration of the rotameters was performed by the EEB staff by setting the flow rate at 2.0 lpm and measuring the actual flow with a bubble meter. The average of the measured flows was then assigned as the sample collection flow rate. The flow rates were audited with a NIST traceable 0-3 lpm mass flow meter (see Attachment I). The difference between the reported and the true flow rates averaged 0.9% and ranged from -1.0% to 3.8% (Table 3).

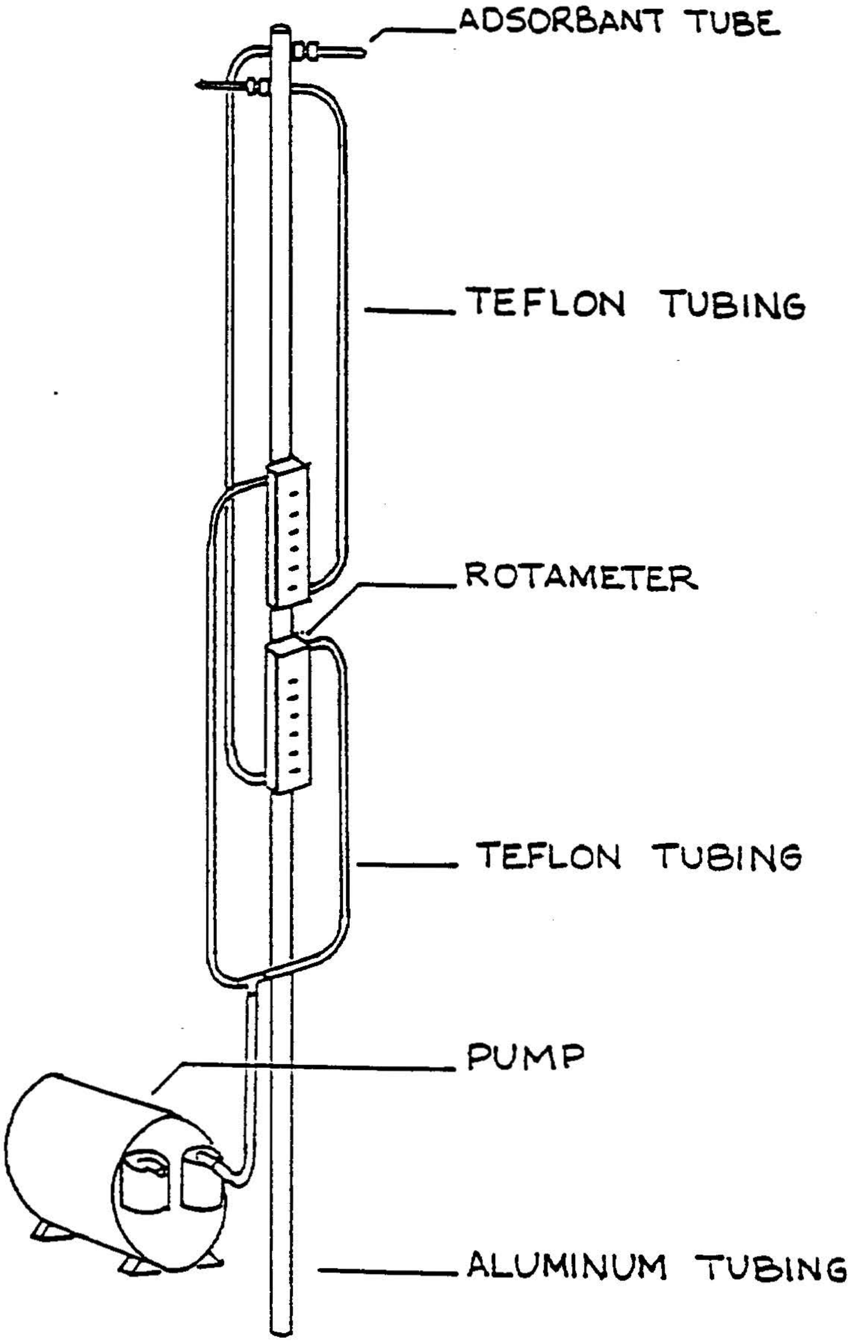


Figure 1. Air Sampler used in the monitoring of Oxydemeton-methyl and Dioxydemeton-methyl

Table 2. Results of the flow rate audit of the ERI samplers.

Site Location	Rotameter ID	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
Salinas	Upper	3.9	3.9	0.0
La Jolla Elementary School	Lower	3.9	3.9	0.0
Salinas	Upper	4.0	4.0	0.0
Monterey Co. Health Department	Lower	3.9	3.9	0.0
Chualar	Upper	3.9	3.9	0.0
Fire Department	Lower	3.9	3.9	0.0
Soledad	Upper	4.0	3.9	2.6
Gonzales Forest Fire Station	Lower	3.9	3.8	2.6
Greenfield	Upper	3.9	3.9	0.0
Oak Ave. at 13th St.	Lower	4.0	3.9	2.6

Table 3. Results of the flow rate audit of the EEB samplers.

Sampler Number	Rotameter ID	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
2	2A	1.93	1.89	2.1
	2B	1.93	1.94	-0.5
4	4A	1.93	1.94	-0.5
	4B	1.93	1.95	-1.0
6	6A	1.93	1.91	1.0
	6B	1.93	1.90	1.6
7	7A	1.93	1.86	3.8
	7B	1.93	1.91	1.0

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

LABORATORY AUDIT

A system audit of the Engineering Research Institute's laboratory operations in support of the Oxydemeton-methyl and Dioxydemeton-methyl monitoring project was conducted between August 26, 1992 and February 11, 1993, by Gabriel Ruiz. The audit was conducted primarily through electronic mail and telephone conversations with Brenda Royce of the ERI, and it consisted of a review of the instrumentation, a review of the quality control measures used to monitor data quality, and an analytical performance audit. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected every 24-hours, stored inside individual screw cap glass culture tubes in an ice chest, and delivered to the laboratory on a daily basis. The samples were then stored in a freezer at -10 to -15°C and extracted within ten days. The extracts were stored in the freezer, and analyses were performed within two months. The unused part of the extracts was retained until the end of the study.

Laboratory Instrumentation

Analysis of the samples was performed with a Hewlett Packard 5890A Gas Chromatograph equipped with Hall electrolytic conductivity detector in the sulfur mode. The chromatograph was interfaced to a Hewlett Packard 3396A integrator. The integrator was used for area counts only, and the concentrations were determined by separate calculations.

Sample Analysis

The analytical procedure was developed by the ERI's laboratory staff and was recorded in a document entitled "Standard Operating Procedure for the Sampling and Determination of Oxydemeton-methyl and Dioxydemeton-methyl in Ambient Air". The method entails extraction with acetonitrile, analysis of Dioxydemeton-methyl by GC, oxidation of Oxydemeton-methyl to Dioxydemeton-methyl, and determination of Oxydemeton-methyl by difference. (Refer to the SOP available in the QA office for further details.)

The detection limit of the method was determined as 11.2 ug total mass for Oxydemeton-methyl and 8.4 ug for Dioxydemeton-methyl, using three standard deviations at the lowest calibration point plus the absolute value of the intercept. Since the Hall detector had a non-linear calibration curve, a second-order best fit curve of area count vs. concentration was used to determine the concentrations.

Extraction efficiency studies were conducted for triplicate sets of samples spiked with 20.9, 94 and 188 ug Oxydemeton-methyl, and 16.4, 74 and 148 Dioxydemeton-methyl, and for single samples spiked with 522 ug Oxydemeton-methyl and 411 ug Dioxydemeton-methyl. The average recovery rates were 127.0%, 88.0%, 71.6%, and 91.0% for Oxydemeton-methyl, and 109.4%, 87.8%, 81.0%, and 78.8% for Dioxydemeton-methyl, respectively.

The retention efficiency of the tubes was determined by drawing ambient air at 4 lpm for 24-hours through four sets of tubes spiked with 52, 104, 209, and 418 ug Oxydemeton-methyl, and 41, 82, 164, and 329 ug Dioxydemeton-methyl. The average recovery rates were 90.8%, 65.2%, 103.1%, and 87.8% for Oxydemeton-methyl, and 87.8%, 74.5%, 82.9%, and 96.0% for Dioxydemeton-methyl, respectively.

The stability of samples spiked with 94 ug Oxydemeton-methyl and 74 ug Dioxydemeton-methyl was investigated under different storage conditions. Samples were analyzed in triplicate after 3, 7, 10, 18, 23, and 30 days of storage in a freezer at -10 to -15°C. The average recovery rates were 41.9%, 95.0%, 86.9%, 86.4%, 92.2%, and 93.9% for Oxydemeton-methyl, and 140.8%, 76.1%, 89.2%, 89.1%, 87.6%, and 86.1% for Dioxydemeton-methyl, respectively. For samples stored in an ice chest at 0°C for 3, 7, and 10 days, the average recovery rates were 86.8%, 79.5%, and 80.2% for Oxydemeton-methyl, and 86.7%, 93.0%, and 107.0% for Dioxydemeton-methyl, respectively. For samples stored at room temperature for 3 and 7 days, the average recoveries were 84.0% and 92.5% for Oxydemeton-methyl, and 117.3% and 105.7% for Dioxydemeton-methyl, respectively.

Quality control activities performed routinely to monitor and document the data quality included the following: daily four-point calibration, a calibration update every 10 samples, analysis of one control sample per batch of field samples, plotting of control charts with control limits defined at ±3 standard deviations, analysis of a field duplicate per sampling day, replicate analyses of 5% of the samples, and analysis of an oxydation spike and an oxydation blank per analytical batch.

Documentation

The ERI's laboratory staff followed adequate chain-of-custody procedures. All samples were accompanied by field data sheets and chain-of-custody records. A unique laboratory sample number independent of the field sample number was assigned to each sample when it was logged in. In addition, the extracts were given a separate laboratory number, and all the numbers were cross-referenced.

Sample logs, laboratory records, and instrument run and maintenance logs were kept in bound notebooks with numbered pages. The entries included sample number, sample type, date sample was received, date of analysis, raw analytical data, results of the analysis, and receptor of the analytical data.

The chromatograms, integrator printouts, and summary sheets for the analysis sequence were saved in an accessible form. Data reduction and calculations were performed on an electronic spreadsheet and the finalized data were stored on electronic media.

Analytical Performance Audit

The performance of the ERI's analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of Oxydemeton-methyl and Dioxydemeton-methyl. The samples were prepared by Gabriel Ruiz on September 17, 1992, following the procedures outlined in Attachment II. The samples were extracted within ten days, and analyses were completed by mid-December, following the laboratory's standard operating procedures.

The analytical results for Oxydemeton-methyl showed a positive bias. The difference between the reported and the assigned values averaged 88.9%, and ranged from -2.9% to 188.9% (Table 4). The results indicate that the accuracy of the method improves as the concentration increases. Also, the results for duplicate samples ODM2 and ODM5, and ODM3 and ODM7 show that the precision of the method increases with the concentration.

The analytical results for Dioxydemeton-methyl showed a negative bias averaging -12.5% and ranging from -30.0% to 2.5% (Table 5). Again, the results show that the accuracy and the precision of the method improve as the concentration increases.

CONCLUSIONS

The ERI followed good quality control procedures overall. The sampling was conducted following good practices, sample handling and storage were appropriate, the analytical method was validated, and the documentation was adequate. The analytical audit results showed a fair agreement between the assigned and the reported mass of both compounds.

The only deficiencies noticed were the exclusion of field blanks and field spikes. Field blanks should be analyzed periodically to investigate post-sampling sources of contamination, such as container cleanliness or permeability, or transportation effects. Field spikes should be included, whenever possible, with the daily batch of samples submitted to the laboratory to monitor sample recovery.

Table 4. Results of the analytical performance audit for Oxydemeton-methyl.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
ODM-1	124.6	121	-2.9
ODM-2	31.2	90	188.9
ODM-3	62.3	91	46.1
ODM-4	0.0	15	N/A
ODM-5	31.2	76	144.0
ODM-6	0.0	0	N/A
ODM-7	62.3	105	68.5

Table 5. Results of the analytical performance audit for Dioxydemeton-methyl.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
ODM-1	0.0	0	N/A
ODM-2	60.0	54	-10.0
ODM-3	30.0	27	-10.0
ODM-4	120.0	123	2.5
ODM-5	60.0	51	-15.0
ODM-6	0.0	0	N/A
ODM-7	30.0	21	-30.0

Flow Audit Procedure for Pesticide Samplers

Introduction

The pesticide sampler is audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable primary standard gas flow calibration system.

The audit device is placed in series with the sample probe 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 reported flow rate is then compared to the true flow rate, and a percent difference is determined.

Equipment

The basic equipment required for the pesticide 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.
6. 1/4" I.D. Tygon tubing.

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 probe inlet with a small section of Tygon tubing.
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 reported flow rate.

ATTACHMENT II

Performance Audit Procedure For The Laboratory Analysis Of Oxydemeton-methyl

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Oxydemeton-methyl and its breakdown product Dioxydemeton-methyl. The audit is conducted by submitting audit samples prepared by spiking XAD-7 resin tubes with measured amounts of Oxydemeton-methyl and Dioxydemeton-methyl. 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. Oxydemeton-methyl, 97.0% pure

2. Dioxydemeton-methyl, 90.0% pure

3. Methanol, residue analysis grade

4. XAD-7 Resin Tubes

5. 25 ul Microsyringe

Safety Precautions

Oxydemeton-methyl and Dioxydemeton-methyl may be harmful if inhaled, swallowed, or absorbed through the skin. Avoid direct physical contact. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

6 mg/ml Oxydemeton-methyl Spiking Solution: Weigh about 62 mg of Oxydemeton-methyl into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

6 mg/ml Dioxydemeton-methyl Spiking Solution: Weigh about 67 mg of Dioxydemeton-methyl into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

Sample Preparation

Prepare seven audit samples from the Oxydemeton-methyl and Dioxydemeton-methyl spiking standards according to the following table:

Sample	Oxydemeton-methyl 6 ug/ml Std	Dioxydemeton-methyl 6 ug/ml Std
ODM-1	20 ul	0 ul
ODM-2	5	10
ODM-3	10	5
ODM-4	0	20
ODM-5	5	10
ODM-6	0	0
ODM-7	10	5

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 spiking 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 at or below 4°C until ready for analysis.

APPENDIX F

METHOD VALIDATION RESULTS

OXYDEMETON-METHYL METHOD VALIDATION DATA

DESCRIPTION		OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
		FORTIF µg*	RESULTS µg*	RECOV %	FORTIF µg*	RESULTS µg*	RECOV %
EXTRACTION EFFICIENCIES							
Level 1		20.9	24.2	115.6%	16.4	18.3	111.5%
			28.4	135.7%		18.3	111.5%
			27.1	129.7%		17.3	105.3%
	Average:		26.5	127.0%		17.9	109.4%
	Std Dev:		2.2	10.3%		0.6	3.6%
Level 2		94	83.2	88.5%	74	68.8	92.9%
			89.9	95.6%		58.7	79.3%
			75.1	79.9%		67.5	91.2%
	Average:		82.7	88.0%		65.0	87.8%
	Std Dev:		7.4	7.9%		5.5	7.4%
Level 3		188	132.2	70.3%	148	114.6	77.5%
			140.9	75.0%		118.9	80.3%
			130.6	69.5%		126.4	85.4%
	Average:		134.6	71.6%		119.9	81.0%
	Std Dev:		5.5	2.9%		5.9	4.0%
Level 4		522	474.8	91.0%	411	323.8	78.8%

* Method Validation results are reported in total µg. The lowest fortification level was selected to be approximately twice the LOD (expressed in µg).

OXYDEMETON-METHYL METHOD VALIDATION DATA

		OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
DESCRIPTION		FORTIF	RESULTS	RECOV	FORTIF	RESULTS	RECOV
		µg*	µg*	%	µg*	µg*	%
RETENTION EFFICIENCIES (4L/min*24h)							
Blank		0	0.0	—	0	0.0	—
Level 1		52	56.1	107.8%	41	33.0	80.6%
			41.7	80.1%		40.9	99.8%
			43.9	84.4%		34.1	83.1%
	Average:		47.2	90.8%		36.0	87.8%
	Std Dev:		7.8	14.9%		4.3	10.5%
Level 2		104	61.7	59.4%	82	63.1	77.0%
			73.9	71.0%		59.0	71.9%
	Average:		67.8	65.2%		61.0	74.5%
	Std Dev:		8.6	8.2%		3.0	3.6%
Level 3		209	240.7	115.1%	164	119.5	72.8%
			203.5	97.4%		146.4	89.3%
			202.2	96.8%		142.0	86.6%
	Average:		215.5	103.1%		136.0	82.9%
	Std Dev:		21.8	10.4%		14.5	8.8%
Level 4		418	366.8	87.8%	329	315.7	96.0%

* Method Validation results are reported in total µg. The lowest fortification level was selected to be approximately twice the LOD (expressed in µg).

OXYDEMETON-METHYL METHOD VALIDATION DATA

	OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
	FORTIF	RESULTS	RECOV	FORTIF	RESULTS	RECOV
DESCRIPTION	µg*	µg*	%	µg*	µg*	%
STABILITY SAMPLES						
Freezer Stability						
03 Day	94	42.9	45.6%	74	99.9	135.0%
		30.7	32.6%		112.6	152.1%
		44.6	47.5%		100.1	135.3%
Average:		39.4	41.9%		104.2	140.8%
Std Dev:		7.6	8.1%		7.2	9.8%
07 Day	94	84.9	90.4%	74	56.3	76.1%
		91.6	97.4%		53.9	72.9%
		91.4	97.2%		58.6	79.2%
Average:		89.3	95.0%		56.3	76.1%
Std Dev:		3.8	4.0%		2.4	3.2%
10 Day	94	75.7	80.5%	74	65.5	88.5%
		78.4	83.4%		66.5	89.9%
		90.9	96.7%		66.1	89.3%
Average:		81.6	86.9%		66.0	89.2%
Std Dev:		8.1	8.6%		0.5	0.7%
18 Day	94	88.7	94.4%	74	64.7	87.4%
		81.9	87.1%		67.6	91.3%
		73.2	77.8%		65.5	88.5%
Average:		81.2	86.4%		65.9	89.1%
Std Dev:		7.8	8.3%		1.5	2.0%

* Method Validation results are reported in total µg. The lowest fortification level was selected to be approximately twice the LOD (expressed in µg).

OXYDEMETON-METHYL METHOD VALIDATION DATA

	OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
	FORTIF	RESULTS	RECOV	FORTIF	RESULTS	RECOV
DESCRIPTION	µg*	µg*	%	µg*	µg*	%
23 Day	94	84.1	89.4%	74	64.3	86.9%
		84.3	89.7%		68.5	92.6%
		91.7	97.5%		61.7	83.4%
Average:		86.7	92.2%		64.8	87.6%
Std Dev:		4.3	4.6%		3.4	4.6%
30 Day	94	83.5	88.8%	74	64.7	87.4%
		85.9	91.4%		61.4	82.9%
		95.3	101.3%		65.0	87.9%
Average:		88.2	93.9%		63.7	86.1%
Std Dev:		6.2	6.6%		2.0	2.8%
Ice Chest Stability						
03 Day	94	83.0	88.3%	74	66.0	89.2%
		83.8	89.2%		64.6	87.3%
		77.7	82.7%		61.9	83.7%
Average:		81.5	86.8%		64.2	86.7%
Std Dev:		3.3	3.5%		2.1	2.8%
07 Day	94	88.3	94.0%	74	65.3	88.2%
		62.1	66.0%		70.0	94.6%
		73.7	78.4%		71.1	96.1%
Average:		74.7	79.5%		68.8	93.0%
Std Dev:		13.2	14.0%		3.1	4.2%
10 Day	94	80.0	85.2%	74	68.9	93.1%
		65.2	69.4%		81.0	109.4%
		80.9	86.0%		87.8	118.6%
Average:		75.4	80.2%		79.2	107.0%
Std Dev:		8.8	9.4%		9.6	12.9%

* Method Validation results are reported in total µg. The lowest fortification level was selected to be approximately twice the LOD (expressed in µg).

OXYDEMETON-METHYL METHOD VALIDATION RESULTS

	OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
	FORTIF	RESULTS	RECOV	FORTIF	RESULTS	RECOV
DESCRIPTION	μg*	μg*	%	μg*	μg*	%
Room Temperature Stability						
03 Day	94	65.9	70.1%	74	93.5	126.3%
		81.0	86.2%		80.2	108.4%
		90.1	95.8%		86.8	117.3%
Average:		79.0	84.0%		86.8	117.3%
Std Dev:		12.2	13.0%		6.6	8.9%
07 Day	94	84.5	89.9%	74	76.3	103.0%
		91.8	97.6%		85.9	116.0%
		84.5	89.9%		72.6	98.1%
Average:		86.9	92.5%		78.2	105.7%
Std Dev:		4.2	4.4%		6.9	9.3%

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* Method Validation results are reported in total μg. The lowest fortification level was selected to be approximately twice the LOD (expressed in μg).

OXYDEMETON-METHYL METHOD VALIDATION DATA

	OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
DESCRIPTION	FORTIF µg*	RESULTS µg*	RECOV %	FORTIF µg*	RESULTS µg*	RECOV %
EXTRACTION CONTROLS						
Level 1	75	73.2	97.6%	75	70.2	93.6%
		71.2	95.0%		68.6	91.5%
		74.8	99.7%		73.1	97.5%
		75.1	100.1%		68.5	91.3%
		60.3	80.4%		70.9	94.6%
		69.6	92.8%		75.5	100.7%
		61.4	81.9%		73.8	98.4%
		71.7	95.6%		70.5	93.9%
		60.3	80.4%		70.8	94.4%
		69.5	92.7%		72.2	96.3%
		67.5	90.0%		75.8	101.1%
		62.4	83.1%		69.9	93.2%
		67.1	89.5%		70.8	94.4%
		67.2	89.6%		68.8	91.7%
		68.0	90.6%		70.8	94.4%
		73.8	98.4%		71.8	95.7%
Average:		68.3	91.1%		71.4	95.2%
Std Dev:		2.6	3.5%		1.2	1.5%

* Method Validation results are reported in total µg. The lowest fortification level was selected to be approximately twice the LOD (expressed in µg).

	OXYDEMETON-METHYL			DIOXYDEMETON-METHYL		
	FORTIF	RESULTS	RECOV	FORTIF	RESULTS	RECOV
DESCRIPTION	µg*	µg*	%	µg*	µg*	%
EXTRACTION CONTROLS						
Level 2	94	88.2	93.8%	74	75.6	102.1%
		90.8	96.6%		78.0	105.3%
Average:		89.5	95.2%		76.8	103.7%
Std Dev:		1.9	2.0%		1.7	2.3%
Level 3	155	134.2	86.6%	102	109.9	107.7%
	155	127.3	82.1%	0	0.0	—
	155	138.4	89.3%	0	0.0	—
Average:		133.3	86.0%		—	—
Std Dev:		5.6	3.6%		—	—
Level 4	209	201.9	96.6%	164	134.4	81.8%
		198.9	95.2%		125.2	76.2%
		193.3	92.5%		141.4	86.1%
		203.9	97.6%		152.8	93.0%
Average:		199.5	95.1%		138.4	85.1%
Std Dev:		4.6	2.2%		11.6	7.1%

* Method Validation results are reported in total µg. The lowest fortification level was selected to be approximately twice the LOD (expressed in µg).

OXYDEMETON-METHYL METHOD VALIDATION DATA

	OXYDEMETON-METHYL			OXYDEMETON-METHYL (cont'd)		
DESCRIPTION	FORTIF	RESULTS	RECOV	FORTIF	RESULTS	RECOV
	μg*	μg*	%	μg*	μg*	%
OXIDATION SPIKES (Fortified with ODM only)						
	74.7	68.9	92.2%	74.7	66.4	88.9%
		62.4	83.6%		65.3	87.4%
		65.4	87.6%		68.1	91.2%
		71.0	95.0%		67.9	90.9%
		65.7	87.9%		66.7	89.3%
		66.4	88.9%		67.0	89.6%
		70.5	94.3%		67.6	90.5%
		64.3	86.1%		64.5	86.4%
		74.7	100.0%		66.9	89.6%
		71.7	96.0%		74.6	99.9%
		75.6	101.2%		76.5	102.4%
		65.5	87.7%		73.3	98.2%
		82.8	110.8%		75.2	100.6%
		78.4	104.9%		74.7	100.1%
		81.3	108.8%		64.9	86.9%
		78.7	105.4%		81.0	108.5%
		68.3	91.4%		63.8	85.4%
		67.6	90.5%		65.0	87.0%
Average:					70.2	94.0%
Std Dev:					5.6	7.5%

OXIDATION BLANKS

17 oxidation blanks were run; no interfering peaks were identified

* Method Validation results are reported in total μg. The lowest fortification level was selected to be approximately twice the LOD (expressed in μg).