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Airborne Concentrations of Pesticides in California

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13. ABSTRACT *(Maximum 200 Words)*

Staff from California State University, Fresno (CSUF) determined the ambient airborne concentrations of the following pesticides (associated breakdown products in parentheses): naled (and dichlorvos), methidathion (and methidaoxon), and oxydemeton-methyl (and dioxydemeton-methyl). Ambient monitoring consisted of deploying several air samplers in small towns near application sites. Ambient air was pulled through XAD-2 resin-filled tubes at the flow rate of four liters per minute for 24 hours. After extraction with solvent, the samples were stored until analysis. Analysis was conducted by gas chromatography with a variety of detectors. Monitoring sites and times were chosen based upon determinations of areas and seasons of peak use for the respective pesticide. Detectable levels of naled and dichlorvos were identified at four of the five monitoring sites. The highest level found was 77 ng per cubic meter. For dichlorvos, the highest level found was 59 ng per cubic meter. Methidathion was found at two of the five monitoring sites. The highest level of methidathion found was 560 ng per cubic meter, and the highest level of methidaoxon found was 100 ng per cubic meter. Neither oxydemeton-methyl nor its oxidation product dioxydemeton-methyl were detected at any of the five monitoring sites. Either these compounds do not persist in the ambient air long enough to be detected, or the sampling system was unable to capture these compounds in the vapor phase.

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AIRBORNE CONCENTRATIONS OF PESTICIDES IN CALIFORNIA

Final Report
Contract No. A032-094

Prepared for:

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JUNE 1993

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ACKNOWLEDGMENTS

The authors of this report acknowledge the valuable assistance provided by the staff of the Air Resources Board, particularly Ralph Propper, Lynn Baker, Mike Poore, Ruth Tomlin, and Don Fitzell. We would also thank personnel of the Tulare County Agriculture Commissioner's office and the Monterey County Agriculture Commissioner's office for the valuable information provided to us regarding pesticide application, as well as George Hurley of Western Farm Service in Salinas for his assistance and cooperation in identifying and making available sites for application monitoring.

This project was submitted in fulfillment of ARB Contract No. A032-094 *Monitoring Pesticides in Air* by the Engineering Research Institute, California State University, Fresno under the sponsorship of the California Air Resources Board. Work was completed as of February 28, 1993.

TABLE OF CONTENTS

OVERVIEW OF SAMPLING AND ANALYSIS PROGRAM

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

Brenda R. Royce
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Barry H. Gump

June 24, 1993

BACKGROUND

The Department of Pesticide Regulation, as part of its mission, is collecting the data required to evaluate the persistence and toxicity of airborne pesticides used in California. The Air Resources Board assists in the collection of this data. Under contract number A032-094 with the Air Resources Board, California State University, Fresno (CSUF) personnel have completed air monitoring studies of three pesticides and their degradation products. These compounds are:

- Naled and Dichlorvos in Tulare County
- Methidathion and Methidaoxon in Tulare County
- Oxydemeton-methyl and Dioxydemeton-methyl in Salinas Valley.

Ambient monitoring was completed for all three pairs of compounds. Application monitoring was carried out for methidathion and oxydemeton-methyl. Due to an unforeseen change in application patterns, a naled application monitoring study could not be carried out.

CSUF provided method development and validation of each sampling and analysis event along with the analysis of all monitoring samples.

Additionally, work was carried out in two successive years on developing sampling and analytical methods for two dithiocarbamate pesticides, ziram and mancozeb, and their breakdown products, tetramethyl thiourea and ethylene thiourea, respectively. These compounds presented some unique difficulties with both sampling and analytical methods not experienced in preparing for the other three groups of compounds. Most notably, dithiocarbamate compounds have very low solubilities in every common laboratory solvent, and they also have very low vapor pressures making direct chromatographic techniques impractical. Analytical techniques identified in the literature were not sensitive enough to meet the detection limits required by the Department of Pesticide Regulation. In addition, the parent compounds and their breakdown products have distinctly different physical characteristics, especially their volatilities and

solubilities. This factor greatly compounded the process of developing methods for simultaneous monitoring for both types of compounds. As a result, monitoring for both ziram and mancozeb was postponed until adequate methods could be developed.

Site selection and sampling for the naled study, as well as the application monitoring studies for methidathion and oxydemeton-methyl, were provided by ARB personnel. CSUF personnel were responsible for sampling and ambient monitoring of methidathion and oxydemeton-methyl. In addition, the oxydemeton-methyl monitoring was used as a training run for application monitoring for CSUF personnel. After observing one application monitoring event performed by ARB staff, CSUF set up and carried out a second application monitoring event under the observation of ARB personnel. Hence, with the completion of the monitoring for oxydemeton-methyl in Monterey County during September 1992, CSUF personnel have been checked out for both setting up and operating samplers for both ambient monitoring and application monitoring events.

Some notable similarities existed in the methods developed for these compounds. Ambient air sampling was carried out on XAD-2 resin-filled tubes for both naled and methidathion under the identical flow rates of 4 liters per minute for 24 hours. Both of these compounds and their degradation products were also extracted from resin using toluene. All three compounds were found to extract readily into the appropriate solvent by sonication. The smaller resin and solvent volumes used made sample handling and storage reasonably easy. The XAD-2 and XAD-7 resin-extraction solvent systems used also had minimal to no background on the detector systems used for analysis. The greatest background was found using the electron-capture detector for methidathion. The use of a more specific detector for naled (electrolytic conductivity detector, HECD, in the halogen mode) and oxydemeton-methyl (HECD in the sulfur mode) resulted in virtually no background which could be attributed to the sampling system.

The greatest problem facing the CSUF personnel was the development of procedures for analyzing the study compounds. This problem was at least partly overcome for the development of the procedure for the analysis of dioxydemeton-methyl when more effective communications were set up between ARB and CSUF analytical chemistry personnel. Nevertheless, the development of analytical procedures should proceed long before the compound is to be sampled in the field to avoid the delay or cancellation of critical sampling events that typically can be carried out during only relatively short periods of the year.

NALED AND DICHLORVOS

Ambient monitoring for naled and its oxidation product, dichlorvos, was performed in Tulare County during May and June of 1991. No application monitoring was completed in 1991 due to the substitution of another pesticide for naled at many of the fields in the application area. Application monitoring for these compounds was carried out by ARB personnel in Fresno County in 1992. The report for the application monitoring is in the naled monitoring report.

Detectable levels of naled and dichlorvos were identified at four of the five monitoring sites, including the background site. At three of these sites (Sunnyside, Jefferson, and Kaweah), levels above the MDL generally occurred between May 20 and May 23, 1991. Detectable levels were found at the background site between May 30 and June 4, 1991. A data summary is in Tables 1 and 2.

Table 1. Summary of Naled Results

Site Highest	Value	Second Highest Value	Mean of Results >LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	0.065	0.057	0.061	2	16
Jefferson Elementary School	0.062*	0.050	0.056	2	16
Kaweah High School	0.060	0.052	0.049	5	16
UC Lindcove Field Station	<LOQ	<LOQ	—	0	16
ARB Monitoring Station, Visalia	0.077	0.060	0.068	2	16

NOTE: LOQ for naled is 0.04 $\mu g/m^3$
* Average of duplicate samples

Table 2. Summary of Dichlorvos Results

Site	Highest Value	Second Highest Value	Mean of Results >LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	0.050*	0.029	0.034	3	16
Jefferson Elementary School	0.024*	0.024	0.023	4	16
Kaweah High School	0.059*	0.039	0.036	4	16
UC Lindcove Field Station	<LOQ	<LOQ	—	0	16
ARB Monitoring Station, Visalia	0.026	0.026	0.026	3	16

NOTE: LOQ for dichlorvos is 0.02 $\mu g/m^3$
* Average of duplicate samples

The Lindcove Field Station is planted to citrus, including oranges, with other orange groves nearby. None of the study pesticides were applied at the UC Lindcove Field Station during the study. No naled or dichlorvos was detected at the Lindcove Field Station sample site during the sampling period. On the other hand, both naled and dichlorvos were detected at the Visalia site which was the "background" site.

Since naled is not a restricted use pesticide, possible applications in or near Visalia other than for oranges may have lead to detectable levels at the background site between May 30 and June 4, 1991.

METHIDATHION AND METHIDAOXON

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. Tables 3 and 4 contains a summary of the findings. Appendices A, B and C of the Methidathion monitoring report contain a more detailed presentation of the monitoring data.

Table 3. 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 $\mu g/m^3$

Table 4. 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 $\mu g/m^3$

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.

All data presented in the 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.

OXYDEMETON-METHYL AND DIOXYDEMETON-METHYL

Both ambient and application monitoring for oxydemeton-methyl and its oxidation product, dioxydemeton-methyl, were performed in the Salinas Valley during August to 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.

All data presented in the 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 oxydemeton-methyl and dioxydemeton-methyl compounds in the vapor phase.

Airborne Concentrations of Naled and Dichlorvos in Central Tulare County from Sampling Conducted in May and June 1991

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

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JUNE 24, 1993

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ACKNOWLEDGMENTS

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 Ralph Propper, Don Fitzell, Lynn Baker, and Ruth Tomlin. 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

Ambient monitoring for naled and its oxidation product, dichlorvos, were performed in Tulare County during May and June of 1991. No application monitoring was completed in 1991 due to the substitution of another pesticide for naled at many fields in the study area. Application monitoring for these compunds was carried out by ARB personnel inFresno County in 1992. The report for the application monitoring is in Appendix F. All data presented in the report for naled and dichlorvos have been determined and accepted subject to a rigorous quality assurance program.

Detectable levels of naled and dichlorvos were identified at four of the five monitoring sites, including the background site. At three of these sites (Sunnyside, Jefferson, and Kaweah), levels above the MDL generally occurred between May 20 and May 23, 1991. Detectable levels were found at the background site between May 30 and June 4, 1991. Tables 1.and 2 present a summary of results for naled and dichlorvos, respectively.

Table 1. Summary of Naled Results

Site	Highest Value	Second Highest Value	Mean of Results >LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	0.065	0.057	0.061	2	16
Jefferson Elementary School	0.062*	0.050	0.056	2	16
Kaweah High School	0.060	0.052	0.049	5	16
UC Lindcove Field Station	<LOQ	<LOQ	—	0	16
ARB Monitoring Station, Visalia	0.077	0.060	0.068	2	16

NOTE: LOQ for naled is 0.04 $\mu g/m^3$
* Average of duplicate samples

Table 2. Summary of Dichlorvos Results					
Site	Highest Value	Second Highest Value	Mean of Results >LOQ	Number of Samples Above LOQ	Total Samples
Sunnyside Union Elementary School	0.050*	0.029	0.034	3	16
Jefferson Elementary School	0.024*	0.024	0.023	4	16
Kaweah High School	0.059*	0.039	0.036	4	16
UC Lindcove Field Station	<LOQ	<LOQ	—	0	16
ARB Monitoring Station, Visalia	0.026	0.026	0.026	3	16

NOTE: LOQ for dichlorvos is 0.02 $\mu g/m^3$
* Average of duplicate samples

The Lindcove Field Station is planted to citrus, including oranges, with other orange groves nearby. None of the study pesticides were applied at the UC Lindcove Field Station during the study. No naled or dichlorvos was detected at the Lindcove Field Station sample site during the sampling period. On the other hand, both naled and dichlorvos were detected at the Visalia site which was the "background" site.

Since naled is not a restricted use pesticide, possible applications in or near Visalia other than for oranges may have lead to detectable levels at the background site between May 30 and June 4, 1991.

INTRODUCTION

Very low volume (4 *lpm*) ambient air samples were collected at 5 sites (including a background site) in Tulare County for analysis of two organophosphates, naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate) and its breakdown product, dichlorvos (2,2-dichlorovinyl dimethyl phosphate). Naled, which is not a restricted use pesticide, is currently used to control citrus thrips on orange corps. It is also used on other crops in Tulare County, including grapes. The location and time period for sampling were based on reported applications of naled in recent years. Tulare county was selected as the study area since it lead the state in reported applications in 1988 (59,732 pounds active ingredient). Typically, peak usage in Tulare County falls in May when naled is applied to the orange crop.

SITE DESCRIPTION

Five sampling sites were selected by ARB personnel from the areas of Tulare County where citrus farming is predominant. Sites were selected for their proximity to the orchards with considerations for both accessibility and security of the sampling equipment. The five sites, as shown on Figure 1, were at the following locations: Sunnyside Union Elementary School, Strathmore; Jefferson Elementary School, Lindsay; Kaweah High School, Exeter; UC, Lindcove Field Station, Exeter; ARB Ambient Air Monitoring Station, Visalia (background). Addresses for the sites are listed in Table 3.

TABLE 3. Ambient Sampling Sites

Sunnyside Union Elementary School 21644 Avenue 196, Strathmore, CA 93267
Jefferson Elementary School 333 Westwood Avenue, Lindsay, CA 93247-1801
Kaweah High School 21215 Avenue 300, Exeter, CA 93221
University of California, Lindcove Field Station 22963 Carson Avenue, Exeter, CA 93221
Air Resources Board, Ambient Air Monitoring Station 310 N. Church St., Visalia, CA (Background site)

Sunnyside Union Elementary School is situated in a sparsely populated area of Strathmore surrounded by agricultural fields, including oranges. The sampling unit was placed on the roof of one of the classroom building which are all single story. There are no buildings or trees near enough to the sampling point to obstruct free air flow.

of one of the classroom building which are all single story. There are no buildings or trees near enough to the sampling point to obstruct free air flow.

Jefferson Elementary School is located near the edge of a residential area off Highway 65 in Lindsay. The sampling equipment was placed on one of the tallest building of the school Trees located near one edge of the building required positioning the sampling equipment near the center of the roof.

Kaweah High School is located north of Highway 198 on Avenue 300. The campus is immediately surrounded by orange groves on all four sides. The sampling equipment was placed on the north building which is centrally located on the small campus. There were no large structures or trees within prescribed limits to the sampling site.

The fourth sampling site was located at the University of California, Lindcove Field Station. The site is located at the edge of the foothills just west of Highway 198. A variety of citrus trees are planted at the field station. Other orange orchards are located throughout the surrounding area. There were no accessible roof tops at this site for the sampling equipment. An open area near the middle of the field station was selected where an existing meteorological station is positioned.

The background monitoring was conducted at the ARB Monitoring Station in downtown Visalia. The sampling apparatus was placed on a second story roof near the other ARB monitoring equipment. 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 Air Resources Board (ARB) personnel over a four week period from May 9 to June 7, 1991. The samples were then transported to California State University, Fresno (CSUF) for analysis.

SAMPLING

Ambient samplers consisted of a glass tube (8mm x 110mm) containing two sections of XAD-2 resin (400 mg primary section with 200 mg backup section) 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 the end of each sampling period. Sampling periods were nominally 24 hours and varied from 23 to 25 hours. The sampling data are presented in Appendix B. At the end of the sampling period, each tube was removed and capped, labeled, and placed in a screw cap glass culture tube. The culture tubes 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 week to CSUF for analysis. At CSUF samples were stored in a freezer at -15oC until extracted for analysis.

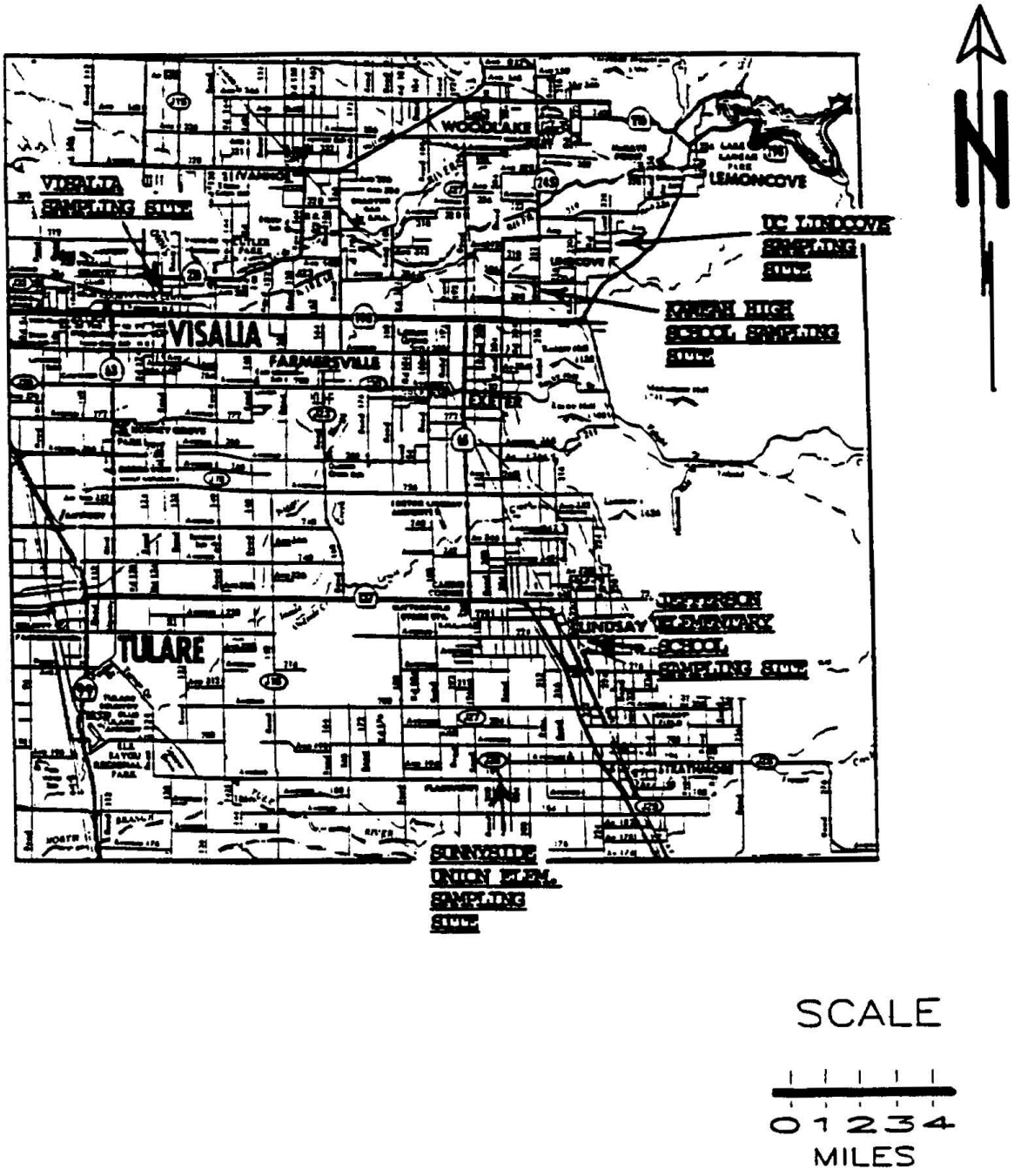


Figure 1. Site Map

LABORATORY ANALYSIS

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 extract was allowed to settle, filtered through a plug of glass wool, and transferred to a 4 *mL* vial for GC analysis. No additional cleanup was required. All sample extractions were completed within 14 days of sampling.

The samples were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with an OI model 4420 electrolytic conductivity detector operated in the halogen mode. The chromatograph was also equipped with a Hewlett-Packard model 3396A integrator. A J&W Scientific DB-5 megabore column (30m x 0.53mm ID) provided the separation. The table below shows the instrument conditions.

Table 4. 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 He	Make Up He	Detector H_2
200	950*	150	1	20	220	9	8	22	100

* HECD Reactor Temperature

A four point calibration curve was prepared by injecting 2 uL of each of the working standards onto the gas chromatograph. The resulting peak areas were entered onto Cricket Graph to generate a second-order equation for the standard curve. Two microliters of each sample was injected on the GC for comparison to the standards. The detection limits for naled and dichlorvos in air were 0.04 $\mu g/m^3$ and 0.02 $\mu g/m^3$, respectively. An example of the chromatograms and equations for one set of standard curves can be found in Appendix C.

The naled and dichlorvos sample data are found in Appendix A at the end of this report. A summary of these data are presented in Tables 1 and 2.

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 one or both of the study compounds were identified, the replicate sample was also extracted and analyzed.

PESTICIDE SAMPLING APPARATUS

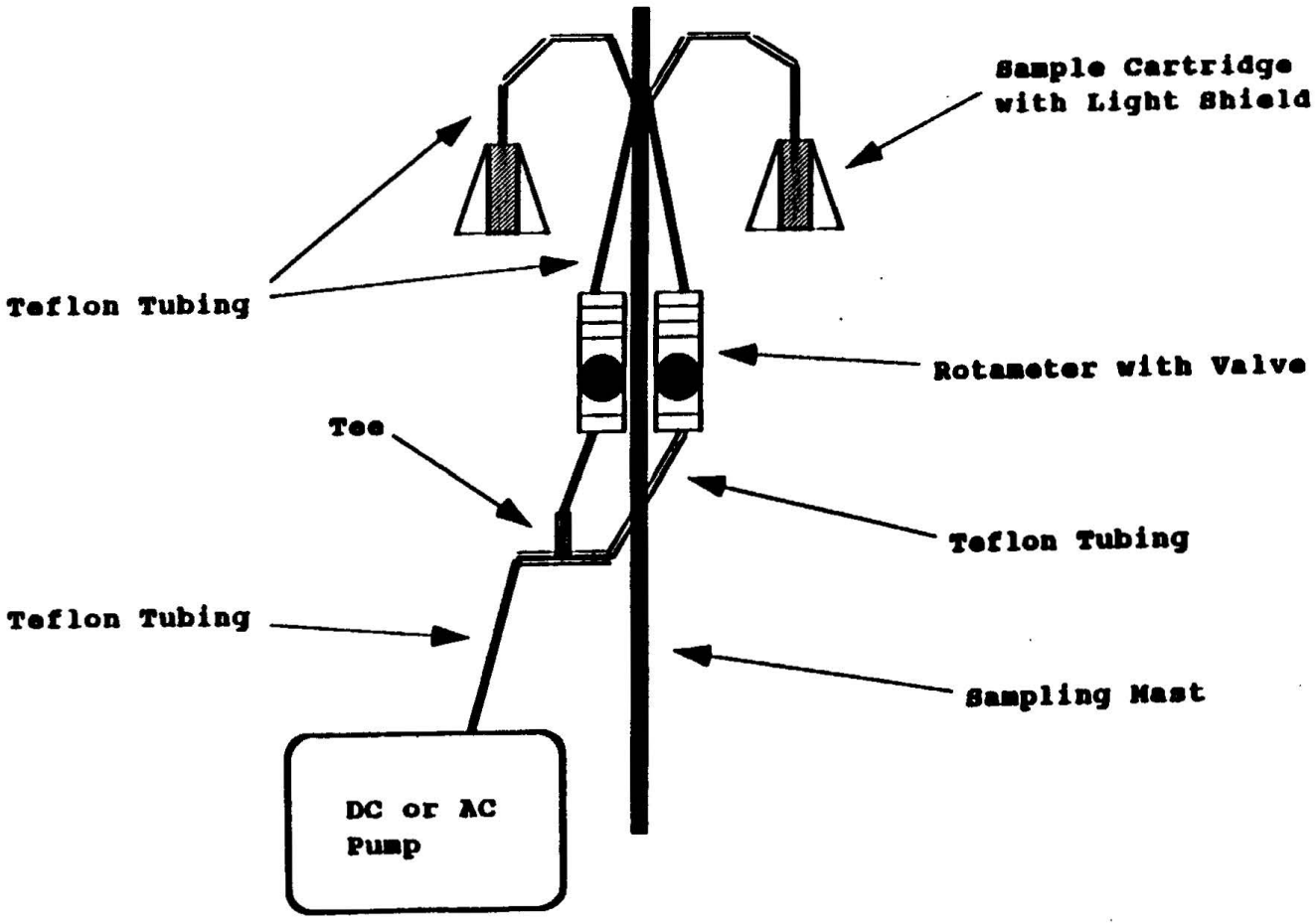


Figure 2 SAMPLING APPARATUS

A set of control samples were prepared and submitted to CSUF by Gabriel Ruiz (ARB) during the monitoring period. These were analyzed and the data returned to ARB for evaluation. During the evaluation of the data, it appeared that, while dichlorvos results were deemed acceptable, there may have been a problem with one of the naled standards used to either prepare or analyze the controls. Portions of each of the neat standards from ARB and CSUF were compared at both ARB and CSUF. The ARB neat standard used to prepare the controls was found to have 85% of the pesticide concentration of the CSUF stock used for analysis of the samples. A stock remade from the CSUF neat standard was within 5% of the stock standard used for the sample analysis.

New controls were prepared and analyzed against the ARB standard used to prepare the controls. Three of the four controls ranged from 79-104% recovery. During the extraction of the fourth control, which came out at only 68% recovery, a very small portion of the resin was lost when the tube was opened. This may account for the lower recovery on this sample.

A number of parameters were studied as part of the method validation. These include storage stability, extraction efficiencies, and retention efficiencies. A summary of the method validation data are presented in Table 5. Appendix D contains the complete validation data.

Sample stability was evaluated under field and laboratory storage conditions. Field conditions were simulated by placing capped spiked sampling tubes in resealable plastic bags in ice chests on ice. Samples were analyzed in triplicate after three, seven, and ten days. Laboratory storage stability was evaluated by placing capped spiked sampling tubes in resealable plastic bags in the laboratory sample freezer. Samples were analyzed in triplicate (except 14 day samples which were analyzed in duplicate) at three, seven, fourteen, twenty-one, and eighty day intervals.

Ice chest stability samples showed increasing degradation for naled over the ten day period, beginning with 73.1% recovery at 3 days and ending with 59.3% recovery at 10 days. Dichlorvos on the other hand, showed a corresponding increase in recovery over the same period (67.5% at 3 days, to 91.1% at 10 days). This observation is in line with the expected degradation of naled to dichlorvos. The low recovery of both naled and dichlorvos at three days may indicate some degradation of both compounds under these storage conditions.

Naled and dichlorvos stability under freezer storage showed a slight degradation during the first three weeks without a clear trend of continuing degradation. Recovery values fell in a range of 88.1% to 95.9% for dichlorvos and 82.1% to 97.8% for naled. The eighty day samples dropped to 73.0% for naled with an accompanying increase in dichlorvos to 108.7%.

Retention efficiencies on the sample collection medium were run at three fortification levels along with unfortified media to measure background. These studies were run by pulling ambient air through the fortified and blank resins at the same flow and duration to be used during sampling.

TABLE 5: VALIDATION SUMMARY					
		AVERAGE PERCENT RECOVERY			
		DICHLORVOS		NALED	
IDENTIFICATION	FORT. LEVEL	% RECOVERY	STD DEV.	% RECOVERY	STD DEV.
STABILITY STUDY					
3-day freezer	1.0 μg	95.9	6.7	98.7	13.7
7-day freezer	1.0 μg	85.5	3.5	88.6	3.5
14-day freezer	1.0 μg	94.2	0.6	82.1	2.5
21-day freezer	1.0 μg	88.1	2.4	92.8	9.9
80-day freezer	0.5 μg	108.7	10.3	73	4.5
3-day ice chest	1.0 μg	67.5	21.4	73.1	16.4
7-day ice chest	1.0 μg	85.3	2.7	69.8	1.8
10-day ice chest	1.0 μg	91.1	8.9	59.3	2.62
7-day rm.temp.	0.5 μg	48.7	*	0	*
RETENTION EFFICIENCIES					
	0.2 μg	103.1	27.9	120.1	42.6
	0.5 μg	79.9	1.0	182.5	6.6
	1.0 μg	108.0	48.3	105.4	0.6
EXTRACTION EFFICIENCIES					
	0.2 μg	113.4	8.1	128.6	5.7
	1.0 μg	111.8	10.5	88.5	3.4
	2.0 μg	94.9	6.3	87.8	5.8
	12.3/15.0 μg	118.1	*	99.9	*
*No Replicate Values					

Blank resins under these conditions indicated no interfering background. Average recovery from the spiked resins were 103.1%, 79.9% and 108.0% for 02 μg, 05 μg, and 10 μg respectively.

Two breakthrough samples were prepared at 12.3 to 21.0 μg for each compound. These had ambient air drawn through them for 24 hours at 4 *L/min* and the back-up sections of resin were analyzed for breakthrough. No naled was found in either backup section. No dichlorvos was identified in the sample spiked at 21.0 μg dichlorvos. The 12.3 μg spike showed a small amount

of breakthrough (0.52 μg). Since the levels found in the monitoring samples were at least two orders of magnitude lower than the levels used to prepare the breakthrough spikes, no breakthrough would be expected in the samples.

RESULTS AND DISCUSSION

Four of the sites, including the background site, had positive results for naled or dichlorvos during some portion of the ambient monitoring period. Results ranged from below the detection limit to a high of 0.059 $\mu g/m^3$ for dichlorvos at Kaweah High School, and 0.082 $\mu g/m^3$ for naled at Jefferson Elementary School. The UC Field Station at Lindcove is the only site which did not have detectable levels for either naled or dichlorvos.

Detectable levels for the two study compounds were found in samples taken between May 20, 1991 and May 30, 1991 at three of the sites (Sunnyside Union Elementary, Jefferson Elementary, and Kaweah High Schools). At a fourth site, the Visalia background site, low levels were found between May 30, 1991 and June 4, 1991. In addition, samples which contained detectable levels for either naled or dichlorvos were clustered together on consecutive samples. The only sample not following this pattern was the sample taken on May 30 at Kaweah High School. This sample was separated from the previous positive sample by two sampling days.

In three pairs of data from collocated samples one sample was significantly above the detection limit for naled while naled was not detected in the duplicate. In the samples taken on May 22 at Kaweah High School one sample was 0.052 $\mu g/m^3$ while the duplicate was reported below the detection limit. The chromatogram of this sample shows a peak at the naled retention time which is detectable but below a reliable quantitation limit.

The remaining two sample pairs do not have detectable levels of naled or dichlorvos in sample 2, though both compounds were detected in sample 1. The levels found in these samples (0.065 $\mu g/L$ and 0.077 $\mu g/L$) were near the detection limit of 0.04 $\mu g/mL$ where relative variability in duplicates is normally higher. Confidence in these values is increased by the fact that all positive results occur within a period of a few days during the monitoring period.

One additional collocated pair sampled May 23, 1991 at Jefferson Elementary differed by 0.039 $\mu g/m^3$ for naled, a relative percent difference of 62 percent. The quality assurance plan approved for this project requires precision to fall within an amount less than or equal to the detection limit for values up to five times the detection limit. For naled this would allow a difference of 0.04 $\mu g/m^3$ for values up to 2.0 $\mu g/m^3$. The collocated duplicates in this case fall within the allowable limits.

The Lindcove sampling site is elevated slightly above the valley floor at the beginning of the foothills to the Sierra Nevada Mountain Range. This location typically has air movement downslope during the morning hours and upslope later in the day. The effect of this air movement on pesticide detection during the study has not been determined.

Application of naled within approximately one mile of the monitoring sites was confirmed by pesticide use reports from the Tulare County Agricultural Commissioner's office. Near the end of the sampling period, the pesticide Baythroid, a synthetic pyrethroid insecticide, was substituted for naled since naled was not effectively eradicating citrus thrips.

CONCLUSIONS

All data presented in this report for naled and dichlorvos have been determined and accepted subject to a rigorous quality assurance program.

Detectable levels of naled and dichlorvos were identified at four of the five monitoring sites, including the background site. At three of these sites (Sunnyside, Jefferson, and Kaweah) levels above the MDL generally occurred between May 20 and May 23, 1991. Detectable levels were found at the background site between May 30 and June 4, 1991.

The Lindcove Field Station is planted to citrus, including oranges, with other orange groves nearby. None of the study pesticides were applied at the UC Lindcove Field Station during the study. No naled or dichlorvos was detected at the Lindcove Field Station sampling site during the monitoring period. On the other hand, both naled and dichlorvos were detected at the Visalia site which was the "background" site.

Since naled is not a restricted use pesticide, possible application in or near Visalia other than for oranges may have led to detectable levels at the background site between May 30 and June 4, 1991.

APPENDIX A

Naled and Dichlorvos in Air ($\mu g/m^3$)

Naled and Dichlorvos in Air ($\mu g/m^3$)

	Sunnyside Union Elementary				Jefferson Elementary School			
	Dichlorvos		Naled		Dichlorvos		Naled	
Date	1	2	1	2	1	2	1	2
09-May-91	ND		ND		ND		ND	
13-May-91	ND	ND	ND	ND	ND		ND	
14-May-91	ND	ND	ND	ND	ND		ND	
15-May-91	ND	ND	ND	ND	ND		ND	
16-May-91	ND	ND	ND	ND	ND		ND	
20-May-91	ND	ND	ND	ND	0.020	ND	ND	ND
21-May-91	0.023	ND	ND	ND	0.024	0.024	ND	ND
22-May-91	ND	0.029	ND	0.065	0.023	ND	0.040	ND
23-May-91	0.052	0.049	0.059	0.055	0.023	0.025	0.082	0.043
28-May-91	ND		ND		ND		ND	
29-May-91	ND		ND		ND		ND	
30-May-91	ND		ND		ND	ND	ND	ND
03-Jun-91	ND		ND		ND		ND	
04-Jun-91	ND		ND		ND		ND	
05-Jun-91	ND		ND		ND		ND	
06-Jun-91	ND		ND		ND		ND	

	Kaweah High School				UC Lindcove Field Station			
	Dichlorvos		Naled		Dichlorvos		Naled	
Date	1	2	1	2	1	2	1	2
09-May-91	ND		ND		ND		ND	
13-May-91	ND		ND		ND		ND	
14-May-91	ND		ND		ND		ND	
15-May-91	ND		ND		ND		ND	
16-May-91	ND		ND		ND		ND	
20-May-91	0.049	0.029	0.052	0.067	ND		ND	
21-May-91	0.023	ND	ND	0.042	ND		ND	
22-May-91	0.021	ND	0.052	ND	ND		ND	
23-May-91	ND	ND	0.040	ND	ND		ND	
28-May-91	ND	ND	ND	ND	ND		ND	
29-May-91	ND	ND	ND	ND	ND		ND	
30-May-91	0.059	0.059	0.054	0.051	ND		ND	
03-Jun-91	ND		ND		ND	ND	ND	ND
04-Jun-91	ND		ND		ND	ND	ND	ND
05-Jun-91	ND		ND		ND	ND	ND	ND
06-Jun-91	ND	ND	ND	ND	ND	ND	ND	ND

	ARB Monitoring Station, Visalia (Background)			
	Dichlorvos		Naled	
Date	1	2	1	2
09-May-91	ND		ND	
13-May-91	ND		ND	
14-May-91	ND		ND	
15-May-91	ND		ND	
16-May-91	ND		ND	
20-May-91	ND		ND	
21-May-91	ND		ND	
22-May-91	ND		ND	
23-May-91	ND		ND	
28-May-91	ND		ND	
29-May-91	ND		ND	
30-May-91	0.029	ND	0.077	ND
03-Jun-91	0.023	ND	ND	ND
04-Jun-91	0.024	0.028	0.062	0.059
05-Jun-91	ND	ND	ND	ND
06-Jun-91	ND	ND	ND	ND

Limit of quantitation

Dichlorvos = 0.02 ug/m^3

Naled = 0.04 ug/m^3

APPENDIX B

Naled Ambient Monitoring - Tulare County

Sample Collection Data

Naled Ambient Monitoring -- Tulare County

SAMPLE COLLECTION DATA							
	Start		End				
FIELD ID	Date	Time	Date	Time	Sampling Period (h)	Flow (1pm)	Volume (m^3)
0 S	09-May-91	9:00	10-May-91	8:15	23.3	3.9	5.441
0 J	09-May-91	9:50	10-May-91	8:30	22.7	3.9	5.304
0 K	09-May-91	11:00	10-May-91	9:10	22.2	3.9	5.187
0 UC	09-May-91	15:15	10-May-91	9:00	17.8	3.9	4.154
0 B	09-May-91	11:45	10-May-91	9:30	21.8	3.9	5.090
1 S	13-May-91	10:30	14-May-91	9:25	22.9	3.9	5.363
1 J	13-May-91	10:45	14-May-91	9:40	22.9	3.9	5.363
1 UC	13-May-91	11:15	14-May-91	10:20	23.1	3.9	5.402
1 K	13-May-91	11:30	14-May-91	10:35	23.1	3.9	5.402
1 B	13-May-91	11:50	14-May-91	10:55	23.1	3.9	5.402
2 S	14-May-91	9:25	15-May-91	9:35	24.2	3.9	5.655
2 J	14-May-91	9:40	15-May-91	9:50	24.2	3.9	5.655
2 UC	14-May-91	10:20	15-May-91	10:40	24.3	3.9	5.694
2 K	14-May-91	10:35	15-May-91	10:15	23.7	3.9	5.538
2 B	14-May-91	10:55	15-May-91	11:40	24.8	3.9	5.792
3 S	15-May-91	9:35	16-May-91	9:30	23.9	3.9	5.597
3 J	15-May-91	9:50	16-May-91	9:45	23.9	3.9	5.597
3 UC	15-May-91	10:40	16-May-91	10:15	23.6	3.9	5.519
3 K	15-May-91	10:15	16-May-91	10:25	24.2	3.9	5.655
3 B	15-May-91	11:40	16-May-91	10:55	23.3	3.9	5.441
4 S	16-May-91	9:30	17-May-91	9:50	24.3	3.9	5.694
4 J	16-May-91	9:45	17-May-91	10:10	24.4	3.9	5.714
4 UC	16-May-91	10:15	17-May-91	10:40	24.4	3.9	5.714
4 K	16-May-91	1:25	17-May-91	10:50	33.4	3.9	7.820

Key: S= Sunnyside Elementary School, J= Jefferson Elementary School, K= Kaweah High School, UC= University of California Lindcove Field Station, B= Ambient Air Monitoring Station, Visalia (background).

SAMPLE COLLECTION DATA							
	Start		End				
FIELD ID	Date	Time	Date	Time	Sampling Period (h)	Flow (1pm)	Volume (m^3)
4 B	16-May-91	10:55	17-May-91	11:15	24.3	3.9	5.694
5 S	20-May-91	10:20	21-May-91	9:30	23.2	3.9	5.421
5 J	20-May-91	10:35	21-May-91	9:50	23.3	3.0	5.441
5 UC	20-May-91	11:00	21-May-91	11:05	24.1	3.9	5.636
5 K	20-May-91	11:15	21-May-91	10:50	23.6	3.9	5.519
5 B	20-May-91	11:35	21-May-91	10:25	22.8	3.9	5.343
6 S	21-May-91	9:30	22-May-91	9:30	24.0	3.9	5.616
6 J	21-May-91	9:50	22-May-91	9:50	24.0	3.9	5.616
6 UC	21-May-91	11:05	22-May-91	11:05	24.0	3.9	5.616
6 K	21-May-91	10:50	22-May-91	10:50	24.0	3.9	5.616
6 B	21-May-91	10:25	22-May-91	10:25	24.0	3.9	5.616
7 S	22-May-91	9:30	23-May-91	9:30	24.0	3.9	5.616
7 J	22-May-91	9:50	23-May-91	9:45	23.9	3.9	5.597
7 UC	22-May-91	11:05	23-May-91	11:00	23.9	3.9	5.597
7 K	22-May-91	10:50	23-May-91	10:45	23.9	3.9	5.597
7 B	22-May-91	10:25	23-May-91	10:15	23.8	3.9	5.577
8 S	23-May-91	9:30	24-May-91	9:20	23.8	3.9	5.577
8 J	23-May-91	11:00	24-May-91	9:35	22.6	3.9	5.285
8 UC	23-May-91	10:45	24-May-91	10:00	23.3	3.9	5.441
8 K	23-May-91	10:15	24-May-91	10:10	23.9	3.9	5.597
8 B	23-May-91	10:30	24-May-91	10:30	24.0	3.9	5.616
9 S	28-May-91	10:35	29-May91	9:25	22.8	3.9	5.343
9 J	28-May-91	10:56	29-May-91	9:45	22.8	3.9	5.339
9 UC	28-May-91	11:20	29-May-91	10:10	22.8	3.9	5.343
9 K	28-May-91	11:33	29-May91	10:25	22.9	3.9	5.351
9 B	28-May-91	11:57	29-May-91	10:55	23.0	3.9	5.374

Key: S= Sunnyside Elementary School, J= Jefferson Elementary School, K= Kaweah High School, UC= University of California Lindcove Field Station, B= Ambient Air Monitoring Station, Visalia (background).

SAMPLE COLLECTION DATA							
	Start		End				
FIELD ID	Date	Time	Date	Time	Sampling Period (h)	Flow (lpm)	Volume (m^3)
10 S	29-May-91	9:25	30-May-91	9:28	24.1	3.9	5.628
10 J	29-May-91	9:45	30-May-91	9:46	24.0	3.9	5.620
10 UC	29-May-91	10:10	30-May-91	10:15	24.1	3.9	5.636
10 K	29-May-91	10:25	30-May-91	10:33	24.1	3.9	5.647
10 B	29-May-91	10:50	30-May-91	11:00	24.2	3.9	5.655
11 S	30-May-91	9:28	31-May-91	9:20	23.9	3.9	5.585
11 J	30-May-91	9:46	31-May-91	9:35	23.8	3.9	5.573
11 UC	30-May-91	10:15	31-May-91	10:10	23.9	3.9	5.597
11 K	30-May-91	10:33	31-May-91	9:55	23.4	3.9	5.468
11 B	30-May-91	11:00	31-May-91	10:35	23.6	3.9	5.519
12 S	03-Jun-91	9:55	04-Jun-91	9:30	23.6	3.9	5.519
12 J	03-Jun-91	10:15	04-Jun-91	9:40	23.4	3.9	5.480
12 UC	03-Jun-91	10:50	04-Jun-91	10:20	23.5	3.9	5.599
12 K	03-Jun-91	10:40	04-Jun-91	10:05	23.4	3.9	5.480
12 B	03-Jun-91	11:26	04-Jun-91	10:55	23.5	3.9	5.495
13 S	04-Jun-91	9:30	05-Jun-91	9:25	23.9	3.9	5.597
13 J	04-Jun-91	9:40	05-Jun-91	9:55	24.3	3.9	5.675
13 UC	04-Jun-91	10:20	05-Jun-91	10:35	24.3	3.9	5.675
13 K	04-Jun-91	10:05	05-Jun-91	10:21	24.3	3.9	5.678
13 B	04-Jun-91	10:55	05-Jun-91	11:10	24.3	3.9	5.675
14 S	05-Jun-91	9:25	06-Jun-91	9:30	24.1	3.9	5.636
14 J	05-Jun-91	9:55	06-Jun-91	9:50	23.9	3.9	5.597
14 UC	05-Jun-91	10:35	06-Jun-91	10:25	23.8	3.9	5.577
14 K	05-Jun-91	10:20	06-Jun-91	10:10	23.8	3.9	5.577
14 B	05-Jun-91	11:10	06-Jun-91	11:00	23.8	3.9	5.577
15 S	06-Jun-91	9:30	07-Jun-91	9:10	23.7	3.9	5.538

Key: S= Sunnyside Elementary School, J= Jefferson Elementary School, K= Kaweah High School, UC= University of California Lindcove Field Station, B= Ambient Air Monitoring Station, Visalia (background).

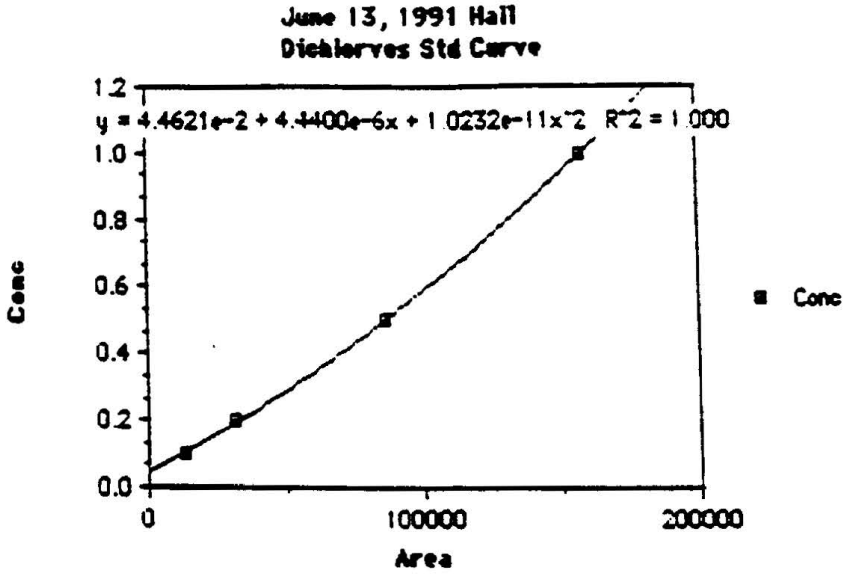
SAMPLE COLLECTION DATA							
	Start		End				
FIELD ID	Date	Time	Date	Time	Sampling Period (h)	Flow (1pm)	Volume (m^3)
15 J	06-Jun-91	9:50	07-Jun-91	9:30	23.7	.9	5.538
15 UC	06-Jun-91	10:25	07-Jun-91	10:10	23.8	3.9	5.558
15 K	06-Jun-91	10:10	07-Jun-91	9:55	23.8	3.9	5.558
15 B	06-Jun-91	11:00	07-Jun-91	10:45	23.8	3.9	5.558

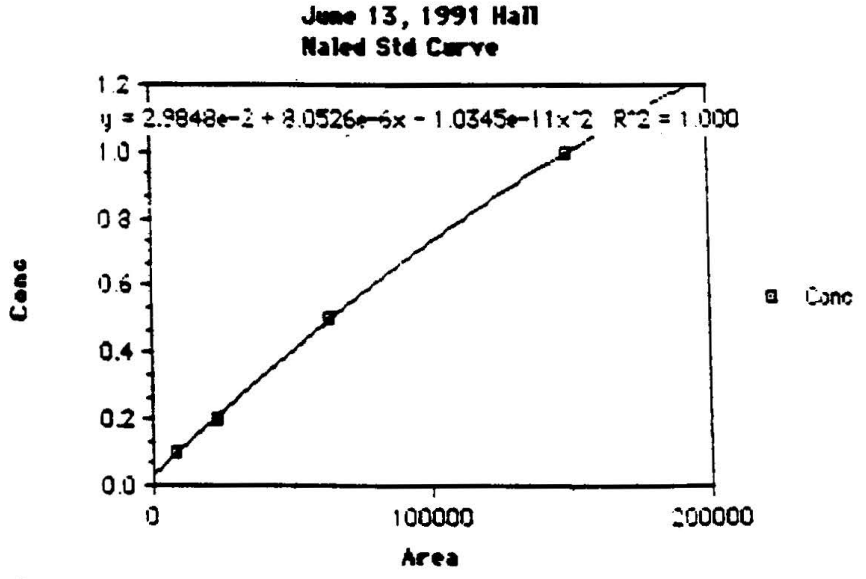
Key: S= Sunnyside Elementary School, J= Jefferson Elementary School, K= Kaweah High School, UC= University of California Lindcove Field Station, B= Ambient Air Monitoring Station, Visalia (background).

APPENDIX C

Standard Curves

STANDARD CURVES DICHLORVOS AND NALED

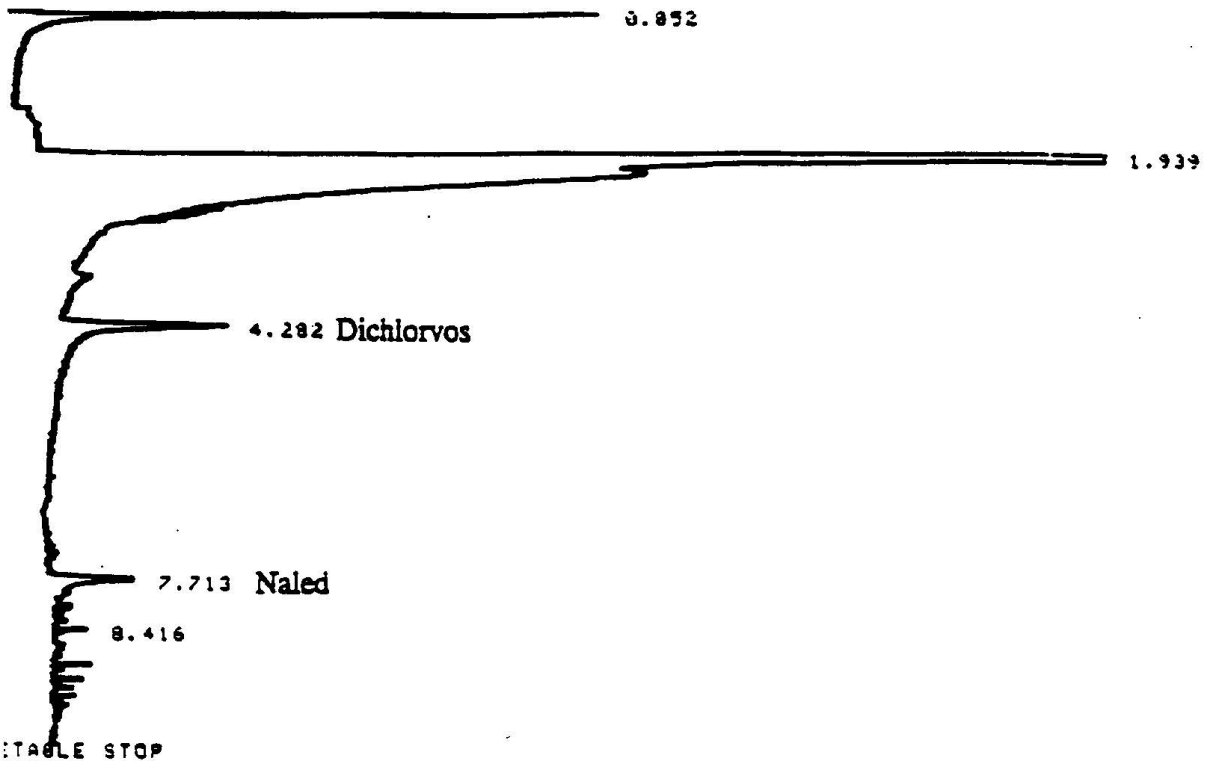




WORKING STANDARD DICHLORVOS AND NALED 0.1 µg/mL

UN # 547 JUN 13, 1991 10:48:57

T



:TABLE STOP

) 547 JUN 13, 1991 10:48:57

HALL DETECTOR

%%

RT	AREA	TYPE	WIDTH	AREA%
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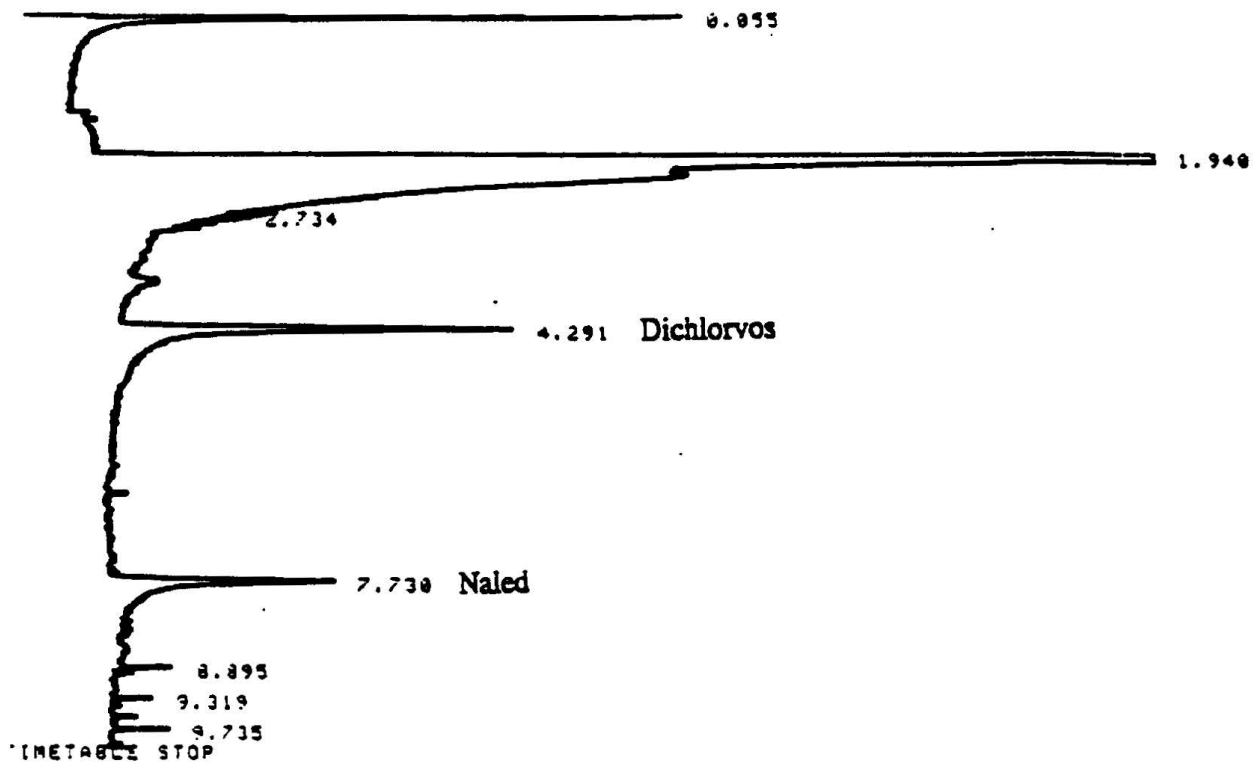
1.939	314899	PB	.030	88.51149
4.282	12968	PV	.088	3.64583
7.713	7980	PV	.184	2.24301
8.416	771	PV	.022	.21671

AL AREA= 355772
FACTOR=1.0000E+00

WORKING STANDARD DICHLORVOS AND NALED 0.2 µg/mL

RUN # 546 JUN 13, 1991 10:36:46
START



TIMETABLE STOP

RUN# 546 JUN 13, 1991 10:36:46

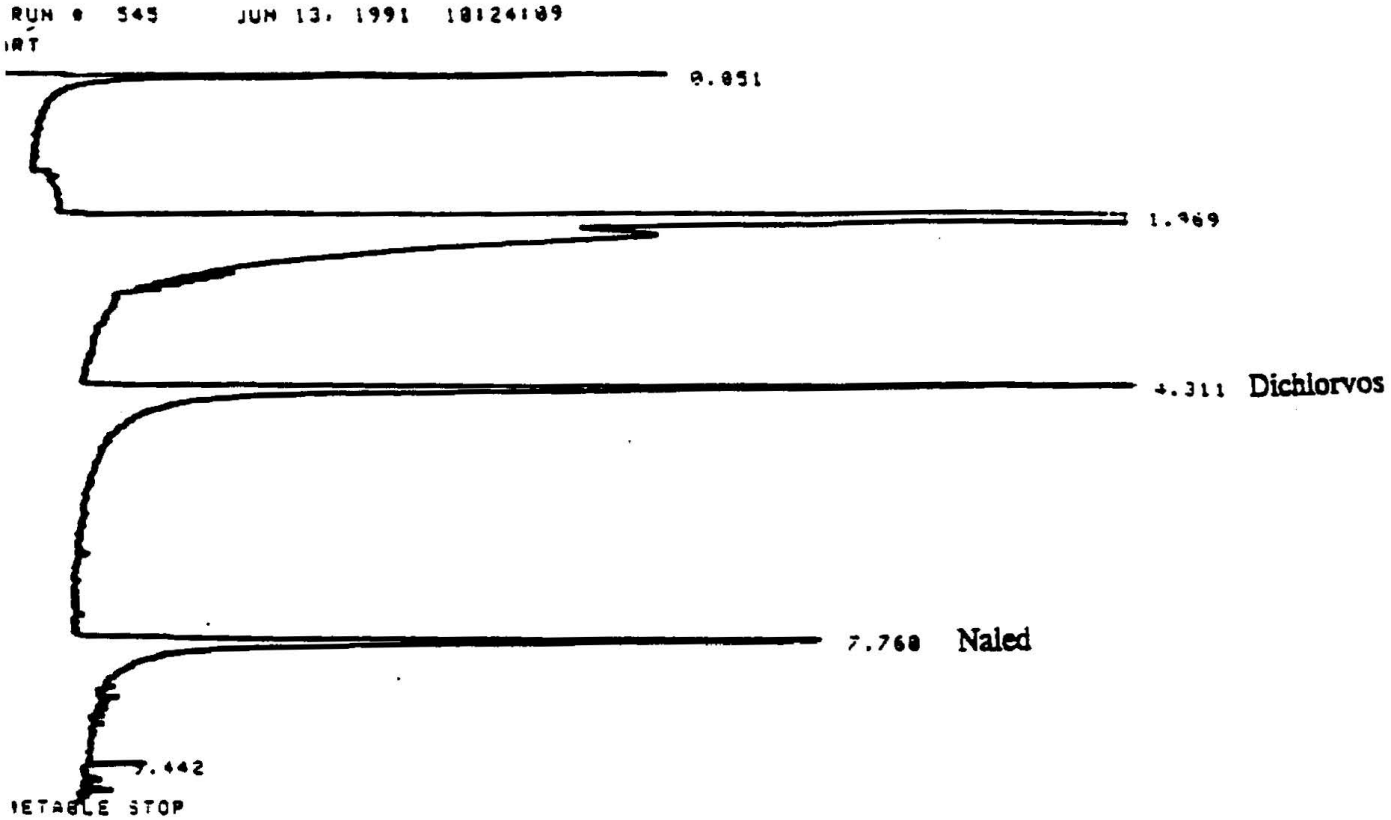
FOA HALL DETECTOR

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.855	18955	PB	.835	5.83277
1.940	246738	PB	.827	75.92544
2.734	1612	PB	.844	.49604
4.291	31375	BB	.889	9.65462
7.730	23069	PV	.112	7.09972
8.895	1240	PP	.823	.38157
9.319	826	PP	.820	.25417
9.735	1159	PB	.822	.35664

TOTAL AREA= 324974
MUL FACTOR=1.0000E+00

WORKING STANDARD DICHLORVOS AND NALED 0.5 µg/mL



545 JUN 13, 1991 10:24:09

HALL DETECTOR

EA%

RT	AREA	TYPE	WIDTH	AREA%
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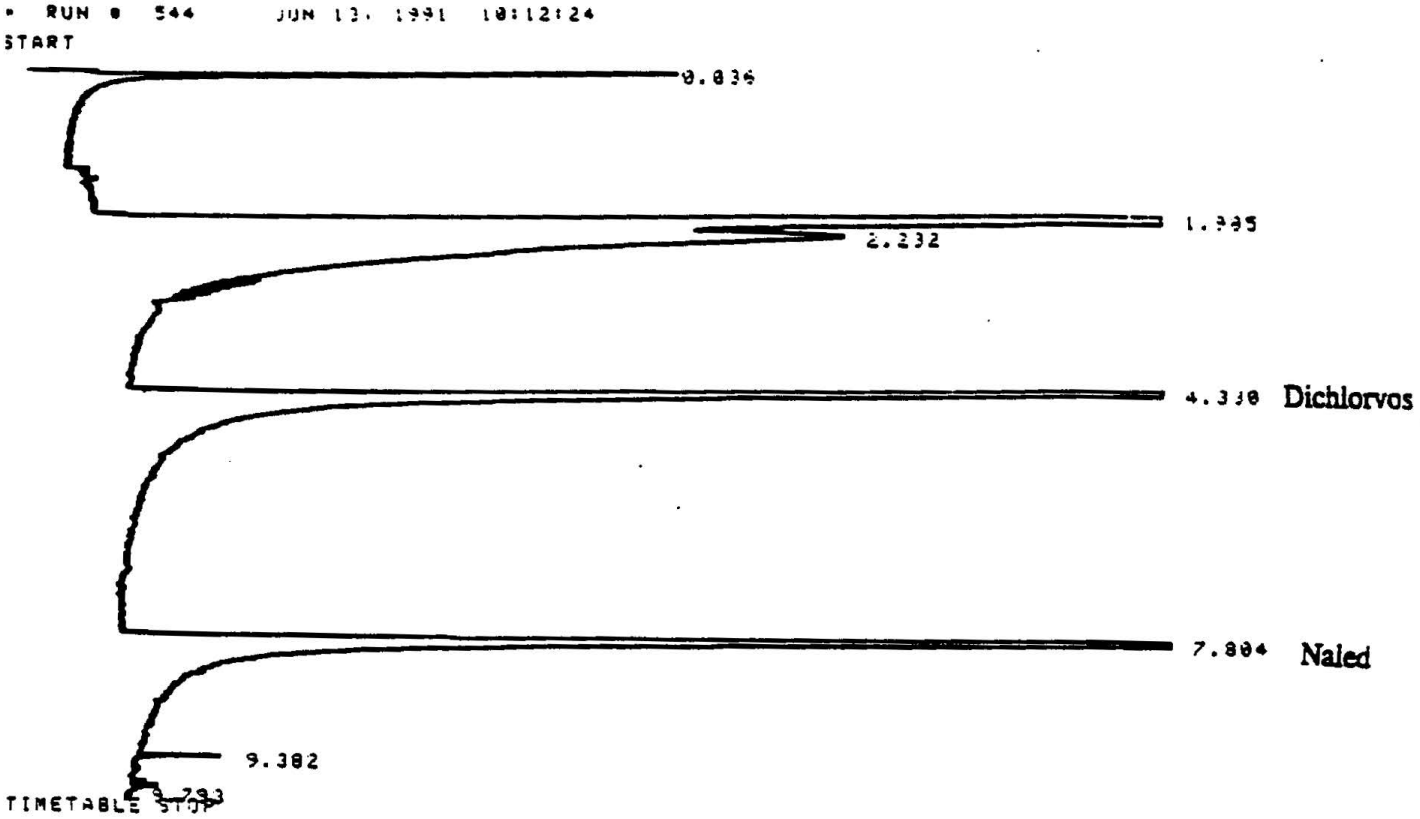
1.969	353967	PB	.840	67.69357
4.311	86085	PB	.889	16.46312
7.768	62976	PB	.896	12.04369
9.442	687	BB	.812	.13138

TAL AREA= 522896
. FACTOR=1.0000E+00

WORKING STANDARD DICHLORVOS AND NALED 1.0 µg/mL



RUN# 544 JUN 13, 1991 10:12:24

VOA HALL DETECTOR

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.836	22080	PB	.041	2.59480
1.385	361284	PV	.041	42.45739
2.232	158822	VB	.273	18.66446
4.338	157719	PB	.077	18.53483
7.804	149097	PB	.087	17.52159
9.382	1094	BP	.014	.12856
9.793	837	PB	.027	.09836

TOTAL AREA= 850933
MUL FACTOR=1.0000E+00

APPENDIX D

Quality Assurance Report

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

PETE WILSON, Governor

August 28, 1992

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

RE: Naled Monitoring Audit Report

Dear Ms. Royce:

Please find attached the final audit report on the Naled and Dichlorvos monitoring project conducted in Tulare County by the Engineering Research Institute and the ARB's Engineering Evaluation Branch in May of 1991. The report consists of the results of a field audit conducted on May 9, 1991, and the results of a system and analytical audit conducted between May 8 and June 18, 1991.

Thank you for reviewing the report prior to it finalization. The comments or changes suggested by you or your staff have been incorporated. If you have any questions, please contact Gabriel Ruiz of my staff at (916) 327-0885.

Sincerely,

Alice Westerinen

Alice Westerinen, Manager
Quality Assurance Section
Monitoring and Laboratory Division

Attachment

cc: Gabriel Ruiz

August 28, 1992

Audit Report
Naled and Dichlorvos Monitoring in Tulare County

SUMMARY

Field Audit

On May 9, 1991, staff of the Quality Assurance Section of the California Air Resources Board conducted a field audit of the five samplers used in the Naled and Dichlorvos air monitoring project 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. Sampling was conducted by staff of the Engineering Evaluation Branch.

The siting criteria were met in most cases. Four samplers were located within 20 meters of a tree dripline, but in all cases the distance between the sampler and the tree was more than twice the height that the tree protruded above the sampler. Also, the probe of the sampler at the University of California field station in Lindcove was only 1.8 meters above the ground, but it is our belief that the integrity of the samples was not compromised.

Although the field standard operating procedures were not documented, the records for field operations were appropriate and consistent with good practice. The flow rate audits resulted in an average percent difference of 3.6%, with individual differences ranging from 1.0% to 6.0%.

Laboratory Audit

An audit of the laboratory operations in support of the Naled and Dichlorvos monitoring project was conducted between May 8 and June 18. The laboratory audit was composed of both a system and an analytical performance audit. The system audit consisted of a review of 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 Naled and Dichlorvos by QA staff and submitted to the laboratory for analysis.

In general, good quality control practices were observed in the areas of method validation, sample analysis, sample documentation, and, to a lesser degree, data quality monitoring. Deficiencies were noted in the storage conditions of the field samples and the monitoring of sample recoveries; the integrity of the samples was probably compromised by the storage conditions, but the situation was not detected because field spikes were not included in the study. Field blanks were not included either, but sample contamination problems were not apparent.

The samples for the analytical performance audit were prepared on May 23 and analyzed on May 30. The results for Dichlorvos averaged -11.3 percent difference, with a range of -24.6% to 10.8%. The Naled results showed a negative bias averaging -77.0% and ranging from -83.3% to -74.0%, probably because of Naled breakdown.

Further tests were conducted to investigate the possibility of Naled breakdown. Replicate sets of audit samples were analyzed after two and seven days in storage. The average percent differences were -25.7% with a range of -38.4% to -10.7%, and -57.4% with a range of -75.9% to -35.7%, respectively.

In the initial stability study, Naled samples were stored in a freezer at -10°C for 3, 7, 14, and 21 days, and the average recovery rates were 97.8%, 88.6%, 82.1%, and 92.8%, respectively. A second study was conducted after the monitoring operations were completed. The Naled samples were stored in an ice chest for 3, 7, and 10 days, and the average recovery rates were 73.1%, 69.8%, and 59.3%, respectively.

FIELD AUDIT

On May 9, 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 Naled and Dichlorvos 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). The flow of each sampling apparatus was audited with a mass flow meter traceable to the National Institute of Standards and Technology (NIST).

Sampler Siting

The five monitoring sites were located at the ARB air monitoring station in Visalia, the Kaweah 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 EEB staff, following the guidelines specified in the Quality Assurance Plan for Pesticide Monitoring.

The samplers at all sites, except at the Kaweah High School, 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. The sampler at the University of California field station in Lindcove was installed on the ground, and the probe's height was only 1.8 meters. 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. No other deviations from the siting criteria were observed (Table 1).

Table 1. Summary of the samplers' conformance with the siting criteria.

Site Location	Height from Ground 2-15 meters	Distance from Supporting Structure		20 meters from tree dripline	Distance from obstacles larger than two time the height the obstacle protrudes above the sampler	Unrestricted airflow 270 degrees around the sampler	10 meters from incineration flues
		Vertical 1 meter	Horizontal 1 meter				
Visalia-ARB Monitoring Station 310 N. Church Street Visalia, CA	Yes	Yes	Yes	No [1]	Yes	Yes	Yes
Kaweah High School 21215 Avenue 300 Exeter, CA	Yes	Yes	Yes	Yes	Yes	Yes	Yes
U.C. Field Station - Lindcove 22963 Carson Avenue Exeter, CA	No [2]	Yes	Yes	No [3]	Yes	Yes	Yes
Jefferson Elementary School 333 Westwood Avenue Lindsay, CA	Yes	Yes	Yes	No [4]	Yes	Yes	Yes
Sunnyside Union Elementary School 21644 Avenue 196 Strathmore, CA	Yes	Yes	Yes	No [5]	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 probe was about 1.8 m from ground.
3. Sampler was 18.5 m from tree dripline. The tree protruded about 0.5 m above the sampler's probe.
4. Sampler was 15.5 m from tree dripline. The tree protruded about 6 m above the sampler's probe.
5. 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 Jack Rogers of the MLD's Engineering Evaluation Branch (EEB). 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 tubes were covered with aluminum foil to protect them from sunlight.

A single-point calibration of the rotameters was performed by the EEB staff by setting the flow rate at 4.0 liters per minute (lpm) and measuring the actual flow with a bubble meter. The samplers were then set up in the field, and the flow rates were reset to 4.0 lpm.

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 standard operating procedures were not documented, but the records for field operations were appropriate and consistent with good practice.

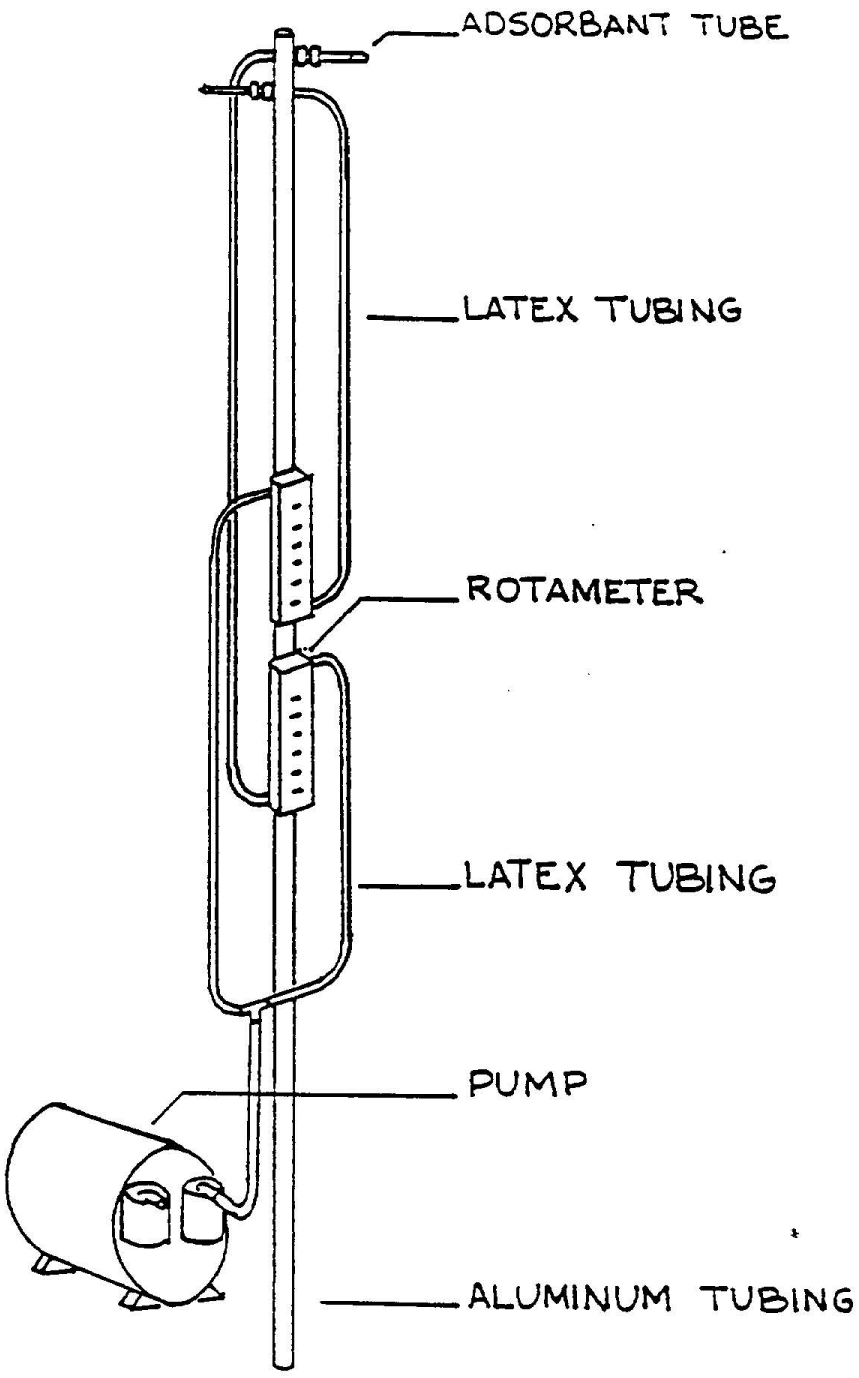


Figure 1. Naled Sampler

Flow Rate Audits

Flow rate audits were conducted with a 0-10 lpm mass flow meter traceable to the NIST and performed according to the procedures outlined in Attachment I. The mass flow meter was certified against a primary standard Brooks automatic flow rate calibrator, model 1050. Results of the flow audits are summarized in Table II. A small bias, averaging 3.6% and ranging from 1.0% to 6.0% was observed in the audit results.

Table II. Results of the Sampler Flow Audits

Site	Rotameter Number	Reported Flow, (lpm)	True Flow, (lpm)	Percent Difference*
Visalia - ARB	20	3.9	3.78	3.2
	9	3.9	3.76	3.7
Kaweah High School	2	3.9	3.75	4.0
	34	3.9	3.68	6.0
U.C. Field Station	19	3.9	3.86	1.0
	18	3.9	3.73	4.6
Jefferson Elementary School	44	3.9	3.81	2.4
	21	3.9	3.81	2.4
Sunnyside Union Elementary School	17	3.9	3.71	5.1
	45	3.9	3.75	4.0

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

LABORATORY AUDIT

A system audit of the Engineering Research Institute's laboratory operations in support of the Naled and Dichlorvos monitoring project was conducted between May 8 and June 18, 1991, 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 for 24-hour periods and stored inside individual screw cap glass culture tubes in an ice chest. The samples were delivered to the laboratory on Friday of each week. The samples were extracted on the day they were received and then stored in a freezer at -10°C. Analyses were peformed within one week, and 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 with a Hall Electrolytic Conductivity Detector. 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 documented in a preliminary draft entitled "Standard Operating Procedures for the Determination of Naled and Dichlorvos 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 0.2 ug total mass for both compounds, 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.

The method recovery rates averaged 101.2% for Naled and 109.6% for Dichlorvos for samples ranging in size from 0.2 ug to 15 ug. A sample stability study was conducted for a set of samples containing 1.0 ug Naled and 1.0 ug Dichlorvos stored in a freezer at -10°C for 3, 7, 14, and 21 days. The average recovery rates for Naled were 97.8%, 88.6%, 82.1% and 92.8%, respectively. The recovery rates for Dichlorvos were 95.9%, 85.5%, 94.2%, and 88.1%, respectively. Breakthrough of the two compounds was investigated for mass loads in excess of 100 ug.

Quality control activities performed routinely to monitor and document the data quality included the following: daily calibration at four points over the 0.1 to 1.0 ug/ml range, 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, and replicate analyses of 5% of the samples. In addition, two laboratory spikes and two solvent blanks were analyzed during the study, and analyses of some samples showing a positive response were repeated. Qualitative confirmations were made for Naled with an Electron Capture Detector. The study did not include any field blanks or field spikes.

Documentation

The ERI's laboratory staff followed the chain-of-custody procedures established by the EEB. 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 known amounts of Dichlorvos and Naled. The samples were prepared by Gabriel Ruiz on May 23, 1991, following the procedures outlined in Attachment II. The samples were stored in a freezer until May 28. They were then transported to the field in an ice chest, where they were kept with other field samples until they were delivered to the laboratory on May 30. The samples were analyzed on May 30, following the laboratory's standard operating procedures.

The analytical results for Dichlorvos showed a random distribution of percent differences averaging -11.3% and ranging from -24.6% to 10.8% (Table III). The Naled results, however, showed a relatively large negative bias averaging -77.0% and ranging from -83.3% to -74.0% (Table IV). An investigation was initiated to determine the source of the bias.

To investigate the possibility of Naled breakdown in the sample tubes, two replicate sets of spiked samples were prepared and delivered to the ERI laboratory on July 8, 1991. The samples from the first set were extracted on July 9 and analyzed on July 10. The results of the analysis showed a negative bias averaging -25.7% and ranging from -38.4% to -10.7% (Table V). The samples in the second set were stored in an ice chest until July 15, when they were extracted and analyzed. The results showed a negative bias averaging -57.4% and ranging from -75.9% to -35.7% (Table VI).

Also, the purity of the Naled neat compound and the concentration of the spiking standard used to prepare the audit samples were verified by ERI by running comparative analyses against their standards. Two 0.5 ppm solutions were prepared from QA's neat compound and spiking standard and compared against ERI's original and a freshly made 0.5 ppm calibration standard. While the results for the QA solutions showed a negative bias (Table VII), the percent difference was only -12% for the neat compound and -20% for the spiking standard. The difference between the neat compounds could be the result of method variability, and in the case of the spiking standard, breakdown of Naled in the QA sample may have been a factor.

The results of the tests supported the hypothesis of Naled breakdown, so the ERI was asked to conduct further stability studies for Naled samples stored in an ice chest. Nine replicate samples, each containing 1.0 ug of Naled, were stored in an ice chest and were analyzed after three, seven, and ten days. The average percent recovery dropped from an initial rate of 88.5% to 73.1% after 3 days, 69.8% after 7 days, and 59.3% after 10 days (Table VIII). By contrast, the average recovery rates for the initial stability study, in which samples were stored in a freezer at -10°C, were 97.8% after 3 days, 88.6% after 7 days, and 82.1% after 14 days (see above).

CONCLUSIONS

In general, good quality control practices were followed throughout the study. The only deficiencies noticed were the lack of written field SOPs, the exclusion of field blanks and field spikes, and the failure to duplicate the actual sample storage conditions during the initial stability study.

The results suggest that the storage conditions of the field samples may have had an adverse effect on their integrity, causing the degradation of Naled. Therefore, the actual Naled ambient concentrations are probably higher than the reported values. While the stability data was sufficient to indicate sample degradation, the Naled breakdown rate is not well characterized, and further studies may be necessary to make a better determination of the actual ambient concentration levels.

We recommend that the following steps be taken to improve the field and laboratory operations in future studies:

1. Field SOPs

   Written and approved field SOPs should be available to the sampling personnel. The SOPs should be followed routinely, and any deviations should be noted in the field data sheets.

2. Field Blanks

   Field blanks should be analyzed periodically to investigate post-sampling sources of contamination, such as container cleanliness or permeability, or transportation effects.

3. Field Spikes

   Whenever possible, field spikes should be included with the weekly batch of samples submitted to the laboratory to monitor sample recovery. The percent recovery should fall within the limits of method variability.

4. Stability Study

   Stability studies should be conducted under conditions that duplicate the actual sample storage environment to determine the length of time that samples can be held without compromising their integrity. The percent recovery for the longest storage time should fall within the limits of method variability.

Table III. Results of ERI's analyses of Dichlorvos audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
1N	1.08	0.92	-14.8%
2N	0.65	0.72	-10.8
3N	0.65	0.49	-24.6
4N	---	ND	---
5N	---	ND	---
6N	2.16	1.8	-16.7

Table IV. Results of ERI's analyses of Naled audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
1N	0.61	0.15	-75.4%
2N	1.02	0.17	-83.3
3N	0.61	0.15	-75.4
4N	---	ND	---
5N	2.04	0.53	-74.0
6N	---	ND	---

ND = Not Detected

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

Table V. Results of ERI's analyses of second set of Naled audit samples after two days of storage.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
7N	0.56	0.43	-23.2%
8N	1.12	0.69	-38.4 *
9N	0.28	0.25	-10.7
10N	0.56	0.39	-30.4

Table VI. Results of ERI's analyses of replicate of second set of Naled audit samples after seven days of storage.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
11N	0.28	0.18	-35.7%
12N	0.56	0.23	-58.9
13N	0.56	0.23	-58.9
14N	1.12	0.27	-75.9

---

* Some sample may have been lost when transferring the resin for extraction.

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

Table VII. Results of the comparison between ERI's and QA's Naled standards.

Sample	Assigned Concentration (ppb)	Measured Concentration (ppb)	Percent Difference
ERI's calibration standard	0.5	0.53	6.0%
ERI's neat standard	0.5	0.51	2.0
QA's neat compound	0.5	0.44	-12.0
QA's spiking standard	0.5	0.40	-20.0

Table VIII. Results of ERI's stability study for 1.0 ug Naled samples stored in an ice chest.

Days in Storage	Average % Recovery
0	88.5%
3	73.1
7	69.8
10	59.3

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

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 Brooks automatic flow calibrator.

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.

Performance Audit Procedure
For The Laboratory Analysis Of Naled

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 Naled and its breakdown product Dichlorvos. The audit is conducted by submitting audit samples prepared by spiking XAD-2 resin tubes with known concentrations of Naled and Dichlorvos. 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. Naled, neat compound
2. Dichlorvos, neat compound
3. Toluene, high purity
4. XAD-2 Resin Tubes
5. 50 ul and 100 ul Microsyringes

Safety Precautions

Naled and Dicholorvos are irritating to skin, eyes, and mucous membranes. Avoid direct physical contact. May be fatal if absorbed through skin. Vapors 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

2 mg/ml Naled Stock Solution: Weigh about 20 mg of Naled into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

2 mg/ml Dichlorvos Stock Solution: Weigh about 20 mg of Dichlorvos into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

20 ug/ml Naled Spiking Standard: Transfer 100 ul of the 2 mg/ml Naled stock solution to a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

20 ug/ml Dichlorvos Spiking Standard: Transfer 100 ul of the 2 mg/ml Naled 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 Naled and Dichlorvos spiking standards according to the following table:

Sample	Naled 20 ug/ml Std	Dichlorvos 20 ug/ml Std
1	-----	-----
2	-----	100 ml
3	30 ml	50
4	30	30
5	50	30
6	100	-----

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 E

Naled MethodValidation Results

NALED METHOD VALIDATION RESULTS						
Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
EXTRACTION EFFICIENCIES						
	0.2	0.210	105.2	0.2	0.248	124.1
	0.2	0.222	111.2	0.2	0.253	126.3
	0.2	0.223	111.6	0.2	0.253	126.4
	0.2	0.224	112.2	0.2	0.277	138.6
	0.2	0.254	127.0	0.2	0.255	127.4
		AVER:	113.4		AVER:	128.6
		STD DEV:	8.09		STD DEV:	5.74
	1.0	1.154	115.4	1.0	0.875	87.5
	1.0	1.020	102.0	1.0	0.880	88.0
	1.0	1.252	125.2	1.0	0.944	94.4
	1.0	1.004	100.4	1.0	0.861	86.1
	1.0	1.161	116.1	1.0	0.867	86.7
		AVER:	111.8		AVER:	88.5
		STD DEV:	10.5		STD DEV:	3.4
	2.0	2.113	105.6	2.0	1.952	97.6
	2.0	1.815	90.7	2.0	1.720	86.0
	2.0	1.859	93.0	2.0	1.774	88.7
	2.0	1.803	90.2	2.0	1.677	83.9
	2.0	1.896	94.8	2.0	1.663	83.1
		AVER:	94.9		AVER:	87.8
		STD DEV:	6.3		STD DEV:	5.9
	12.3	14.523	118.1	15.0	14.989	99.

NALED METHOD VALIDATION RESULTS						
Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
RETENTION EFFICIENCIES						
Blanks	0.0	ND		ND	0.000	
	0.0	ND		ND	0.000	
	0.0	ND		ND	0.000	
Spikes	0.2	0.262	130.8	0.2	0.134	67.0
	0.2	0.247	123.4	0.2	0.341	170.3
	0.2	0.160	79.9	0.2	0.229	114.5
	0.2	0.156	78.1	0.2	0.257	128.5
		AVER:	103.1		AVER:	120.1
		STD DEV:	27.9		STD DEV:	42.6
	0.5	0.402	80.3	0.5	0.883	176.5
	0.5	0.398	79.5	0.5	0.943	188.5
		AVER:	79.9		AVER:	182.5
		STD DEV:	0.6		STD DEV:	8.5
	1.0	1.340	134.0	1.0	1.057	105.7
	1.0	0.819	81.9	1.0	1.051	105.1
		AVER:	108.0		AVER:	105.4
		STD DEV:	36.8		STD DEV:	0.4
Breakthrough-Backup	12.3	0.521	4.2	15.0	ND	-
Breakthrough-Backup	21.0	ND	-	19.6	ND	-

NALED METHOD VALIDATION RESULTS						
Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
STABILITY SAMPLES Freezer Stability						
3-Day Storage	1.0	0.891	89.1	1.0	0.867	86.7
	1.0	0.962	96.2	1.0	0.937	93.7
	1.0	1.025	102.5	1.0	1.132	113.2
		AVER:	95.9		AVER:	97.8
		STD DEV:	6.7		STD DEV:	13.7
7-Day Storage	1.0	0.886	88.6	1.0	0.850	85.0
	1.0	0.862	86.2	1.0	0.921	92.1
	1.0	0.817	81.7	1.0	0.888	88.8
		AVER:	85.5		AVER:	88.6
		STD DEV:	3.5		STD DEV:	3.5
14-Day Storage	1.0	0.938	93.8	1.0	0.803	80.3
	1.0	0.947	94.7	1.0	0.839	83.9
		AVER:	94.2		AVER:	82.1
		STD DEV:	0.6		STD DEV:	2.5
21-Day Storage	1.0	0.899	89.9	1.0	0.977	97.7
	1.0	0.853	85.3	1.0	0.993	99.3
	1.0	0.890	89.0	1.0	0.814	81.4
		AVER:	88.1		AVER:	92.8
		STD DEV:	2.4		STD DEV:	9.9
80-Day Storage	0.5	0.518	103.5	0.5	0.340	68.0
	0.5	0.510	102.0	0.5	0.370	74.1
	0.5	0.603	120.6	0.5	0.384	76.9
		AVER:	108.7		AVER:	73.0
		STD DEV:	10.3		STD DEV:	4.5
Blank 80-Day Storage	0.0	0.011		0.0	0.142	

NALED METHOD VALIDATION RESULTS						
Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
STABILITY SAMPLES Ice Chest Stability						
3-Day Storage	1.0	0.436	43.6	1.0	0.543	54.3
	1.0	0.738	73.8	1.0	0.843	84.3
	1.0	0.851	85.1	1.0	0.807	80.7
		AVER:	67.5		AVER:	73.1
		STD DEV:	21.4		STD DEV:	16.4
7-Day Storage	1.0	0.861	86.1	1.0	0.679	67.9
	1.0	0.823	82.3	1.0	0.704	70.4
	1.0	0.876	87.6	1.0	0.713	71.3
		AVER:	85.3		AVER:	69.8
		STD DEV:	2.7		STD DEV:	1.8
10-Day Storage	1.0	0.808	80.8	1.0	0.571	57.1
	1.0	0.965	96.5	1.0	0.588	58.8
	1.0	0.960	96.0	1.0	0.621	62.1
		AVER:	91.1		AVER:	59.3
		STD DEV:	8.9		STD DEV:	2.6
Room Temperature Stability						
7-Day Storage	0.5	0.244	48.7	0.5	0.000	0.0

APPENDIX F

Application Monitoring

State of California

AIR RESOURCES BOARD

NALED APPLICATION MONITORING REPORT

Ambient Air Monitoring in Fresno County for Naled and Dichlorvos in August 1992 during and after a Naled Application to a Vineyard

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C91-031A

Report Date:

APPROVED:

_____, Project Engineer
Testing Section

_____, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

Naled Monitoring in Fresno County in August 1992

This report presents the results of ambient monitoring for naled after an air burst application at a selected vineyard in Fresno County. The results are based on samples collected and analyzed by the Air Resources Board Monitoring and Laboratory Division staff. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

Jack Rogers assisted in the collection of samples. Mike Ansolabehere of Valent U.S.A. Corp. assisted in arranging for a suitable field to monitor. Assistance was provided by Lynn Baker of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by Don Fitzell of the Engineering Evaluation Branch of the ARB.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

State of California
Air Resources Board

Naled Monitoring in Fresno 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 three-day source impacted ambient monitoring program for naled and its breakdown product, dichlorvos (DDVP), in Fresno County in August 1992.

II. PESTICIDE DESCRIPTION

Naled (molecular weight 381 g/mole) is a non-systemic insecticide-acaricide which is a white solid with a melting point of 27°C. It has a vapor pressure of 5×10^{-4} mm Hg at 25°C. It is practically insoluble in water, slightly soluble in aliphatic solvents, and readily soluble in aromatic solvents.

Dichlorvos (DDVP), a breakdown product of naled, is a colorless liquid with a molecular weight of 221 g/mole. Vapor pressure is 1.2×10^{-2} mm Hg at 20°C. DDVP is also an insecticide and fumigant. DDVP is slightly soluable in water and glycerol, miscible with aromatic and chlorinated hydrocarbons and alcohols.

While naled is not regulated as a restricted use material under Section 6400, Title 3 of the California Administrative Code, it is subject to the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65).

III. SAMPLING LOCATIONS

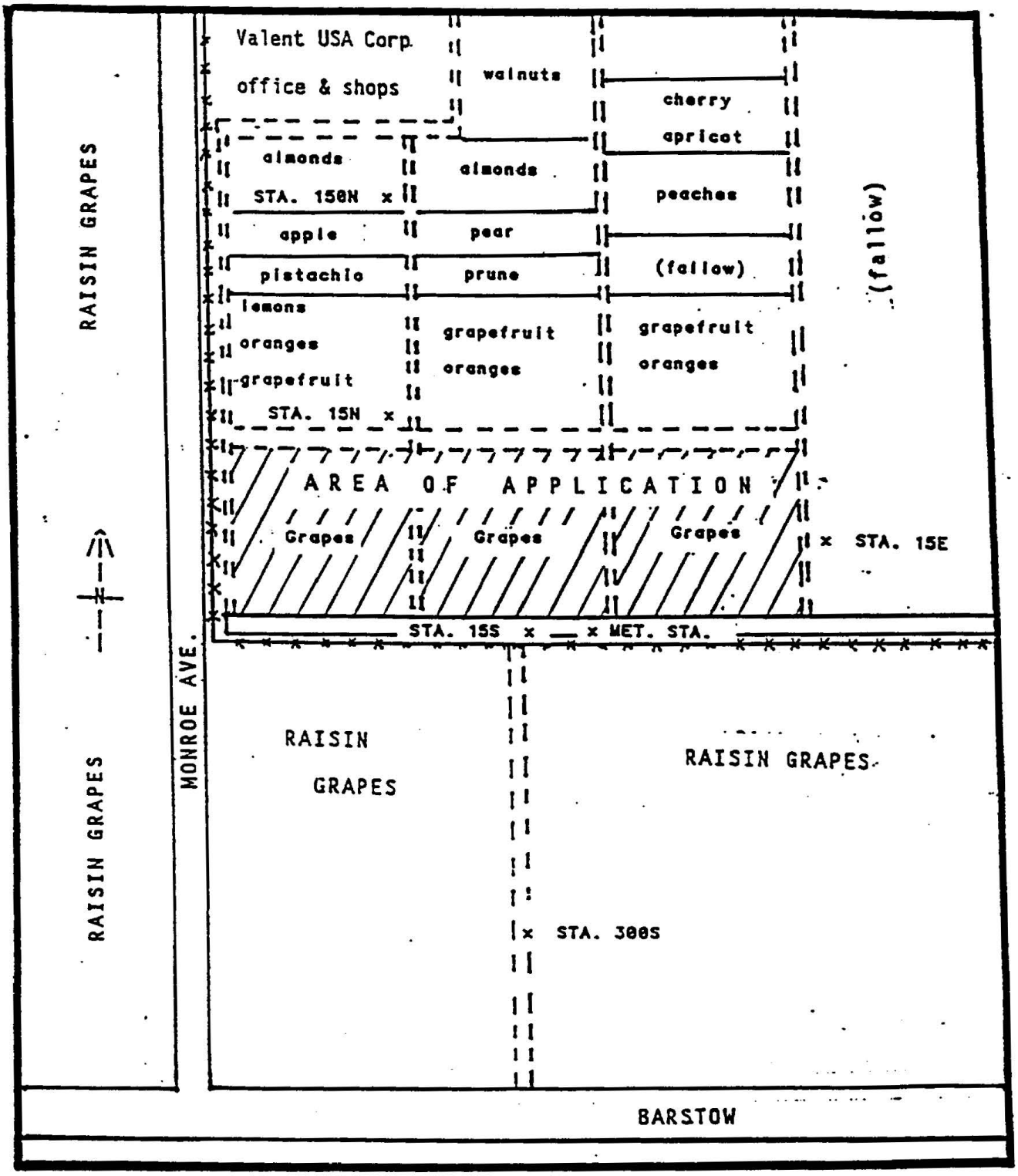
A vineyard of about 9 acres was selected (Figure I) by Mike Ansolabehere of Valent U.S.A. Corp. and approved by ARB staff to use for application monitoring.

The prevailing winds in the area are generally from the north and south (up and down the valley). Four samplers were set up as shown in Figure I. One approximately 15 and another 150 yards north of the field. The third was approximately 15 yards south of the field and another approximately 300 yards south of the field. A meteorological station was set up about 15 yards south of the field and 15 yards east of the south sampler (See Figure I). Three hours after the application (after sample number three) the monitor 15 yards south of the field was moved to 15 yards east of the field. This was done to cover a west wind that

Figure I

Pesticide Application Field

And Monitoring Sites



persisted for much of the sampling time instead of the expected north wind.

The application was by air blast spray (from a tractor pulled trailer) and took about three hours. The application rate was one pint of naled per acre. The naled was put in solution with water and the entire solution was applied at the rate of 55 gal/acre. Tractor speed during application was about 2 mph.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-2 tubes. (See Appendix I.) These tubes are 8mm x 110mm, with 400 mg in the primary section and 200 mg in the secondary (SKC catalog #226-30-06). Any naled 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 ARB Monitoring and Laboratory Division laboratory in Sacramento for analysis.

Sampling trains designed to operate continuously were set up at the sampling sites identified in Figure I. Duplicate samples were obtained from all four samplers.

Sampling tubes were changed, as closely as practical, according to the schedule outlined in the QA Plan for Pesticide Monitoring. (See Appendix II.) The actual sampling schedule is shown in Table 1. Comparing the two schedules, it can be seen the background (pre-application) sampling time was extended from 1 to 4 1/2 hours. This is because sampling was done the afternoon and evening before the application (to prevent the delay of the application), so more time was available to collect these background samples. Also, the QA Plan 8-hour samples were eliminated to avoid a late night trip. As a result, the 4-hour samples were extended to 5 hours and the 9-hour samples were extended to 16 hours.

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 battery-powered vacuum pump. A diagram of the sampling train is shown in Figure II. 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 along with date, time, and site location. Calibration

Table 1

APPLICATION SAMPLING SCHEDULE

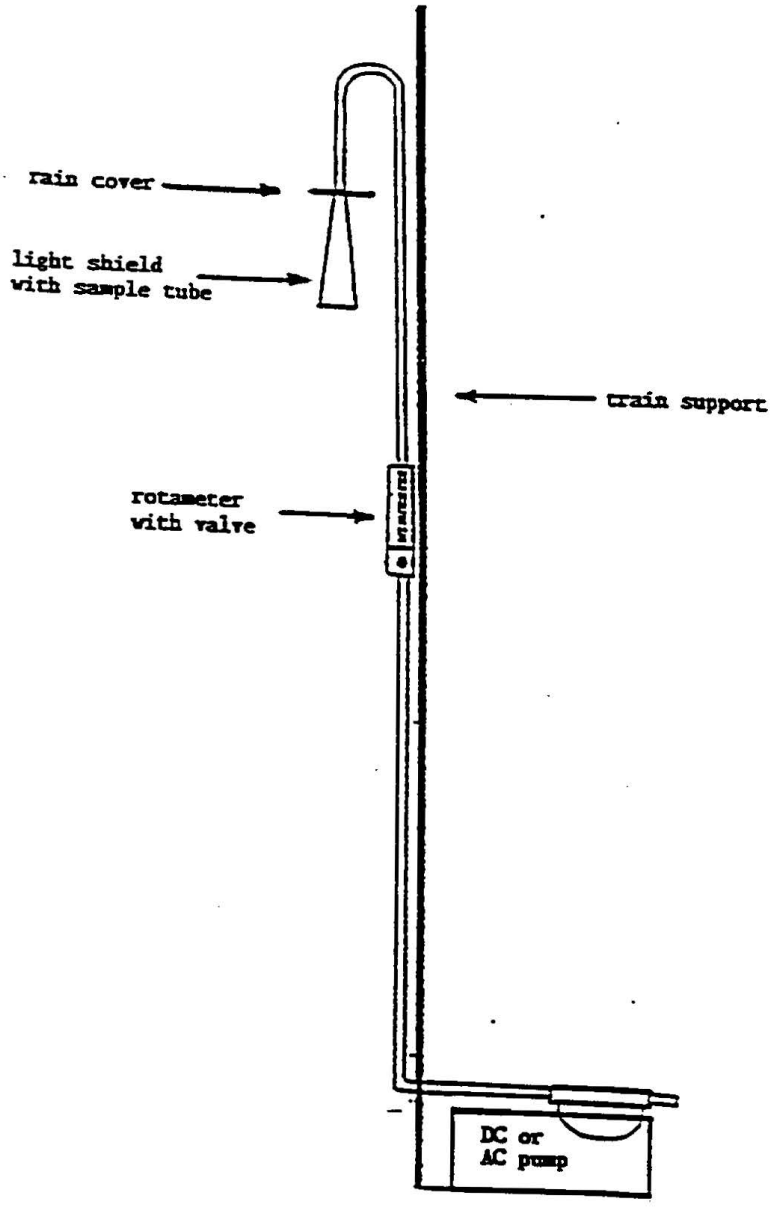
The sampling schedule for each station is as follows:

Sample Number	Description	Sampling Stations 150N: -150 yd North*	15N: -15 yd North*	15S: -15 yd South*	15E: -15 yd East*	300S: -300 yd South*
1	Background sample (-4 1/2 hr. sample starting -12 1/2 hr. prior to application).	2	2	2	-	2
2	Application + 1 hr. after application combined sample.	2	2	2	-	2
3	-2 hr. sample from 1 to 3 hr. after the application.	2	2	2	-	2
4	-5 hr. sample from 3 to 8 hr. after the application.	2	2	-	2	2
5	-16 hr. sample from 8 to 24 hr. after the application.	2	2	-	2	2
6	1st 24 hour sample starting -24 hr. after the application.	2	2	-	2	2
7	2nd 24 hour sample starting -48 hr. after the application.	-	2	-	2	2

* 2 = Duplicate (collocated) samples at each site.
- = No sample collected.

Figure II

Pesticide Sampler



prior to use in the field indicated that an average flow rate of 1.9 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 EEB staff. The XAD-2 in the primary section of each sample tube was extracted by ultrasonication with a 1:1 mixture of hexane and acetone. Analysis was by GC separation on a DB-5 capillary column and measurement by Electron Capture Detector (GC/ECD). For details, see the Analytical S.O.P. in Appendix III. The secondary (backup) sections were saved to check for breakthrough, if necessary.

VI. RESULTS

Table 2 is a summary of the sampling data. It includes the maximum and second maximum at each station. It also includes the average concentration of samples greater than the minimum detection level (MDL), the number of samples collected, the number of samples analyzed, and the number of samples greater than the MDL for each station. For the purposes of Table 2, collocated samples were averaged and treated as a single sample.

Naled and dichlorvos (DDVP) results for each collected sample are presented in Table 3. Sampling and analysis data are presented in Appendix IV. The results indicate naled and DDVP were detected in the near (15 yard) samples and were generally undetected at the far sampling stations (150N and 300S). The highest level for DDVP was for samples 5A and 5B (3.43 and 1.30 ug/scm) at Station 15E. The highest level for naled was also 5A and 5B (6.48 and 6.31 ug/scm) at Station 15E. However, results from Stations 15N and 15S indicate that samples 5A and 5B are second peaks for naled. The first naled peak, collected with the 2A and 2B samples, corresponds with the naled application.

As discussed in "Sampling Locations", the samplers were set up based on the prevailing north-south (valley) winds. As can be seen from Table 4, a summary of the meteorological data, the wind seemed to prevail from the west and was low (<5 mph) during much of the sampling period following application. As a result the near south sampler, 15S, was moved east of the field and redesignated 15E. The far south sampler, 300S, was not moved and was used as a background sampler.

The chemist performing the analysis reported there were problems with the analysis. (See the memo "Naled/DDVP Application Results" in

Table 2

Naled Pesticide Sampling Study

Results Summary *

	Station 15N		Station 150N		Station 15S		Station 15E		Station 300S	
	DDVP	Naled	DDVP	Naled	DDVP	Naled	DDVP	Naled	DDVP	Naled
Max. Conc.										
ug/scm	1.14	2.56	<MDL	<MDL	0.92	3.58	2.41	6.42	0.23	<MDL
ppt	0.12	0.15	<MDL	<MDL	0.10	0.22	0.25	0.38	0.03	<MDL
2nd Max. Conc.					(B)					
ug/scm	0.39	1.59	<MDL	<MDL	0.23	<MDL	0.42	1.01	0.17	<MDL
ppt	0.04	0.10	<MDL	<MDL	0.02	<MDL	0.06	0.06	0.02	<MDL
Average **										
ug/scm	0.41	1.12	<MDL	<MDL	0.92	3.58	0.83	2.53	0.14	<MDL
ppt	0.04	0.07	<MDL	<MDL	0.10	0.22	0.09	0.15	0.01	<MDL
Sample Numbers *										
Total Collected	7	7	6	6	3	3	4	4	7	7
Total Analyzed	7	7	6	6	3	3	4	4	7	7
Total above MDL	5	4	0	0	2	1	4	3	4	0

* For this purpose, collocated samples (all samples were collocated) are averaged and treated as a single sample.

** Uses only those values greater than the minimum detection level (MDL).

(B) Background sample collected before application.

DDVP (dichlorvos) is a breakdown product of naled after application.

Table 3

Naled Pesticide Application Sampling Study

DDVP AND NALED SAMPLING RESULTS, ug/scm

SAMPLE NUMBER	Station 15N		Station 150N		Station 15S		Station 15E		Station 300S		SAMPLE NUMBER
	DDVP	Naled	DDVP	Naled	DDVP	Naled	DDVP	Naled	DDVP	Naled	
1A	< 0.19	< 0.39	< 0.19	< 0.39	0.23	< 0.39			< 0.19	< 0.38	1A
2A	0.43	2.50	< 0.20	< 0.40	0.88	3.33			0.21	< 0.42	2A
3A	< 0.47	< 0.95	< 0.42	< 0.84	< 0.55	< 1.11			< 0.36	< 0.73	3A
4A	0.18	< 0.36	0.18	< 0.37			0.55	1.06	0.17	< 0.35	4A
5A	1.17	1.69	0.06	< 0.11			3.43	6.48	0.13	< 0.11	5A
6A	0.21	0.23	< 0.04	< 0.07			0.26	0.18	0.06	< 0.07	6A
7A	0.08	0.09					0.21	< 0.07	0.05	< 0.08	7A
1B	< 0.19	< 0.39	< 0.19	< 0.39	0.23	< 0.39			< 0.19	< 0.38	1B
2B	0.35	2.61	< 0.20	< 0.40	0.96	3.83			0.25	< 0.42	2B
3B	< 0.47	< 0.95	< 0.42	< 0.84	< 0.55	< 1.11			< 0.36	< 0.73	3B
4B	0.21	< 0.36	< 0.18	< 0.37			0.48	0.96	< 0.17	< 0.35	4B
5B	1.11	1.49	< 0.05	< 0.11			1.38	6.36	0.21	< 0.11	5B
6B	0.23	0.22	< 0.04	< 0.07			0.23	0.16	0.12	< 0.07	6B
7B	0.10	0.09					0.10	< 0.07	0.10	< 0.08	7B

Station 15N was located 15 yards north of the field.
Station 150N was located 150 yards north of the field. Sampling stopped after the first 24 hours as allowed by the Quality Assurance Plan.
Station 15S was located 15 yards south of the field. Moved east of the field after Sample 3.
Station 15E was located 15 yards east of the field. Sampler was moved from south of the field.
Station 300S was located 300 yards south of the field.
DDVP (dichlorvos) is a breakdown product of naled after application.
Number one samples were collected before the naled application.
Number two samples were collected during the naled application.

Table 4

Naled Pesticide Application Sampling Study

Meteorological Survey Results
(from Portable Monitor and Observations at the Application Site)

Hour	Tuesday 8/25/92 Wind mph	dir.	Temp. F	Obsv.	Wednesday 8/26/92 Wind mph	dir.	Temp. F	Obsv.	Thursday 8/27/92 Wind mph	dir.	Temp. F	Obsv.	Friday 8/28/92 Wind mph	dir.	Temp. F	Obsv.
2400					2	W	56		4	WNW	63		1	W	65	
0100					2	W	54		3	WNW	61		1	N	65	
0200					2	W	53		2	NW	59		1	N	60	
0300					1	W	51		2	NW	57		1	N	60	
0400					1	NW	49		1	NE	55		1	N	58	
0500					0		48		0		50		1	N	54	
0600	Application:				0		46		1	S	48		2	W	62	
0700	0800 - 1100				0		49	Sunny,	0		50		1	WSW	60	Sunny
0800	1	WNW	60	Sunny,	0.5	NW	56	No	2	NW	60		0		65	& Clear
0900	1	SW	68	No	1	NNE	64	Clouds,	1	WNW	65		2	NW	67	
1000	2	W	74	Clouds,	1	NE	64	& Hazy	3	W	72		1	W	75	
1100	4	WNW	76	& Hazy	2	ESE	79		2	W	78	Sunny	2	W	77	Sunny
1200	4	WNW	80		2	S	87	Sunny,	2	W	83	& Clear				& Clear
1300	4	WNW	83	Sunny,	3	WNW	90	No	3	W	85					
1400	5	W	85	No	5	WNW	92	Clouds,	3	W	88					
1500	3	W	87	Clouds,	4	WNW	94	& Hazy	3	WNW	90					
1600	4	WNW	80	& Hazy	5	WNW	94		3	W	92					
1700	4	W	85		4	WNW	93	Sunny,	3	NW	90	Sunny,				
1800	3	WNW	80		3	W	92	Partly	3	NW	90	Partly				
1900	3	W	74	Sunny,	2	W	88	Cloudy,	3	NW	90	Cloudy				
2000	2	W	68	No	2	W	78	& Hazy	2	NW	87					
2100	2	W	66	Clouds,	2	W	66		2	W	72					
2200	2	NW	64	& Hazy	3	W	68		2	W	67					
2300	2	WNW	61		3	W	65		2	W	65					

Appendix IV.) As a quality assurance check, select samples were also run on a GC with a mass spectrometer (GC/MS). For naled, the GC/MS results were 62 to 169% of the GC/ECD results. For DDVP, the GC/MS results were 44 to 760% of the GC/ECD. They should only be 50 to 150%. None of the results have been changed based upon these quality assurance checks. Therefore, the reported values for naled may be lower than actual and the reported results for DDVP may be higher than actual.

VII. QUALITY ASSURANCE

All of the procedures outlined in the Pesticide Quality Assurance Plan (Appendix II) were followed. Reproducibility, linearity, collection and extraction efficiency and minimum detection limit are described in the S.O.P. for naled (Appendix III). Breakthrough and storage stability are reported in the Method Validation (Appendix IV). Spikes were prepared by the Quality Management and Operations Support Branch of the ARB and reported in the QA Section Audit Report (Appendix VI).

The precision (standard deviation) of the collocated collected samples are shown in Tables 5a for naled and 5b for DDVP. The standard deviation averaged 0.07 for naled and 0.10 for DDVP.

Data completeness is 100%. Including background samples collected before the application, 54 sample tubes were collected and 54 tubes were analyzed. No samples were invalidated in the field or by the laboratory.

Table 5A

Naled Pesticide Sampling Study
Naled Sampling Precision*

Sample Number	Sample Concentration: Primary (A) Sample, ug/scm	Sample Concentration: Duplicate (B) Sample, ug/scm	Standard Deviation
15N-2	2.50	2.61	0.06
15N-5	1.69	1.49	0.10
15N-6	0.23	0.22	0.01
15N-7	0.09	0.09	0.00
		Sta. 15N Average =	0.04
15S-2	3.33	3.83	0.25
15E-4	1.06	0.96	0.05
15E-5	6.48	6.36	0.06
15E-6	0.18	0.16	0.01
		Sta. 15S/E Average =	0.09
(Stations 15S & 15E shared the same sampler.)			
Sta. 15ON & 30OS had no detectable quantities of Naled.			

* Only samples with detectable quantities were used to determine standard deviation.

Table 5B

Naled Pesticide Sampling Study
DDVP Sampling Precision*

Sample Number	Sample Concentration: Primary (A) Sample, ug/scm	Sample Concentration: Duplicate (B) Sample, ug/scm	Standard Deviation
15N-2	0.43	0.35	0.04
15N-4	0.18	0.21	0.02
15N-5	1.17	1.11	0.03
15N-6	0.21	0.23	0.01
15N-7	0.08	0.1	0.01
		Sta. 15N Average =	0.02
15S-1	0.23	0.23	0.00
15S-2	0.88	0.96	0.04
15E-4	0.55	0.48	0.04
15E-5	3.43	1.38	1.03
15E-6	0.26	0.23	0.02
15E-7	0.21	0.10	0.06
		Sta. 15S/E Average =	0.20
(Stations 15S & 15E shared the same sampler.)			
30OS-2	0.21	0.25	0.02
30OS-5	0.13	0.21	0.06
30OS-6	0.06	0.12	0.03
30OS-7	0.04	0.09	0.03
		Sta. 30OS Average =	0.04
Station 15ON had no detectable DDVP in the B samples.			

* Only samples with detectable quantities of DDVP were used to determine standard deviation. DDVP (dichlorvos) is a breakdown product of naled.

APPENDIX I

SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Naled Application Monitoring in Fresno County during August, 1992

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C91-031A

Date: July 24, 1992

APPROVED:

David F. Todd, for Project Engineer
Testing Section

Peter K. Ouchida, Manager
Testing Section

George Lew, Chief
Engineering Evaluation Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for Naled Application Monitoring
in Fresno County during August, 1992

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) will conduct a 3-day source impacted ambient monitoring program for naled in Fresno County during the month of August. Naled is used on a wide variety of crops. A report on the measured concentrations will be submitted to DPR.

II. Sampling

Prior to application, background samples will be taken to establish if any naled is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with XAD-2 tubes using battery powered pumps capable of flows of approximately 2 liters per minute. Sample collection will follow the timetable outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" as closely as is reasonably possible.

Calibrated rotometers will be used to control sample flow rates. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in a log book, along with any other pertinent information.

Three samplers will be used; 1) one 15 yards upwind of the field, 2) one 15 yards downwind and 3) one 150 yards downwind. These distances are approximate and dependent on the physical obstacles surrounding the field. Duplicates of each sample will be taken. ARB's "Quality Assurance Plan for Pesticide Monitoring" will be followed as closely as possible.

III. Analysis

All samples will be analyzed by the ARB's Engineering Evaluation Branch (EEB) using gas chromatography and electron capture detection (GC/ECD). All samples will be stored on ice until delivery to EEB.

IV. Quality Assurance

Field sampling and laboratory analytical quality assurance activities are described in the ARB's "Quality Assurance Plan for Pesticide Monitoring."

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample flow rates will be calibrated prior to and after sampling in the field.

A chain of custody sheet will accompany all samples. A field log book will be used to record start and stop times, sample ID's and any other significant data, including field size, application rate, formulation, and length of the application.

V. Personnel

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

APPENDIX II

QUALITY ASSURANCE PLAN

State of California
Air Resources Board

Quality Assurance Plan for Pesticide Monitoring

Prepared by the

Monitoring and Laboratory Division
and
Stationary Source Division

September 28, 1990

APPROVED:

Veronica A. Sherman, Chief,
Toxic Air Contaminant
Identification Branch
Stationary Source Division

_____, Chief,
Quality Management and
Operations Support Branch
Monitoring and Laboratory Division

George Lew, Chief,
Engineering Evaluation Branch
Monitoring and Laboratory Division

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

LIST OF TABLES

APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

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

II. Quality Assurance Policy Statement

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

III. Quality Assurance Objectives

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

IV. Siting

Siting criteria for ambient pesticide monitoring are listed in TABLE 1. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. Background sites should be located away from any applications.

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

A. Monitoring Site Description

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

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

V. Sampling

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Sampling will be conducted following the Environmental Protection Agency (EPA) ambient monitoring guidelines of 40 CFR 58 for calibration, precision, accuracy and data validation. The ARB Quality Assurance Section upon request will review quality assurance/quality control procedures and will evaluate pesticide monitoring activities.

A. Protocol

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

1. Identification of the sample site locations.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.)
3. Description of the analytical method.
4. Quality assurance/quality control plan for sampling, including calibration procedures for flow meters.
5. Test schedule.
6. Test personnel.

Specific sampling methods and activities will be described in a monitoring plan (protocol) for review by ARB and DFA. Criteria which apply to all sampling are: 1) chain of custody forms will accompany all samples (APPENDIX I.), 2) light and rain shielding will be used for samples during monitoring and, 3) samples will be stored in an ice chest until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to this specific pesticide.

B. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample type (e.g., charcoal tube), sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Field blanks should be included with each batch of samples submitted to the lab for analysis. The average of the initial and final flow rates for the sampling period will be used if a flow controller is not used.

C. Collocation

For ambient monitoring, sampling precision or the standard deviation of the data set will be calculated from at least 2 samples collocated at a site. The collocated sampler will be rotated between sampling sites so that at least three duplicate samples are collected at each site. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. One sample will be designated as the primary sample and the other sample will be designated as the duplicate.

D. Calibration

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

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

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

E. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc. should be made by sampling personnel.

TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY

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

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. APPLICATION SAMPLING SCHEDULE

The sampling schedule for each station is as follows:

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

* duplicate collocated samples at each site.

VI. Analysis

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

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

A. Standard Operating Procedures

1. Instrument and Operating Parameters

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

2. Sample Preparation

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

3. Calibration Procedures

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

4. Quality Assurance

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as; use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of lab analysis and after every tenth sample. Control samples should be found to be within control

limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked tubes at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VII. Data Reduction and Reporting

The mass of pesticide (microgram, ug) found in each sample will be used along with the sample air volume from the field data sheet to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in ug/m^3 as well as ppb or ppt (as appropriate). Wind speed and direction data will also be reported for application site monitoring.

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

A. Quality Assurance

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

1. Precision and Accuracy

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

2. Data Completeness

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

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

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: _____
Sample/Run #: _____ Time: _____
Plant name: _____
Sample Location: _____
Type of Sample: _____
Log #: _____ Initials: _____

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

Disposition of Sample: Immediate Analysis ____ Refrigerator ____
Storage ____ Freezer ____

RELATED ID'S	DESCRIPTION

RETURN THIS FORM TO: Don Fitzell (445-0618)

APPENDIX III

ANALYTICAL S.O.P.

Air Resources Board

Engineering Evaluation Branch

Standard Operating Procedure for the Analysis of Naled and Dichlorovos in Ambient Air

August 1992

1. SCOPE

This document describes the analytical procedure for the analysis of naled and dichlorvos (DDVP) in ambient air. This method is based on the method developed by the Engineering Research Institute, California State University, Fresno and the method developed by the California Department of Food and Agriculture, Chemistry Laboratory Services, Environmental Monitoring Section.

2. SUMMARY

Samples are collected on XAD-2 resin. The samples are extracted by ultrasonication with a 1:1 mixture of hexane and acetone. Both compounds are analyzed by gas chromatography using and electron capture detector (GC/ECD). Separation is accomplished using a DB-5 capillary column. The compounds are identified and quantitated by comparison of retention times and response with standards of known concentrations.

3. INTERFERENCES AND LIMITIATIONS

3.1 Compounds responding to the ECD and having similar retention times may interfere. This could result in misidentification and/or erroneous quantitation.

3.2 Samples are to be stored in the laboratory freezer at or below $-4^{\circ}C$ to prevent degradation. Samples must also be delivered to the laboratory for analysis prior to any indication of significant degradation under field storage conditions. These conditions are typically storage in an ice chest for up to one week.

4. EQUIPMENT

4.1 A Varian 3400 gas chromatograph equipped with an electron capture detector and a Varian 604 data system (or equivalent).

4.2 A DB-5 fused silica capillary column (30 m x 0.2 mm i.d., 0.25 um film).

4.3 Amber glass vials, 8 ml, with teflon-faced septa and screw caps for extraction and storage of sample extracts and standards.

4.4 Ultrasonic bath for extraction.

4.5 Microliter syringes, 10 ul to 500 ul sizes.

4.6 Volumetric and graduated pipets, various volumes.

4.7 Disposable glass transfer pipets.

4.8 XAD-2 resin sample tubes: 400 mg primary section, 200 mg secondary section, 110 mm x 8 mm.

5. REAGENTS

5.1 Hexane: high purity (pesticide residue quality).

5.2 Acetone: high purity (pesticide residue quality).

5.3 Stock standard: transfer approximately 10 to 20 mg of Naled (Chem Service) to a 100 ml volumetric flask, dilute to mark with hexane:acetone (1:1). Repeat for Dichlorvos (Chem Service). Store stock solutions in the freezer. Record all data in a log book.

5.4 Calibration standards: Dilute appropriate aliquots of the stock solutions in amber screw cap vials with teflon liners. Combining appropriate amounts of both naled and dichlorvos into one standard will simplify quantitation. Store calibration standards in the freezer. Record all data in a log book.

6. INSTRUMENT CONDITIONS

6.1 Injector 250°C

6.2 Detector 300°C, Range 10

6.3 Make up; nitrogen, 30 ml/min.

6.4 Carrier; helium, 1.0 ml/min, 12 psi

6.5 Splitter; 52 ml/min, on at 0.8 min.

6.6 Column conditions; initial 50°C, hold 0.0 min., ramp to 112°C @ 50°C/min, hold 5 min., ramp to 115°C @ 1°C/min., hold 0.0 min., ramp to 210°C @ 50°C/min., hold 5 min., ramp to 240 °C @ 50°C/min., hold 4 min.

7. EXTRACTION

7.1 Carefully break the sample tube so that the wire spring can be remove. Remove the glass wool plug on top of the primary section

and place it into an 8 ml amber sample vial. Also pour the XAD-2 of the primary section into the sample vial. Add 2 ml hexane:acetone (1:1) and ultrasonicate for 20 minutes. After completion, use a disposable glass pipet to transfer the solvent into another amber sample vial with screw cap and teflon liner. Store in the refrigerator or freezer until ready for analysis.

8. INSTRUMENT CALIBRATION

8.1 Inject 2 ul of the solvent into the GC to check for interferences. If interferences or contamination is found, replace the solvent or take steps to remove the contamination.

8.2 Run a three point calibration each day that samples are run. Be sure that the sample concentrations are bracketed by the highest and lowest calibration points.

9. LINEARITY, SENSITIVITY AND PRECISION

Table I.

Standard Concentration (ug/ml)	Dichlorvos (Counts)	Naled (Counts)
0.078125	53,775	112,649
0.078125	50,698	92,618
0.078125	42,948	101,799
0.078125	59,743	93,693
0.156250	105,644	297,346
0.156250	102,800	349,752
0.156250	123,729	418,284
0.312500	258,418	1,418,055
0.312500	254,885	1,545,931
0.625000	541,051	4,542,666
0.625000	509,143	4,568,771

Standard Curves

Dichlorovos $Y = 1.1457 \times 10^{-6} + 0.0225$ $C = .9998$

Naled $Y = 1.1728 \times 10^{-7} + 0.1026$ $C = .992$

Precision

For the lowest calibration point:

Table II.

Dichlorovos			Naled		
Counts	(ug/ml)		Counts	(ug/ml)	
53,775	0.084110		112,649	0.115811	
50,698	0.080585		92,618	0.113462	
42,948	0.071706		101,799	0.114639	
59,743	0.090948		93,693	0.113588	
	0.081837	± 0.008008		0.114350	± 0.001086
		± 9.8%			± 0.9%

Minimum Detection Limit

Minimum Detection Limit (MDL) = |intercept| x 3($s.d._{low}$)

where: |intercept| = the absolute value of the intercept of the standard curve

$s.d._{low}$ = standard deviation of the lowest calibration standard used to produce the standard curve. This value must be expressed in concentration; therefore the standard curve must first be used to convert the area counts into concentration before the standard deviation is determined.

Dichlorovos MDL = |0.0225| + 3(0.008) = 0.05 ug/ml x 2 ml = 0.10 ug/tube

Naled MDL = |0.1026| + 3(0.001) = 0.11 ug/ml x 2 ml = 0.22 ug/tube

10. COLLECTION/CONVERSION

Nine XAD-2 sample tubes were spiked with known amounts of naled and dichlorvos. These tubes, along with 3 tubes not spiked (blanks), were set up to sample ambient air in Sacramento in the same manner as proposed for the field. Ambient air was drawn through the tubes for approximately 20 hours at a rate of about 2 liters per minute.

Table III.

Amount Spiked (ug)	Dichlorvos Recovered (ug)	(%)	Naled Recovered (ug)	(%)
0.00 (Blank)	0.15	--	<0.00	--
0.00 (Blank)	0.10	--	<0.00	--
0.00 (Blank)	<0.00	--	<0.00	--
0.50	0.72	144	0.70	140
0.50	0.48	96	0.66	132
1.00	1.28	128	1.40	140
1.00	1.16	116	1.54	154
2.00	2.32	116	2.34	116
2.00	2.28	114	2.46	123
5.00	4.50	90	4.95	99
5.00	4.26	85	5.79	116
5.00	5.76	115	6.36	127

Because of the false positives detected in the collection/conversion study, any dichlorovos detected in field samples will have to be confirmed and quantitated by GC/MSD or similar method which does not have this interference.

11. STORAGE STABILITY AND BREAKTHROUGH

Storage stability and breakthrough studies were conducted by the Engineering Research Institute at the California State University, Fresno and were not repeated for this S.O.P. (see attached).

APPENDIX IV

METHOD VALIDATION

NALED METHOD VALIDATION RESULTS

Engineering Research Institute

California State University, Fresno

(from "Airborne Concentrations of Naled and Dichlorvos in Central Tulare County from Sampling Conducted in May and June 1991")

NALED METHOD VALIDATION RESULTS

Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
EXTRACTION EFFICIENCIES						
	0.2	0.210	105.2	0.2	0.248	124.1
	0.2	0.222	111.2	0.2	0.253	126.3
	0.2	0.223	111.6	0.2	0.253	126.4
	0.2	0.224	112.2	0.2	0.277	138.6
	0.2	0.254	127.0	0.2	0.255	127.4
		AVER:	113.4		AVER:	128.6
		STD DEV:	8.09		STD DEV:	5.74
	1.0	1.154	115.4	1.0	0.875	87.5
	1.0	1.020	102.0	1.0	0.880	88.0
	1.0	1.252	125.2	1.0	0.944	94.4
	1.0	1.004	100.4	1.0	0.861	86.1
	1.0	1.161	116.1	1.0	0.867	86.7
		AVER:	111.8		AVER:	88.5
		STD DEV:	10.5		STD DEV:	3.4
	2.0	2.113	105.6	2.0	1.952	97.6
	2.0	1.815	90.7	2.0	1.720	86.0
	2.0	1.859	93.0	2.0	1.774	88.7
	2.0	1.803	90.2	2.0	1.677	83.9
	2.0	1.896	94.8	2.0	1.663	83.1
		AVER:	94.9		AVER:	87.8
		STD DEV:	6.3		STD DEV:	5.9
	12.3	14.523	118.1	15.0	14.989	99.

NALED METHOD VALIDATION RESULTS

Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
RETENTION EFFICIENCIES						
Blanks	0.0	ND		ND	0.000	
	0.0	ND		ND	0.000	
	0.0	ND		ND	0.000	
Spikes	0.2	0.262	130.8	0.2	0.134	67.0
	0.2	0.247	123.4	0.2	0.341	170.3
	0.2	0.160	79.9	0.2	0.229	114.5
	0.2	0.156	78.1	0.2	0.257	128.5
		AVER:	103.1		AVER:	120.1
		STD DEV:	27.9		STD DEV:	42.6
	0.5	0.402	80.3	0.5	0.883	176.5
	0.5	0.398	79.5	0.5	0.943	188.5
		AVER:	79.9		AVER:	182.5
		STD DEV:	0.6		STD DEV:	8.5
	1.0	1.340	134.0	1.0	1.057	105.7
	1.0	0.819	81.9	1.0	1.051	105.1
		AVER:	108.0		AVER:	105.4
		STD DEV:	36.8		STD DEV:	0.4
Breakthrough-Backup	12.3	0.521	4.2	15.0	ND	-
Breakthrough-Backup	21.0	ND	-	19.6	ND	-

NALED METHOD VALIDATION RESULTS

Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
STABILITY SAMPLES Freezer Stability						
3-Day Storage	1.0	0.891	89.1	1.0	0.867	86.7
	1.0	0.962	96.2	1.0	0.937	93.7
	1.0	1.025	102.5	1.0	1.132	113.2
		AVER:	95.9		AVER:	97.8
		STD DEV:	6.7		STD DEV:	13.7
7-Day Storage	1.0	0.886	88.6	1.0	0.850	85.0
	1.0	0.862	86.2	1.0	0.921	92.1
	1.0	0.817	81.7	1.0	0.888	88.8
		AVER:	85.5		AVER:	88.6
		STD DEV:	3.5		STD DEV:	3.5
14-Day Storage	1.0	0.938	93.8	1.0	0.803	80.3
	1.0	0.947	94.7	1.0	0.839	83.9
		AVER:	94.2		AVER:	82.1
		STD DEV:	0.6		STD DEV:	2.5
21-Day Storage	1.0	0.899	89.9	1.0	0.977	97.7
	1.0	0.853	85.3	1.0	0.993	99.3
	1.0	0.890	89.0	1.0	0.814	81.4
		AVER:	88.1		AVER:	92.8
		STD DEV:	2.4		STD DEV:	9.9
80-Day Storage	0.5	0.518	103.5	0.5	0.340	68.0
	0.5	0.510	102.0	0.5	0.370	74.1
	0.5	0.603	120.6	0.5	0.384	76.9
		AVER:	108.7		AVER:	73.0
		STD DEV:	10.3		STD DEV:	4.5
Blank 80-Day Storage	0.0	0.011		0.0	0.142	

NALED METHOD VALIDATION RESULTS

Description	Dichlorvos			Naled		
	Fortif. µg	Results µg	Recov. %	Fortif. µg	Results µg	Recov. %
STABILITY SAMPLES						
Ice Chest Stability						
3-Day Storage	1.0	0.436	43.6	1.0	0.543	54.3
	1.0	0.738	73.8	1.0	0.843	84.3
	1.0	0.851	85.1	1.0	0.807	80.7
		AVER:	67.5		AVER:	73.1
		STD DEV:	21.4		STD DEV:	16.4
7-Day Storage	1.0	0.861	86.1	1.0	0.679	67.9
	1.0	0.823	82.3	1.0	0.704	70.4
	1.0	0.876	87.6	1.0	0.713	71.3
		AVER:	85.3		AVER:	69.8
		STD DEV:	2.7		STD DEV:	1.8
10-Day Storage	1.0	0.808	80.8	1.0	0.571	57.1
	1.0	0.965	96.5	1.0	0.588	58.8
	1.0	0.960	96.0	1.0	0.621	62.1
		AVER:	91.1		AVER:	59.3
		STD DEV:	8.9		STD DEV:	2.6
Room Temperature Stability						
7-Day Storage	0.5	0.244	48.7	0.5	0.000	0.0

APPENDIX V

SAMPLING and LABORATORY REPORT

NALED PESTICIDE SAMPLING STUDY

RESULTS SUMMARY, UG/SCM

SAMPLE NUMBER	Station 15N		Station 150N		Station 15S		Station 15E		Station 300S		SAMPLE NUMBER
	DDVP	Naled	DDVP	Naled	DDVP	Naled	DDVP	Naled	DDVP	Naled	
1A	< 0.19	< 0.39	< 0.19	< 0.39	0.23	< 0.39			< 0.19	< 0.38	1A
2A	0.43	2.50	< 0.20	< 0.40	0.88	3.33			0.21	< 0.42	2A
3A	< 0.47	< 0.95	< 0.42	< 0.84	< 0.55	< 1.11			< 0.36	< 0.73	3A
4A	0.18	< 0.36	0.18	< 0.37			0.55	1.06	0.17	< 0.35	4A
5A	1.17	1.69	0.06	< 0.11			3.43	6.48	0.13	< 0.11	5A
6A	0.21	0.23	< 0.04	< 0.07			0.26	0.18	0.06	< 0.07	6A
7A	0.08	0.09					0.21	< 0.07	0.05	< 0.08	7A
1B	< 0.19	< 0.39	< 0.19	< 0.39	0.23	< 0.39			< 0.19	< 0.38	1B
2B	0.35	2.61	< 0.20	< 0.40	0.96	3.83			0.25	< 0.42	2B
3B	< 0.47	< 0.95	< 0.42	< 0.84	< 0.55	< 1.11			< 0.36	< 0.73	3B
4B	0.21	< 0.36	< 0.18	< 0.37			0.48	0.96	< 0.17	< 0.35	4B
5B	1.11	1.49	< 0.05	< 0.11			1.38	6.36	0.21	< 0.11	5B
6B	0.23	0.22	< 0.04	< 0.07			0.23	0.16	0.12	< 0.07	6B
7B	0.10	0.09					0.10	< 0.07	0.10	< 0.08	7B

Station 15N was located 15 yards north of the field.
Station 150N was located 150 yards north of the field. Sampling stopped after the first 24 hours as allowed by the Quality Assurance Plan.
Station 15S was located 15 yards south of the field. Moved east of the field after Sample 3.
Station 15E was located 15 yards east of the field. Sampler was moved from south of the field.
Station 300S was located 300 yards south of the field.
DDVP (dichlorvos) is a breakdown product of naled after application.
Number one samples were collected before the naled application.
Number two samples were collected during the naled application.

NALED PESTICIDE SAMPLING STUDY
SAMPLING TUBE DATA
(for Rotometers)

Station: 15N-#A & #B

SAMPLE NUMBER	MONTH	START			STOP			SAMPLE TIME, min.	FLOW, lpm	VOLUME, scm	SAMPLE, ug		CONC, ug/scm		CONC, ppt		SAMPLE NUMBER
		dy	hr	mn	dy	hr	mn				DDVP	Naled	DDVP	Naled	DDVP	Naled	
1A	Aug.	24	14	55	24	19	26	271	1.9	0.515	< 0.10	< 0.20	< 0.19	< 0.39	< 0.02	< 0.02	1A
2A		25	7	50	25	12	20	270	1.9	0.513	0.22	1.28	0.43	2.50	0.04	0.15	2A
3A		25	12	20	25	14	11	111	1.9	0.211	< 0.10	< 0.20	< 0.47	< 0.95	< 0.05	< 0.06	3A
4A		25	14	11	25	19	5	294	1.9	0.559	0.10	< 0.20	0.18	< 0.36	0.02	< 0.02	4A
5A		25	19	5	26	10	56	951	1.9	1.807	2.12	3.06	1.17	1.69	0.12	0.10	5A
6A		26	10	56	27	10	58	1442	1.9	2.740	0.58	0.64	0.21	0.23	0.02	0.01	6A
7A		27	10	58	28	10	30	1412	1.9	2.683	0.22	0.24	0.08	0.09	0.01	0.01	7A
1B	Aug.	24	14	55	24	19	26	271	1.9	0.515	< 0.10	< 0.20	< 0.19	< 0.39	< 0.02	< 0.02	1B
2B		25	7	50	25	12	20	270	1.9	0.513	0.18	1.34	0.35	2.61	0.04	0.15	2B
3B		25	12	20	25	14	11	111	1.9	0.211	< 0.10	< 0.20	< 0.47	< 0.95	< 0.05	< 0.06	3B
4B		25	14	11	25	19	5	294	1.9	0.559	0.12	< 0.20	0.21	< 0.36	0.02	< 0.02	4B
5B		25	19	5	26	10	56	951	1.9	1.807	2.00	2.70	1.11	1.49	0.11	0.09	5B
6B		26	10	56	27	10	58	1442	1.9	2.740	0.64	0.60	0.23	0.22	0.02	0.01	6B
7B		27	10	58	28	10	30	1412	1.9	2.683	0.28	0.24	0.10	0.09	0.01	0.01	7B

DDVP (dichlorvos) is a breakdown product of Naled after application.

NALED PESTICIDE SAMPLING STUDY

SAMPLING TUBE DATA

(for Rotometers)

Station: 150N-#A & #B

SAMPLE NUMBER	MONTH	START			STOP			SAMPLE TIME, min.	FLOW, lpm	VOLUME, scm	SAMPLE, ug		CONC, ug/scm		CONC, ppt		SAMPLE NUMBER
		dy	hr	mn	dy	hr	mn				DDVP	Naled	DDVP	Naled	DDVP	Naled	
1A	Aug.	24	14	50	24	19	22	272	1.9	0.517	< 0.10	< 0.20	< 0.19	< 0.39	< 0.02	< 0.02	1A
2A		25	7	50	25	12	10	260	1.9	0.494	< 0.10	< 0.20	< 0.20	< 0.40	< 0.02	< 0.02	2A
3A		25	12	10	25	14	15	125	1.9	0.238	< 0.10	< 0.20	< 0.42	< 0.84	< 0.04	< 0.05	3A
4A		25	14	15	25	19	0	285	1.9	0.542	0.10	< 0.20	0.18	< 0.37	0.02	< 0.02	4A
5A		25	19	0	26	11	12	972	1.9	1.847	0.12	< 0.20	0.06	< 0.11	0.01	< 0.01	5A
6A		26	11	12	27	11	13	1441	1.9	2.738	< 0.10	< 0.20	< 0.04	< 0.07	< 0.00	< 0.00	6A
		Sta. 150 taken out at 1113 on Aug. 27.															
1B	Aug.	24	14	50	24	19	22	272	1.9	0.517	< 0.10	< 0.20	< 0.19	< 0.39	< 0.02	< 0.02	1B
2B		25	7	50	25	12	10	260	1.9	0.494	< 0.10	< 0.20	< 0.20	< 0.40	< 0.02	< 0.02	2B
3B		25	12	10	25	14	15	125	1.9	0.238	< 0.10	< 0.20	< 0.42	< 0.84	< 0.04	< 0.05	3B
4B		25	14	15	25	19	0	285	1.9	0.542	< 0.10	< 0.20	< 0.18	< 0.37	< 0.02	< 0.02	4B
5B		25	19	0	26	11	12	972	1.9	1.847	< 0.10	< 0.20	< 0.05	< 0.11	< 0.01	< 0.01	5B
6B		26	11	12	27	11	13	1441	1.9	2.738	< 0.10	< 0.20	< 0.04	< 0.07	< 0.00	< 0.00	6B
7B		Sta. 150 taken out at 1113 on Aug. 27.															7B

DDVP (dichlorvos) is a breakdown product of Naled after application.

NALED PESTICIDE SAMPLING STUDY

SAMPLING TUBE DATA

(for Rotometers)

Station: 15S-#A & #B

SAMPLE NUMBER	MONTH	START dy	START hr	START mn	STOP dy	STOP hr	STOP mn	SAMPLE TIME, min.	FLOW, lpm	VOLUME, scm	SAMPLE, ug DDVP	SAMPLE, ug Naled	CONC, ug/scm DDVP	CONC, ug/scm Naled	CONC, ppt DDVP	CONC, ppt Naled	SAMPLE NUMBER
1A	Aug.	24	15	0	24	19	30	270	1.9	0.513	0.12	< 0.20	0.23	< 0.39	0.02	< 0.02	1A
2A		25	7	50	25	12	25	275	1.9	0.523	0.46	1.74	0.88	3.33	0.09	0.20	2A
3A		25	12	25	25	14	0	95	1.9	0.181	< 0.10	< 0.20	< 0.55	< 1.11	< 0.06	< 0.07	3A
4A		Station 15S moved to east of field at 1400 on Aug 25 and changed to Station 15E.															4A
5A																	5A
6A																	6A
7A																	7A
1B	Aug.	24	15	0	24	19	30	270	1.9	0.513	0.12	< 0.20	0.23	< 0.39	0.02	< 0.02	1B
2B		25	7	50	25	12	25	275	1.9	0.523	0.50	2.00	0.96	3.83	0.10	0.23	2B
3B		25	12	25	25	14	0	95	1.9	0.181	< 0.10	< 0.20	< 0.55	< 1.11	< 0.06	< 0.07	3B
4B		Station 15S moved to east of field at 1400 on Aug 25 and changed to Station 15E.															4B
5B																	5B
6B																	6B
7B																	7B

DDVP (dichlorvos) is a breakdown product of Naled after application.

NALED PESTICIDE SAMPLING STUDY
SAMPLING TUBE DATA
(for Rotometers)

Station: 300S-#A & #B

SAMPLE NUMBER	MONTH	START			STOP			SAMPLE TIME, min.	FLOW, lpm	VOLUME, scm	SAMPLE, ug		CONC, ug/scm		CONC, ppt		SAMPLE NUMBER
		dy	hr	mn	dy	hr	mn				DDVP	Naled	DDVP	Naled	DDVP	Naled	
1A	Aug.	24	14	35	24	19	10	275	1.9	0.523	< 0.10	< 0.20	< 0.19	< 0.38	< 0.02	< 0.02	1A
2A		25	7	50	25	12	0	250	1.9	0.475	0.10	< 0.20	0.21	< 0.42	0.02	< 0.02	2A
3A		25	12	0	25	14	25	145	1.9	0.276	< 0.10	< 0.20	< 0.36	< 0.73	< 0.04	< 0.04	3A
4A		25	14	25	25	19	28	303	1.9	0.576	0.10	< 0.20	0.17	< 0.35	0.02	< 0.02	4A
5A		25	19	28	26	11	20	952	1.9	1.8088	0.24	< 0.20	0.13	< 0.11	0.01	< 0.01	5A
6A		26	11	20	27	11	13	1433	1.9	2.7227	0.16	< 0.20	0.06	< 0.07	0.01	< 0.00	6A
7A		27	11	13	28	10	20	1387	1.9	2.6353	0.12	< 0.20	0.05	< 0.08	0.00	< 0.00	7A
1B	Aug.	24	14	35	24	19	10	275	1.9	0.523	< 0.10	< 0.20	< 0.19	< 0.38	< 0.02	< 0.02	1B
2B		25	7	50	25	12	0	250	1.9	0.475	0.12	< 0.20	0.25	< 0.42	0.03	< 0.02	2B
3B		25	12	0	25	14	25	145	1.9	0.276	< 0.10	< 0.20	< 0.36	< 0.73	< 0.04	< 0.04	3B
4B		25	14	25	25	19	28	303	1.9	0.576	< 0.10	< 0.20	< 0.17	< 0.35	< 0.02	< 0.02	4B
5B		25	19	28	26	11	20	952	1.9	1.8088	0.38	< 0.20	0.21	< 0.11	0.02	< 0.01	5B
6B		26	11	20	27	11	13	1433	1.9	2.7227	0.34	< 0.20	0.12	< 0.07	0.01	< 0.00	6B
7B		27	11	13	28	10	20	1387	1.9	2.6353	0.26	< 0.20	0.10	< 0.08	0.01	< 0.00	7B

DDVP (dichlorvos) is a breakdown product of Naled after application.

State of California

M E M O R A N D U M

To : David Todd
Assoc. Air Pollution Spec.

Date : November 20, 1992

Subject : Naled/DDVP
Application Results

Through: Peter Ouchida, Manager
Testing Section

Don Fitzell
Assoc. Air Pollution Spec.

From : Air Resources Board

Since you will be writing the naled application report, I thought it would be valuable to you to describe the difficulties during analysis which makes the data not as accurate as we normally expect. The accuracy of the results is indicated by:

1. First and most obvious is the difference between the results I obtained by ECD vs. the results obtained by NLB staff using MSD. (Attachment I). For naled, the MSD results were from 62-169% of the ECD results and for DDVP, the MSD results were from 44-760% of the ECD results. A reasonable expectation would be ±50%. The ECD analysis was run on Sept. 1-11, 1992 with standards prepared on Sept. 1. The MSD analysis was done Oct. 27-28 using one of the standards prepared on Sept. 1.

2. The next obvious indication is the performance audit conducted by QMOSB (Attachment II). As indicated by Gabe, my naled results were approximately 50% below the assigned mass and my DDVP results were approximately 60% above the assigned mass. I have no explanation for this. Gabe suggests breakdown of naled into DDVP. I don't think this is the case because:

   1) The spiked tubes prepared by Gabe would have had to degrade in order for me to get low naled and high DDVP results. I analyzed his spikes within 12-24 hours after he prepared them and FSU's stability data indicates good recovery for up to 21 days when stored in the freezer.

   2) If the standards I used to measure the spikes had degraded, the results would be the reverse: naled results would be high (because my calibrating standard would actually be less than I thought) and the DDVP results would be low (because breakdown of naled into DDVP would make it appear there was more of my standard present than I thought).

Also, it should be noted that for sample DN3, I measured 0.22 ug DDVP for a tube which was a blank.

Part of the above noted facts can be explained by an analysis of the chromatograms. First, it should be mentioned that the normal data system used with the Varian 3400 was down for repair and could not be repaired because of the lack of a State budget. The only available data system for me to use had no long term storage capability and did not indicate on the chromatogram how the peak was integrated. This can be important in the analysis of broad peaks.

The DDVP peak appears broad (possible interferences) and the naled peak appears sharp. This resulted in DDVP being measured when none was present (sample DN3) and probably increased the value measured when DDVP was present.

In summary, the values reported should be considered "ballpark" (the same order of magnitude) with regard to accuracy, even though the precision appears good. The values reported for DDVP are most likely a "worst case" situation. The contribution of the interferences would make it appear that more DDVP was present than collected in the sample tube. The breakdown of naled into DDVP under storage conditions would also increase the apparent concentration of DDVP. For this same reason, the naled results reported are probably lower than the actual amount collected in the sample tube.

cc: Lynn Baker
Ruth Tomlin
Gabe Ruiz
George Lew

DDVP and Naled Results (ug/tube)

Sample ID	ECD		MSD		Sample Volume (m^3)
	DDVP	Naled	DDVP	Naled	
15N-1A	--	--			0.52
15N-1B	--	--			0.52
15S-1A	0.12	--			0.52
15S-1B	0.12	--			0.52
150N-1A	--	--			0.52
150B-1B	--	--			0.52
300S-1A	--	--			0.52
300S-1B	--	--			0.52
15N-2A	0.22	1.28			0.52
15N-2B	0.18	1.34			0.52
15S-2A	0.46	1.74			0.51
15S-2B	0.50	2.00			0.51
150N-2A	--	--			0.49
150N-2B	--	--			0.49
300S-2A	0.10	--			0.48
300S-2B	0.12	--			0.48
15N-3A	--	--			0.21
15N-3B	--	--			0.21
15S-3A	--	--			0.18
15S-3A	--	--			0.18
150N-3A	--	--			0.24
150N-3B	--	--			0.24
300S-3A	--	--			0.27
300S-3B	--	--			0.27
15N-4A	0.10	--			0.56
15N-4B	0.12	--			0.56
15E-4A	0.32	0.62			0.58
15E-4B	0.28	0.56			0.58
150N-4A	0.10	--			0.54
150N-4B	--	--			0.54
300S-4A	0.10	--			0.58
300S-4B	--	--			0.58
15N-5A	2.12	3.06	4.30	4.90	1.81
15N-5B	2.00	2.70	1.92	2.54	1.81
15E-5A	6.20	11.70	5.13	6.92	1.81
15E-5B	2.50	11.50	5.64	7.09	1.81
150N-5A	0.12	--	0.06	--	1.85
150N-5B	--	--			1.85
300S-5A	0.24	--	0.05	0.11	1.79
300S-5B	0.38	--	0.05	--	1.79
15E-6A	0.70	0.48			2.74
15E-6B	0.64	0.44			2.74
15N-6A	0.58	0.64			2.74
15N-6B	0.64	0.60			2.74
300S-6A	0.16	--			2.72
300S-6B	0.34	--			2.72
15E-7A	0.56	--			2.64
15E-7B	0.28	--			2.64
15N-7A	0.22	0.24			2.68
15N-7B	0.28	0.24			2.68
300S-7A	0.12	--			2.68
300S-7B	0.26	--			2.68