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AIR RESOURCES BOARD

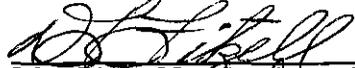
**Ambient Air Monitoring in Merced County for Telone (1,3-Dichloropropene)  
During DowElanco's Commercial Reintroduction, March-April, 1995**

Engineering and Laboratory Branch  
Monitoring and Laboratory Division

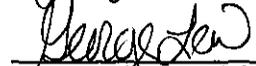
Test Report No. C94-071-M

Report Date: November 9, 1995

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**Ambient Air Monitoring in Merced County for Telone (1,3-Dichloropropene)  
During DowElanco's Commercial Reintroduction, March-April, 1995**

This report presents the results of ambient air monitoring for Telone during DowElanco's "Commercial Reintroduction Project" in March and April of 1995 in Merced County. The Air Resources Board (ARB) located five samplers throughout Merced County: Merced, El Nido, Dos Palos "Y", Stevinson and Hilmar. These are the same sites used during the 1990 ambient air monitoring which resulted in the suspension of all permits for its use throughout the state.

Low levels of Telone were detected: 24-hour concentrations ranged from 0.11 to 7.4  $\mu\text{g}/\text{m}^3$ . One hundred and sixty-seven of the two hundred and sixteen<sub>3</sub> samples collected were below the detection limit (approximately 0.10  $\mu\text{g}/\text{m}^3$ ). Only four samples were above 1.0  $\mu\text{g}/\text{m}^3$ . The remaining 45 samples ranged between the detection limit and 1.0  $\mu\text{g}/\text{m}^3$ . Mitigating measures, reduced number of applications and the unusually rainy weather were contributors to the low levels found.

## Acknowledgments

The Instrument Technicians were: Jack LaBrue, Ken Lewis, Jack Rogers and Bud Thoma of the ARB. Assistance was provided by the Merced County Agricultural Commissioner's Office. Lynn Baker, Ruth Tomlin, and Cara Roderick of the ARB's Air Quality Measures Branch also assisted in this project.

## TABLE OF CONTENTS

		<u>PAGE</u>
I.	INTRODUCTION	1
II.	PESTICIDE DESCRIPTION	1
III.	SAMPLING LOCATIONS	2
IV.	SAMPLING METHODOLOGY	2
V.	ANALYTICAL METHODOLOGY	3
VI.	RESULTS	3
VII.	QUALITY ASSURANCE	4

### LIST OF FIGURES

I.	TELONE MONITORING AREA	5
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### LIST OF TABLES

I.	TELONE MONITORING SITES	6
II.	TELONE AMBIENT MONITORING DATA	7
III.	SUMMARY OF TELONE DATA	13
IV.	TELONE QA/QC DATA	14

### APPENDICES

I.	ELB TELONE PROTOCOL	
	ATTACHMENT A. Sampling Apparatus	
	ATTACHMENT B. Standard Operating Procedure for the Analysis of Telone (1,3-dichloropropene) in Ambient Air	
	ATTACHMENT C. Quality Assurance Plan for Pesticide Monitoring	
II.	DPR REQUEST FOR TELONE MONITORING	

State of California  
Air Resources Board

**Ambient Air Monitoring in Merced County for Telone (1,3-Dichloropropene)  
During DowElanco's Commercial Reintroduction, March-April, 1995**

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Air Quality Measures Branch, the ARB Engineering and Laboratory Branch (ELB) conducted a two-month source impacted ambient monitoring program for Telone in Merced County during the months of March and April 1995. This monitoring, in conjunction with subsequent monitoring in Kern County, is to confirm that mitigating measures developed by DowElanco to reduce emissions of Telone from the soil are effective. Mitigating measures include: maximum use of 12 gallons per acre, 300 foot buffer zones around each application, injection depth of 18 inches, and compaction of the soil following application. The commercial reintroduction of Telone is a result of a series of studies undertaken in California by DowElanco designed to mitigate the release of Telone into the air. These monitoring studies began after results from a study conducted by the ARB in April 1990, "Telone (1,3-dichloropropene) Monitoring in Merced County," indicated the presence of unacceptably high ambient concentrations of Telone during the peak application period in Merced County. This resulted in a statewide suspension of the permits of all users for this soil fumigant.

Since the statewide reintroduction, the DPR has allowed application of Telone in thirteen counties in California. The ARB staff chose to monitor in Merced and Kern Counties because of the high use in these areas. The Kern study is being conducted June-November 1995. The five ambient sites in Merced County used in the 1990 study were also used in this monitoring. Using the sampling apparatus shown in APPENDIX I, Attachment A, samples were collected at these locations, shown in Figure I.

The ARB staff collected 24-hour samples, Monday through Friday for nine weeks, which included a week of background monitoring prior to application of Telone in the area. This monitoring was designed to verify the predictive models developed by DowElanco and to obtain an idea of the maximum annual exposure California's residents might expect.

II. PESTICIDE DESCRIPTION

Telone is a volatile (vapor pressure 27.8 mm Hg at 20°C), colorless to amber liquid consisting of cis and trans isomers of the compound 1,3-dichloropropene. It has a molecular weight of 111.0, a boiling point of 104°C to 112°C and a solubility in water of approximately 2.3 gm/liter (The Merck Index, 11th Edition, 1989 and APPENDIX II).

Telone is a restricted use pesticide under Title 3, California Code of Regulations, Section 6400. The EPA has classified it as a Class B2 carcinogen (probable human carcinogen) (APPENDIX II). The State of California has determined under Proposition 65 that 1,3-dichloropropene is a potential carcinogen (California Code of Regulations, 1994).

It is used on a wide variety of crops and is injected as a preplant soil treatment to control nematodes, fungi, insects, weeds and other soil pests. Prior to the suspension of its use, the DPR Pesticide Use Report for 1988 reported statewide use of 16,518,814 pounds. Historical application rates varied from five to thirty-six gallons per acre depending on the soil type and crop (APPENDIX II).

### III. SAMPLING LOCATIONS

The five sites chosen were the same as used in the 1990 ambient study in Merced County: Merced, El Nido, Dos Palos "Y", Stevinson, and Hilmar. The addresses of these locations and their sample identifications are listed in TABLE I. The Merced, Stevinson and Hilmar samplers were all located on the roof of a single-story building. The Dos Palos "Y" sampler was positioned approximately 1 to 1 1/2 meters above a solid wooden fence. The El Nido sampler was approximately 1 to 1 1/2 meters above a covered picnic table. The sites were selected on the basis of the criteria listed in the QA Plan for Pesticide Monitoring (APPENDIX I, ATTACHMENT C). Other considerations in selecting the monitoring sites were: proximity to expected application sites, possible population exposure, reasonable access, availability of AC power and security.

### IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through charcoal tubes (see APPENDIX I). These tubes are 8 mm x 110 mm, coconut-base charcoal with 400 mg in the primary section with 200 mg in the secondary (SKC catalog #226-09). Any Telone present in the sampled ambient air is captured by the charcoal adsorbent contained in the tubes. Subsequent to sampling, the tubes were stored and transported in an insulated container with ice to the ARB's ELB in Sacramento for analysis.

Each sample train consisted of a charcoal tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 115V AC vacuum pump. A diagram of the sampling train is shown in APPENDIX I, Attachment A. 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 placed around the tube to protect any collected Telone from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute

(lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration on February 22, 1995 with a digital bubble meter 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. This average value was used to calculate all sample volumes.

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 charcoal 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 charcoal tubes recovered from each sampler were analyzed by the ARB ELB staff using the same procedure as in all previous studies. The charcoal in the primary section of each sample tube was extracted with carbon disulfide, followed by GC separation on a DB-624 capillary column and measurement by Electron Capture Detector (APPENDIX I, ATTACHMENT B). All samples were analyzed the week following collection. Based on the levels found in previous studies, no primary sections were deemed high enough to require the analysis of the secondary section.

#### VI. RESULTS

The concentration data for Telone results are shown in TABLE II. A summary of the Telone concentration data is shown in TABLE III. Quality Assurance data is summarized in TABLE IV.

Low levels of Telone were detected: from 0.11 to 7.4  $\mu\text{g}/\text{m}^3$ . One hundred and sixty-seven of the two hundred and sixteen samples collected were below the detection limit (approximately 0.10  $\mu\text{g}/\text{m}^3$ ). Only four samples were above 1.0  $\mu\text{g}/\text{m}^3$ . The remaining 45 samples ranged between the detection limit and 1.0  $\mu\text{g}/\text{m}^3$ . Mitigating measures, reduced number of applications and the unusually rainy weather were contributors to the low levels found.

The results from the 1990 study in Merced County indicated much higher values at the same sampling sites. The average of the values above the minimum detection limit ranged from 0.8  $\mu\text{g}/\text{m}^3$  at Merced to 24.5  $\mu\text{g}/\text{m}^3$  at the Hilmar site. A single high sample was found to be 160.7  $\mu\text{g}/\text{m}^3$  at the Hilmar site.

During analysis of the background samples, a consistent low level of Telone was found in all samples including the blank. Further work indicated the solvent used for extraction had become contaminated with

laboratory standard. After this background contamination was subtracted from all samples the values were all below the detection limit. A fresh solvent was used for all subsequent extractions.

QA data is presented in TABLE IV. Recovery levels seem to be consistently low. No explanation for these values is offered at this time. A review of all Telone QA data indicates a recurring problem with Telone spikes prepared by the ELB and other laboratories. However, a comparison of duplicate field samples generally results in good agreement. The ELB laboratory will attempt to resolve this problem before the end of the monitoring program in Kern County.

## VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, and minimum detection limit and storage stability were determined prior to the first monitoring program, and are outlined in the S.O.P. for Telone (APPENDIX I, Attachment B).

Prior to this analysis, linearity, reproducibility and the minimum detection limit were checked to ensure reliable results. The values found were comparable to those presented in the S.O.P. for Telone.

This monitoring conducted in Merced County is only part of DowElanco's reintroduction program for Telone. The majority of the applications will occur later this year (June through November, 1995) in Kern County. For this reason a laboratory audit by the ARB's Quality Management and Operations Support Branch (QMOSB) was not conducted at this time. It will be performed sometime during the analysis of the samples from Kern County.

FIGURE I. Telone Monitoring Area

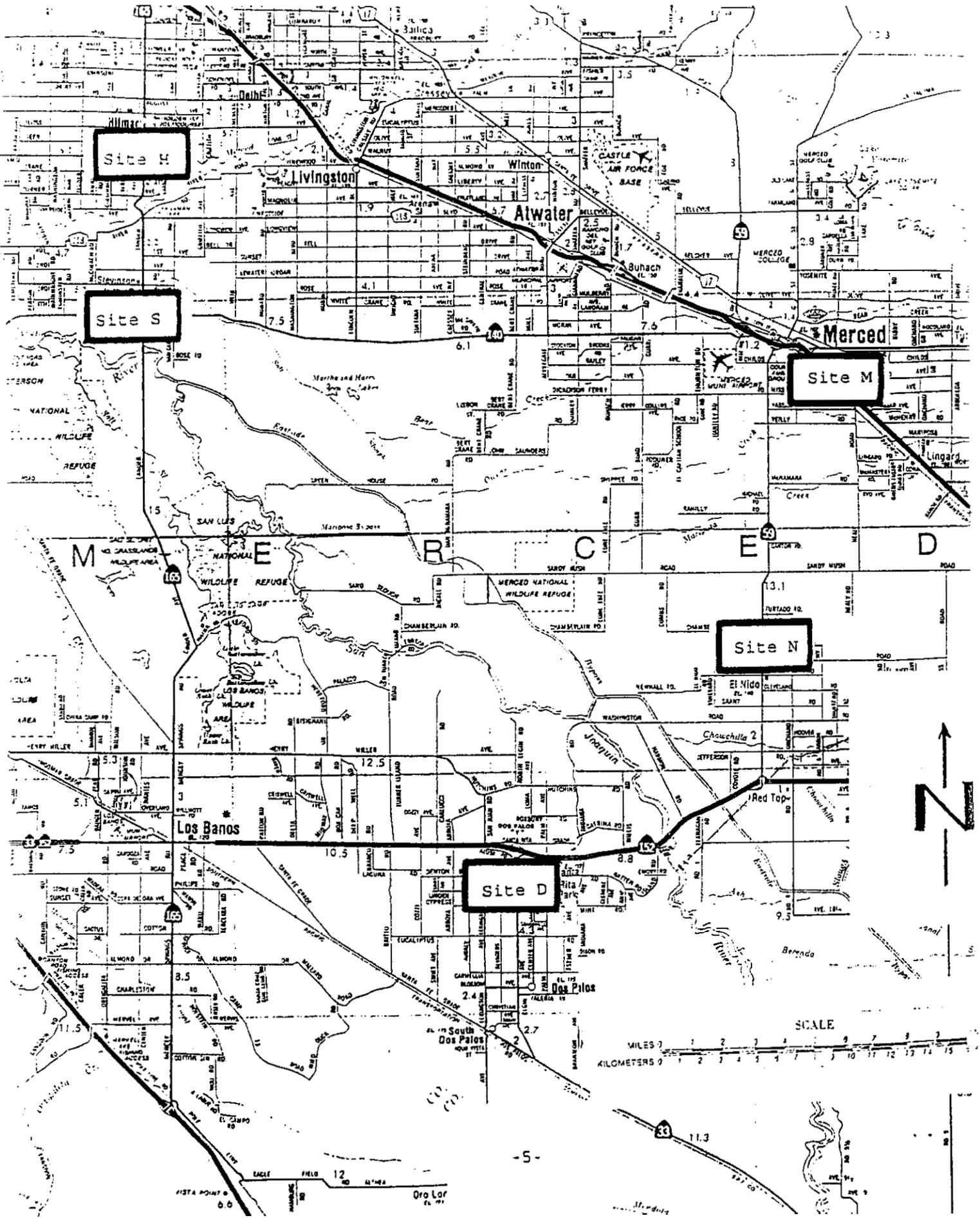


TABLE I. Telone Monitoring Sites

1. Site M  
Merced (urban background)  
Merced Co. Air Pollution Control District  
210 E. 15th St.
  
2. Site N  
El Nido  
Merced Co. Fire Dept. (roof of barbecue pit)  
10537. S. Highway 59 at El Nido Rd.
  
3. Site D  
Dos Palos "Y"  
Merced Co. Fire Dept. (on top of wall by the driveway)  
8047 Dairy Ln. (Highway 33 just south of Highway 152)
  
4. Site S  
Stevinson  
Merquin School (roof of building behind school)  
Third Ave. west of Lander Ave. (Highway 165)
  
5. Site H  
Hilmar  
Hilmar Jr. High School (roof of school building)  
Lander Ave. north of Geer Ave.

TABLE II. Telone Ambient Monitoring Data

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
1M	1465	2.8	ND	--	Background 2/27-28/95
1N	1455	2.8	ND	--	
1D	1460	2.8	ND	--	
1S-1	1440	2.7	ND	--	
1S-2	1440	2.7	ND	--	
1H	1435	2.7	ND	--	
2M	1450	2.8	ND	--	Background 2/28-3/1/95
2N	1450	2.8	ND	--	
2D	1450	2.8	ND	--	
2S-1	1460	2.8	ND	--	
2S-2	1460	2.8	ND	--	
2H	1445	2.7	ND	--	
2B	BLANK	--	ND	--	
3M	1480	2.8	ND	--	Background 3/1-2/95
3N	1485	2.8	ND	--	
3D	1480	2.8	ND	--	
3S-1	1470	2.8	ND	--	
3S-2	1470	2.8	ND	--	
3H	1475	2.8	ND	--	
4M	1425	2.7	ND	--	Background 3/2-3/95
4N	1415	2.7	ND	--	
4D	1415	2.7	ND	--	
4S-1	1420	2.7	ND	--	
4S-2	1420	2.7	ND	--	
4H	1425	2.7	ND	--	
5M	1450	2.8	ND	--	3/6-7/95
5N	1460	2.8	ND	--	
5D	1455	2.8	ND	--	
5S	1450	2.8	0.49	0.18	
5H-1	1470	2.8	ND	--	
5H-2	1470	2.8	ND	--	
6M	1460	2.8	ND	--	3/7-8/95
6N	1450	2.8	ND	--	
6D	1450	2.8	ND	--	
6S	1455	2.8	ND	--	
6H-1	1435	2.7	0.59	0.22	
6H-2	1435	2.7	0.61	0.23	

<sup>1</sup>M = Merced, N = El Nido, D = Dos Palos "Y", S = Stevinson, H = Hilmar. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 1.9 liters per minute.

<sup>3</sup>ND = Not Detected, <0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

TABLE II. Telone Ambient Monitoring Data (cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
7M	1440	2.7	ND	--	3/9-10/95
7N	1440	2.7	ND	--	
7D	1455	2.8	ND	--	
7S	1455	2.8	ND	--	
7H-1	1460	2.8	ND	--	
7H-2	1460	2.8	ND	--	
8M	1410	2.7	ND	--	
8N	1415	2.7	ND	--	
8D	1415	2.7	ND	--	
8S	1400	2.7	ND	--	
8H-1	1415	2.7	ND	--	
8H-2	1415	2.7	ND	--	
8B	BLANK	--	ND	--	
9M-1	1295	2.5	ND	--	3/13-14/95
9M-2	1295	2.5	ND	--	
9N	1360	2.6	ND	--	
9D	1395	2.7	ND	--	
9S	1480	2.8	ND	--	
9H	1515	2.9	ND	--	
9B	BLANK	--	ND	--	
10M-1	1480	2.8	ND	--	3/14-15/95
10M-2	1480	2.8	ND	--	
10N	1460	2.8	ND	--	
10D	1470	2.8	ND	--	
10S	1465	2.8	ND	--	
10H	1465	2.8	ND	--	
11M-1	1435	2.7	ND	--	
11M-2	1435	2.7	ND	--	
11N	1435	2.7	ND	--	
11D	1430	2.7	ND	--	
11S	1435	2.7	0.36	0.13	
11H	1435	2.7	ND	--	
12M-1	1410	2.7	ND	--	3/16-17/95
12M-2	1410	2.7	ND	--	
12N	1415	2.7	ND	--	
12D	1410	2.7	ND	--	
12S	1415	2.7	ND	--	
12H	1415	2.7	ND	--	

<sup>1</sup>M = Merced, N = El Nido, D = Dos Palos "Y", S = Stevinson, H = Hilmar. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 1.9 liters per minute.

<sup>3</sup>ND = Not Detected, <0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

TABLE II. Telone Ambient Monitoring Data (cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
13M	1355	2.6	ND	--	
13N-1	1375	2.6	ND	--	
13N-2	1375	2.6	ND	--	
13D	1420	2.7	ND	--	
13S	1490	2.8	ND	--	
13H	1530	2.9	ND	--	3/20-21/95
13B	BLANK	--	ND	--	
14M	1460	2.8	ND	--	
14N-1	1460	2.8	ND	--	
14N-2	1460	2.8	ND	--	
14D	1460	2.8	ND	--	
14S	1455	2.8	ND	--	3/21-22/95
14H	1455	2.8	0.52	0.19	
15M	1440	2.7	ND	--	
15N-1	1440	2.7	ND	--	
15N-2	1440	2.7	ND	--	
15D	1435	2.7	ND	--	
15S	1430	2.7	ND	--	3/22-23/95
15H	1430	2.7	ND	--	
16M	1415	2.7	ND	--	
16N-1	1415	2.7	ND	--	
16N-2	1415	2.7	ND	--	
16D	1415	2.7	ND	--	
16S	1415	2.7	0.44	0.16	3/23-24/95
16H	1420	2.7	ND	--	
17M	1425	2.7	ND	--	
17N	1415	2.7	0.60	0.22	
17D-1	1430	2.7	ND	--	
17D-2	1430	2.7	ND	--	
17S	1435	2.7	2.4	0.89	3/27-28/95
17H	1425	2.7	ND	--	
18M	1435	2.7	ND	--	
18N	1435	2.7	ND	--	
18D-1	1430	2.7	0.52	0.19	
18D-2	1430	2.7	0.51	0.19	
18S	1435	2.7	ND	--	3/28-29/95
18H	1425	2.7	ND	--	

<sup>1</sup>M = Merced, N = El Nido, D = Dos Palos "Y", S = Stevinson, H = Hilmar. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 1.9 liters per minute.

<sup>3</sup>ND = Not Detected, <0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

TABLE II. Telone Ambient Monitoring Data (cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
19M	1430	2.7	ND	--	
19N	1440	2.7	ND	--	
19D-1	1430	2.7	ND	--	
19D-2	1430	2.7	ND	--	
19S	1430	2.7	11.1	4.1	3/29-30/95
19H	1425	2.7	1.1	0.41	
20B	BLANK	--	ND	--	
20M	1425	2.7	ND	--	
20N	1425	2.7	0.54	0.20	
20D-1	1420	2.7	ND	--	
20D-2	1420	2.7	ND	--	
20S	1420	2.7	20.	7.4	3/30-31/95
20H	1415	2.7	ND	--	
21M	1440	2.7	ND	--	
21N	1440	2.7	ND	--	
21D	1440	2.7	ND	--	
21S-1	1440	2.7	0.63	0.23	
21S-2	1440	2.7	0.58	0.21	
21H	1450	2.8	0.51	0.18	4/3-4/95
21B	BLANK	--	ND	--	
22M	1455	2.8	ND	--	
22N	1455	2.8	0.58	0.21	
22D	1455	2.8	ND	--	
22S-1	1470	2.8	ND	--	
22S-2	1470	2.8	ND	--	4/4-5/95
22H	1460	2.8	ND	--	
23M	1430	2.7	ND	--	
23N	1430	2.7	ND	--	
23D	1435	2.7	0.42	0.16	
23S-1	1425	2.7	ND	--	
23S-2	1425	2.7	ND	--	4/5-6/95
23H	1430	2.7	ND	--	
24M	1455	2.8	0.42	0.15	
24N	1450	2.8	ND	--	
24D	1450	2.8	0.44	0.16	
24S-1	1445	2.7	1.47	0.54	
24S-2	1445	2.7	1.46	0.54	4/6-7/95
24H	1450	2.8	0.88	0.31	

<sup>1</sup>M = Merced, N = El Nido, D = Dos Palos "Y", S = Stevinson, H = Hilmar. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 1.9 liters per minute.

<sup>3</sup>ND = Not Detected, <0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

TABLE II. Telone Ambient Monitoring Data (cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
25M	1410	2.7	ND	--	
25N	1410	2.7	ND	--	
25D	1405	2.7	ND	--	
25S	1410	2.7	8.52	3.2	
25H-1	1405	2.7	1.77	0.66	
25H-2	1405	2.7	1.74	0.64	4/10-11/95
25B	BLANK	--	ND	--	
26M	1425	2.7	0.75	0.28	
26N	1420	2.7	0.60	0.22	
26D	1430	2.7	ND	--	
26S	1420	2.7	ND	--	
26H-1	1420	2.7	0.48	0.18	4/11-12/95
26H-2	1420	2.7	0.48	0.18	
27M	1440	2.7	0.40	0.15	
27N	1440	2.7	0.42	0.16	
27D	1440	2.7	ND	--	
27S	1440	2.7	0.57	0.21	
27H-1	1440	2.7	0.45	0.17	4/12-13/95
27H-2	1440	2.7	0.42	0.16	
28M	1440	2.7	0.48	0.18	
28N	1440	2.7	ND	--	
28D	1440	2.7	0.44	0.16	
28S	1440	2.7	1.86	0.69	
28H-1	1440	2.7	0.90	0.33	4/13-14/95
28H-2	1440	2.7	1.00	0.37	
29M-1	1415	2.7	ND	--	
29M-2	1415	2.7	ND	--	
29N	1410	2.7	ND	--	
29D	1415	2.7	ND	--	
29S	1410	2.7	3.5	1.3	
29H	1405	2.7	0.51	0.19	4/17-18/95
29B	BLANK	--	ND	--	
30M-1	1440	2.7	0.30	0.11	
30M-2	1440	2.7	0.33	0.12	
30N	1440	2.7	ND	--	
30D	1440	2.7	ND	--	
30S	1440	2.7	0.80	0.30	4/18-19/95
30H	1435	2.7	0.44	0.16	

<sup>1</sup>M = Merced, N = El Nido, D = Dos Palos "Y", S = Stevinson, H = Hilmar. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 1.9 liters per minute.

<sup>3</sup>ND = Not Detected, <0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

TABLE II. Telone Ambient Monitoring Data (cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
31M-1	1375	2.6	ND	--	
31M-2	1375	2.6	ND	--	
31N	1380	2.6	ND	--	
31D	1375	2.6	ND	--	
31S	1375	2.6	0.39	0.15	4/19-20/95
31H	1375	2.6	ND	--	
32M-1	1515	2.9	ND	--	
32M-2	1515	2.9	ND	--	
32N	1520	2.9	ND	--	
32D	1515	2.9	ND	--	
32S	1520	2.9	ND	--	4/20-21/95
32H	1525	2.9	ND	--	
33M	1430	2.7	ND	--	
33N-1	1430	2.7	ND	--	
33N-2	1430	2.7	ND	--	
33D	1435	2.7	ND	--	
33S	1440	2.7	ND	--	
33H	1440	2.7	0.30	0.11	4/24-25/95
33B	BLANK	--	ND	--	
34M	1430	2.7	ND	--	
34N-1	1430	2.7	ND	--	
34N-2	1430	2.7	ND	--	
34D	1430	2.7	ND	--	
34S	1425	2.7	ND	--	4/25-26/95
34H	1430	2.7	ND	--	
35M	1420	2.7	ND	--	
35N-1	1420	2.7	ND	--	
35N-2	1420	2.7	ND	--	
35D	1415	2.7	ND	--	
35S	1420	2.7	ND	--	4/26-27/95
35H	1420	2.7	ND	--	
36M	1455	2.8	ND	--	
36N-1	1455	2.8	ND	--	
36N-2	1455	2.8	ND	--	
36D	1485	2.8	ND	--	
36S	1500	2.8	ND	--	4/27-28/95
36H	1500	2.8	ND	--	

<sup>1</sup>M = Merced, N = El Nido, D = Dos Palos "Y", S = Stevinson, H = Hilmar. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 1.9 liters per minute.

<sup>3</sup>ND = Not Detected, <0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

TABLE III. Summary of Telone Data

Location	Number of 24-hour sampling periods <sup>a)</sup>	Number of samples above MDL <sup>b)</sup>	Maximum (ug/m <sup>3</sup> )	Average <sup>c)</sup> (ug/m <sup>3</sup> )
Merced	32	5	0.28	0.18
El Nido	32	5	0.22	0.20
Dos Palos "Y"	32	4	0.19	0.17
Stevinson	32	14	7.4	1.4
Hilmar	32	12	0.65	0.26

Collocated samples are averaged and used as a single sample for all data in this table.

a) Background samples not included.

b) MDL (Minimum detection limit) = 0.3 ug/sample (approx. 0.1 ug/m<sup>3</sup>).

c) Only samples above MDL included.

TABLE IV. Telone QA/QC Data  
Telone Spikes Prepared in Hexane

LABORATORY SPIKES			
ID	Level	Recovered	Percent
Sp-28	0.58	0.45	78
Sp-29	0.58	0.42	72
Sp-32	1.16	0.87	75
Sp-33	1.16	0.87	75
Sp-36	2.33	1.96	84
Sp-37	2.33	1.89	81

Tubes spiked in the laboratory and analyzed the same day.

Field Spikes			
ID	Level	Recovered	Percent
Sp-26	0.58	0.27	47
Sp-27	0.58	ND	--
Sp-30	1.16	0.42	36
Sp-31	1.16	0.45	39
Sp-34	2.33	1.14	49
Sp-35	2.33	0.99	42

Tubes spiked in the laboratory and carried with field samples under identical conditions.

APPENDIX I.  
ELB TELONE PROTOCOL

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

Protocol for the Monitoring of Telone in Merced and Kern Counties  
during the Limited Commercial Reintroduction Starting in Early 1995

Engineering and Laboratory Branch

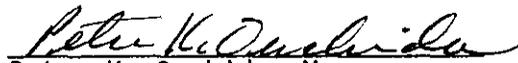
Monitoring and Laboratory Division

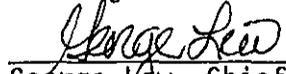
Project No. C94-071

Date: February 14, 1995

APPROVED:

  
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Don Fittell, Project Engineer

  
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George Lew, Chief  
Engineering and Laboratory 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 the Monitoring of Telone in Merced and Kern Counties  
during the Limited Commercial Reintroduction Starting in Early 1995

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the ARB Engineering and Laboratory Branch (ELB) will conduct ambient air monitoring for Telone during the limited commercial reintroduction program scheduled to begin in 1995. The first significant use of Telone is expected in Merced County, prior to sweet potato planting, from March through May. The heaviest use of Telone is anticipated to be in Kern County prior to planting of carrots. These applications are expected to begin around the first of July and continue through October.

The DPR approved of this reintroduction following several steps by DowElanco since permits for the use of Telone were suspended in 1990. This follows the evaluation of DowElanco's reintroduction program by the DPR, ARB, and Office of Environmental Health Hazard Assessment. Mitigation techniques and management practices specified by DowElanco will be used to reduce potential public exposure. The goal of this monitoring program is to assess the annual public exposure to Telone under these mitigation techniques.

II. Sampling

Samples will be collected using the apparatus shown in ATTACHMENT A. Calibrated flow meters will be used to set and monitor sample flow rate through charcoal tubes. The sampling tubes will be protected from direct sunlight and supported about 1.5 meters above the ground. AC powered samplers will be used where feasible, 12VDC powered samplers will be used at all other sites. All samplers will be operated at a flow rate of approximately 2.0 liters per minute (lpm).

Three or four sampling sites will be monitored by ELB staff for two twenty-four hour periods prior to any applications in order to establish that there are no detectable levels of Telone (1,3-dichloropropene) from any other sources. These background samples will be taken in both Merced and Kern Counties. When commercial applications begin, ELB staff will collect samples from these 3 or 4 sites which will be located near areas of expected high use. Planned monitoring sites are in: Hilmar, Stevinson, Merced, El Nido and Dos Palos Y in Merced County and Edison, Weed Patch/Lamont and Rosedale areas in Kern County. A minimum of two (up to a maximum of four) samples will be taken at each site per week, every week until applications end or detected levels are no longer considered significant. Sample collection will be approximately 24 hours long. One site will have duplicate samplers to monitor sampling precision. Samples will be stored in an ice chest until delivered to the laboratory. No meteorological data will be collected on site.

### III. Analysis

All samples will be stored in a freezer until analysis. Analysis of Telone samples will be performed by ELB staff. The analytical method includes extraction with carbon disulfide, separation by gas chromatography using a DB-624 column and measurement by an electron capture detector. The analytical procedure is described in ATTACHMENT B, "Standard Operating Procedure for the Analysis of Telone (1,3-dichloropropene) in Ambient Air." All samples will be analyzed within two weeks of receipt by the laboratory.

### IV. Quality Assurance

The "Quality Assurance Plan for Pesticide Monitoring" (ATTACHMENT C) will be followed. Sampling flow rates will be calibrated prior to and after sampling in the field. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. A field log book will be used to record sample start and stop times, sample IDs, any change in the flow rates, and other pertinent information. A chain of custody sheet will accompany all samples.

The dependent parameters (reproducibility, linearity and minimum detection limit) of the analytical instrument will be checked prior to analysis. Storage stability and collection efficiency have already been determined (ATTACHMENT B). At least one set of field spikes per month and at least one blank per week will be provided.

As part of the quality assurance program, the Quality Management and Operations Support Branch (QMOSB) will independently check the flow rates before the start of the sampling program and after completing the sampling program. QMOSB staff will also provide blind audit samples which will be included with the samples submitted to the laboratory for analysis.

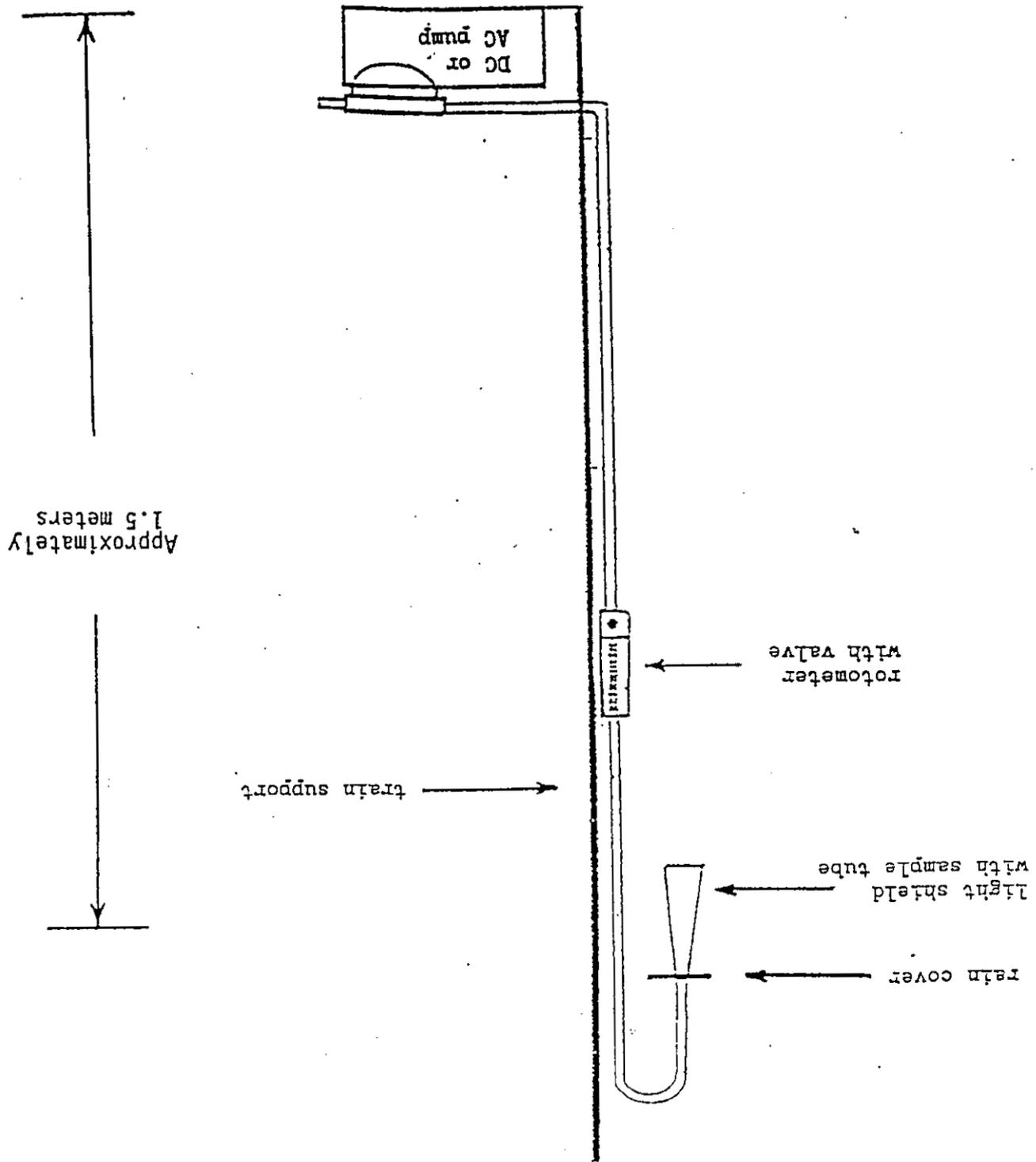
### V. Personnel

ARB Monitoring personnel will consist of Don Fitzell (Project Engineer) and several Instrument Technicians rotating throughout the sampling period.

### VI. Travel/Monitoring Schedule

For each week of sampling, an Instrument Technician will travel to the monitoring area on Monday morning. Sampling will begin as early as possible Monday morning. The charcoal tubes will be collected each day and replaced with a new one. On the last day of monitoring, the final samples will be collected and all samples (on ice) delivered to the laboratory in Sacramento.

ATTACHMENT A  
Pesticide Monitoring Apparatus



Standard Operating Procedure for the Analysis of Telone  
(1,3-dichloropropene) in Ambient Air

ATTACHMENT B

State of California  
Air Resources Board  
Monitoring and Laboratory Division/EEB

Standard Operating Procedure for the Analysis of  
Telone (1,3-dichloropropene) in Ambient Air  
(Revised with breakthrough data Sept. 8, 1994)

1. SCOPE

This is a gas chromatography/electron capture method for the determination of 1,3-dichloropropene from ambient air samples. The method was adapted from NIOSH Method 1003 (Issued 2/14/84.).

2. SUMMARY OF METHOD

The exposed charcoal tubes are stored in an ice chest or refrigerator until desorbed with 3 ml of carbon disulfide. The injection volume is 2  $\mu$ l. A gas chromatograph with an electron capture detector is used for analysis.

3. INTERFERENCES/LIMITATIONS

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

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Varian 3400 gas chromatograph  
Varian 604 Data System

Detector: 350 $^{\circ}$ C

Injector: 250 $^{\circ}$ C

Column : J&W Scientific DB-624, 30 meter, 0.32 mm i.d., 1.0  $\mu$ m film thickness.

Program: Initial 40 $^{\circ}$ C, hold 1 min.; to 70 $^{\circ}$ C @ 50 $^{\circ}$ C/min., hold 1 min.; to 82 $^{\circ}$ C @ 1 $^{\circ}$ C/min., hold 0.0 min.; to 225 $^{\circ}$ C @ 50 $^{\circ}$ C/min., hold 5 min. End = 22.46 min.  $t_R$  cis = 10.4 min.,  $t_R$  trans = 12.2 min.

Splitter open @ 0.8 min.

Flows:

column: He, 1.7 ml/min, 8 psi  
make up: N<sub>2</sub>, 38 ml/min.  
splitter: 37 ml/min.

**B. AUXILIARY APPARATUS:**

1. Glass amber vials, 4 ml capacity with septum caps.
2. Vial Shaker, SKC, or equiv.

**C. REAGENTS**

1. Carbon Disulfide, ACS Grade, or better
2. Telone (cis-1,3-dichloropropene and trans-1,3-dichloropropene mixture), Chem Service PS-152, 99+%, or equiv.

**5. ANALYSIS OF SAMPLES**

1. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which results in possible carry-over contamination.
2. At least one calibration sample must be analyzed for each batch of ten samples. The response of the standard must be within 10 % of previous calibration analyses.
3. Carefully score the primary section end of the sampled charcoal tube above the retainer spring and break at the score. Remove the glass wool plug from the primary end of the charcoal tube with forceps and place it into a 4 ml amber colored sample vial. Pour the charcoal into the vial and carefully add 3.0 ml carbon disulfide. CAUTION: HEAT WILL BE GENERATED. Seal the vial.

Retain the secondary section of the charcoal tube for later analysis to check the possibility of breakthrough.

4. Place the sample vial on a desorption vibrator for 45 minutes. Remove the carbon disulfide extract and store in a second vial at 4°C until analysis.
5. After calibration of the GC system, inject 2.0 ul of the extract. If the resultant peaks for telone have a measured area greater than that of the highest standard injected, dilute the sample and re-inject.
6. Calculate the concentration in ug/ml based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.
7. The atmospheric concentration is calculated according to:

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

6. QUALITY ASSURANCEA. Instrument Reproducibility

Triplicate injections of 3 standards at three different concentrations were made to establish the reproducibility of this instrument. This data is shown in TABLE 1.

TABLE 1. INSTRUMENT REPRODUCIBILITY

AMOUNT INJECTED (ug/ml)		INTEGRATION COUNTS			
trans	cis	trans	(%)	cis	(%)
0.024	0.076	15,099 ± 209	(+1%)	10,808 ± 178	(+2%)
0.24	0.76	141,742 ± 3,675	(+3%)	96,384 ± 1,939	(+2%)
2.4	7.6	1,716,441 ± 28,757	(+2%)	1,372,607 ± 41,371	(+3%)

B. Linearity

A five point calibration curve was made ranging from 0.05 ug/ml to 10.0 ug/ml. The corresponding equation and correlation coefficient is:

$$\text{total (cis + trans)} \quad y = 3.173 \times 10^{-6} X + 0.0650 \quad \text{Corr.} = .9991$$

The standard deviation of these values based on triplicate injections was <3% for each concentration.

C. Minimum Detection Limit

Using the equation above and the data below, the minimum detection limit for Telone was calculated by:

$$\text{MDL} = |i| + 3(\text{s.d.}_{\text{low}})$$

where :  $|i|$  = the absolute value of the intercept of the standard curve (from above).

$\text{s.d.}_{\text{low}}$  = the standard deviation of the lowest concentration used for the standard curve.

$$\text{lowest concentration used} = 0.05 + 0.001 \text{ ug/ml}$$

$$\text{MDL} = |0.0650| + 3(0.001) = 0.068 \text{ ug/ml}$$

Using 3 ml extraction volume and an average of 4.3 m<sup>3</sup> sample volume:

$$\frac{0.068 \text{ ug/ml} \times 3 \text{ ml}}{4.3 \text{ m}^3} = 0.05 \text{ ug/m}^3$$

Because of the high sensitivity, a MDL of 0.1 ug/m<sup>3</sup> is recommended to insure reliability of the data.

D. Collection and Extraction Efficiency (Recovery)

Collection and extraction efficiency data for Telone on charcoal is presented in TABLE 2. Note that no breakthrough occurred at the levels tested.

TABLE 2. COLLECTION AND EXTRACTION EFFICIENCY FOR TELONE ON CHARCOAL

CIS			TRANS			TOTAL		
Amount Spiked (ug)	Amount Recovered (ug)	(%)	Amount Spiked (ug)	Amount Recovered (ug)	(%)	Amount Spiked (ug)	Amount Recovered (ug)	(%)
0.76	0.63 ± 0.07	(83)	0.24	0.27 ± 0.02	(113)	1.0	0.90 ± 0.08	(90)
7.6	7.8 ± 0.3	(103)	2.4	2.0 ± 0.1	(83)	10.0	9.8 ± 0.3	(98)
15.2	14.8 ± 2.2	(97)	4.8	4.4 ± 0.8	(92)	20.0	19.2 ± 3.0	(96)
30.4	25.5 ± 0.7	(84)	9.6	8.8 ± 0.2	(92)	40.0	34.3 ± 0.9	(86)

\* Amount spiked on to primary section of charcoal tube. The tube was then subjected to an air flow of approximately 3 lpm for 24 hours. The primary and secondary sections were then desorbed with 3.0 ml of carbon disulfide and analyzed by capillary column GC/ECD. No Telone was found in the secondary charcoal section.

E. Storage Stability

Storage stability studies were done in triplicate for 1.0 ug telone spikes on charcoal tube primary sections over a period of 38 days. The percent recovery data for storage stability is presented in TABLE 3.

TABLE 3. TELONE STORAGE STABILITY AT 4°C

AMOUNT SPIKED (cis + trans)	PERCENT RECOVERY				
	1 DAY	3 DAYS	5 DAYS	11 DAYS	38 DAYS
1.0 ug	93 ± 8	71 ± 11	72 ± 5	76 ± 5	66 ± 4

F. Breakthrough

The secondary section of two high level field samples were analyzed for breakthrough. The primary sections contained 588 ug and 727 ug of Telone. No Telone was detected in either secondary section.

ATTACHMENT C

Quality Assurance Plan for Pesticide Monitoring

State of California  
California Environmental Protection Agency  
Air Resources Board

QUALITY ASSURANCE PLAN  
FOR PESTICIDE MONITORING

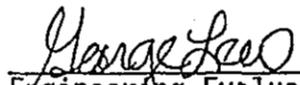
Prepared by the  
Monitoring and Laboratory Division  
and  
Stationary Source Division

Revised: February 4, 1994

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

## TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION . . . . .	1
A. QUALITY ASSURANCE POLICY STATEMENT . . . . .	1
B. QUALITY ASSURANCE OBJECTIVES . . . . .	1
II. SITING . . . . .	1
III. SAMPLING . . . . .	2
A. BACKGROUND SAMPLES . . . . .	2
B. SCHEDULE . . . . .	2
C. BLANKS AND SPIKES. . . . .	2
D. METEOROLOGICAL DATA. . . . .	2
E. COLLOCATION. . . . .	3
F. CALIBRATION. . . . .	3
G. FLOW AUDIT . . . . .	3
H. LOG SHEETS . . . . .	3
I. PREVENTATIVE MAINTENANCE . . . . .	3
J. TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY. . . . .	4
K. TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE . . . . .	5
IV. PROTOCOL . . . . .	6
V. ANALYSIS . . . . .	6
A. STANDARD OPERATING PROCEDURE . . . . .	6
VI. FINAL REPORTS AND DATA REDUCTION . . . . .	8
A. AMBIENT REPORTS . . . . .	8
B. APPLICATION REPORTS . . . . .	8
C. QUALITY ASSURANCE . . . . .	9

## APPENDIX

I. CHAIN OF CUSTODY FORM . . . . .	10
II. APPLICATION CHECKLIST . . . . .	11

## QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

## A. Quality Assurance Policy Statement

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

## B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

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

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

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

### III. Sampling

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

#### A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

#### B. Schedule

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

#### C. Blanks and Spikes

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

#### D. Meteorological Station

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

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

#### E. Collocation

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

#### F. Calibration

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

#### G. Flow Audit

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

#### H. Log Sheets

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

#### I. Preventative Maintenance

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

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

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

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

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

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

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

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

#### IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).
3. Specification of sampling periods and flow rates.
4. Description of the analytical method.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

#### V. Analysis

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

##### A. Standard Operating Procedures

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

#### 1. Instrument and Operating Parameters

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

#### 2. Sample Preparation

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

#### 3. Calibration Procedures

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

#### 4. Quality Control

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

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

## VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as  $\mu\text{g}/\text{m}^3$  (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

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

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

### A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

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

### B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

### C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.



## APPLICATION CHECKLIST

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

APPENDIX II  
DPR REQUEST FOR TELONE MONITORING

# Memorandum

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

Date : February 7, 1990

Place :

From : Department of Food and Agriculture 1220 N Street  
Sacramento, CA 95814

Subject: ARB Monitoring for 1,3-dichloropropene

In order to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), the California Department of Food and Agriculture requests that the Air Resources Board document the airborne levels of 1,3-dichloropropene. This memorandum provides background and recent use information on 1,3-dichloropropene-containing products, and identifies how they are used.

Technical 1,3-dichloropropene is a volatile, colorless-to-amber liquid with a molecular weight of 111.0 and a specific gravity of approximately 1.212 at 20°C. 1,3-dichloropropene's solubility in water is approximately 2300 mg/l and it has a vapor pressure of 27.8 mmHg at 20°C.

The EPA has classified 1,3-dichloropropene as a probable human carcinogen (Class B-2 carcinogen) based largely on tumor data. 1,3-dichloropropene has entered the risk assessment process at the California Department of Food and Agriculture because of oncogenic and teratogenic effects. The oral LD<sub>50</sub> has been reported as 713 mg/kg in male rats and 470 mg/kg in female rats. The inhalation (4 hour) LC<sub>50</sub> for the rat has been measured at 729 ppm. The EPA has classified 1,3-dichloropropene in Toxicity Category II for oral and eye exposure, and Toxicity category III for dermal exposure.

1,3-dichloropropene is a volatile liquid fumigant, which is an active ingredient in 4 currently registered products. 1,3-dichloropropene is used as a preplant soil treatment to control nematodes, fungi, insects, weeds and certain other soil pests. Generally, applications are made in the fall or spring using cultivation equipment, such as chisels, which inject this fumigant 10 to 12 inches below the soil surface. 1,3-dichloropropene is applied either as a full-coverage treatment or it may be banded in the planting row to fields that have been prepared for planting. Application rates for field crops vary from 5 gallons per acre for shallow-rooted crops grown in sandy soils to 36 gallons per acre for deep-rooted crops grown in clay soils. Soil fumigation of orchard and vineyard sites may require rates of up to 102 gallons per acre.

Genevieve Shiroma  
Page 2  
February 7, 1990

To prevent excessive fumigant loss, the soil surface is sealed after application by using a roller or other implement.

1,3-dichloropropene is listed as a restricted use material under Title 3, California Code of Regulations, Section 6400, and users must obtain a permit to purchase or use 1,3-dichloropropene-containing products. Additionally, users are required to file a Notice of Intent prior to application and a Pesticide Use Report after using 1,3-dichloropropene. Individual Pesticide Use Reports are compiled and summarized in the published Pesticide Use Report. This report indicates that 1,3-dichloropropene use totaled 14,057,100 pounds of active ingredient in 1986, and 13,628,366 pounds of active ingredient in 1987.

The following table summarizes 1987 Pesticide Use Report data for 1,3-dichloropropene.

1,3-dichloropropene Use by Crop (pounds of active ingredient)

<u>Crop</u>	<u>1987</u>
Carrot	2,376,669
Tomato	1,522,895
Sugarbeet	1,334,172
Broccoli	1,090,870
Open Land	1,084,115
Cotton	721,004
Sweet Potato	703,646
<b>TOTAL REPORTED USE</b>	<b>13,628,366</b>

Pesticide Use Report data summarized in this table shows the largest reported use of 1,3-dichloropropene occurs on fields planted to carrots but significant use occurs on land planted to several other major crops. Additionally, these data indicate that, when ranked in descending order, counties with highest use are Kern (2,179,310 pounds of active ingredient), Fresno (1,780,323), San Joaquin (1,481,061), Monterey (1,468,748), and Merced (1,324,998). When use report data is summarized by county, month and crop several locations and times of year provide comparable opportunities to document airborne concentrations. In 1987, the highest reported monthly use of 1,3-dichloropropene occurred in Merced County on fields where sugarbeets and sweet potatoes were planted.

Recommendation

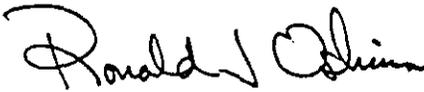
The use pattern for 1,3-dichloropropene suggests that monitoring should take place in Merced County for a 30-day sampling period

Genevieve Shiroma  
Page 3  
February 7, 1990

during April. Three sampling sites should be selected in relatively high-population areas or areas frequented by people. Sampling sites should be in sugarbeet and sweet potato growing areas, but not immediately adjacent to fields that will be planted to these crops. At each site, nineteen 24-hour samples should be taken during the 30-day sampling period. The specific dates for sampling during the period are:

April 2, 4, 5, 6, 7, 8, 9, 12, 13, 18, 21, 22, 23, 25, 26, 27, 28, 29, and 30.

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



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|-----------------|----------------|
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| John Donahue    | Mike J. Tanner |
| Keith Pfeifer   | Lynn Baker     |
| Peter Venturini | Dave Duncan    |
| Bill Fabre      | Ruby Reed      |