State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

FINAL

Report for 1996 Ambient Monitoring of Telone in Kern County

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. C96-045

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Report for 1996 Ambient Monitoring of Telone in Kern County

This report presents the results of ambient air monitoring for Telone from July 1 to August 9, 1996, in Kern County. The Air Resources Board (ARB) located five samplers throughout Kern County: south of Shafter, Rosedale, Bakersfield (urban background), Lamont and Weed Patch.

A wide range of concentrations of Telone were detected: 24-hour values ranged from 0.10 ug/m^3 to a maximum concentration of 13 ug/m^3. Eighty of the 105 samples analyzed were above the limit of detection (0.30 ug/sample or approximately 0.10 ug/m^3). Of these, 28 were 1.0 ug/m^3 or greater.

TABLE OF CONTENTS

LIST OF TABLES

APPENDICES

FINAL

Report for the 1996 Ambient Monitoring of Telone in Kern County

I. Introduction

At the request (April 9, 1996 memo from John Sanders to Genevieve Shiroma, and May 14, 1996 memo from Genevieve Shiroma to George Lew) of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) Engineering and Laboratory Branch (ELB) conducted ambient air monitoring for the pesticide Telone (1,3-dichloropropene). The monitoring was conducted in Kern County from July 1 to August 9, 1996. ARB also conducted monitoring in 1995, the first year of Telone's reintroduction since 1990. The purpose of conducting monitoring in 1996 was to determine ambient air concentrations during the use of Telone under DPR's 1996 revised Telone permit conditions.

The heaviest use of Telone was anticipated to be in Kern County during the period of mid-June through August 1996. The DPR's request specified that the monitoring be similar to that of the 1995 Telone air monitoring study. The Stationary Source Division (SSD) of ARB suggested that "the MLD monitor within the highest usage period in Kern County for either two days a week over a duration of two months, or for four days a week for one month." The SSD also suggested that "MLD use the same five monitoring sites as last year, and include an additional site in the southern area of Kern County near Mettler, if a suitable sampling site can be found," and "Depending on the use pattern, and if an additional monitor is not available, MLD might consider moving the sampler from the Almondale School site to the Mettler area." No such site was found in the Mettler area and so the Almondale School (Rosedale) site was used again for the summer 1996 monitoring project. Sampling sites were chosen based on the above recommendations as well as from consultation with Trical Incorporated, the Telone applicator.

The method development results (from previous studies) and Standard Operating Procedures for telone sampling/analysis are enclosed as Appendix 1.

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, 12th Edition, 1996).

Telone is a restricted use pesticide under Title 3, California Code of Regulations, Section 6400. The United States Environmental Protection Agency (US EPA) has classified it as a Class B2 carcinogen (probable human carcinogen. The State of California has determined under Proposition 65 that 1,3-dichloropropene is a carcinogen (California Code of Regulations, 1989).

III. Sampling Locations

Four sampling sites plus an urban background site were selected by ARB personnel from the areas of Kern County where Telone use is predominant. Sites were selected for their proximity to the fields with considerations for both accessibility and security of the sampling equipment. ELB staff collected samples from these sites which were located near areas of expected high use. Monitoring sites were in: Weed Patch, Lamont, Bakersfield and two west of Bakersfield. Four samples, plus one collocated sample, were taken at each site per week, for 5 weeks. No meteorological data were collected on site. The samples were collected over a five week period from July 1, 1996 to August 9, 1996. Addresses for the sites are listed in Table 1.

Table 1. Ambient Sampling Sites

Site	Contact
Rio Bravo Union School (RB) 6601 Enos Lane Bakersfield, CA 93112 (Highway 43 and Kratzmeyer Road) (South of Shafter)	Gerald Higbey, Superintendent (805) 589-2696
Almondale School (A) 10510 Chippewa Road Bakersfield, CA 93312 (Chippewa and Verdugo Roads) (Rosedale)	Diane Dalton, Principal (805) 588-6060
Air Res. Board Ambient Air Monitoring Site (BF) 5558 California Avenue, Suite 460 Bakersfield, CA 93309 (California Avenue and Stockdale Highway) (urban background)	Peter Ouchida (916) 322-3719
Mt. View School (M) 8201 Palm Avenue Lamont, CA 93241 (Highway 184 and Mt. View Road)	John Chavez, Superintendent (805) 845-0751
Vineland School (V) 14327 Vineland Road Weed Patch, CA 93307 (Vineland and Sunset Roads)	Steven Greenfield, Superintendent (805) 845-3713

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, and 200 mg in the secondary (SKC catalogue #226-09). Sample collection was approximately 24 hours in duration at approximately 2 Lpm. Any Telone present in the sampled ambient air was captured by the charcoal adsorbent contained in the tubes. Subsequent to sampling, the tubes were stored and transported in an insulated container with dry ice to the ARB's ELB laboratory 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 115 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 rotameter was 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 May 22, 1996 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 rotameters were set to 2.0 Lpm. This average flow value was used for all calculations.

V. Analytical Methodology

Upon arrival at the ARB Northgate Laboratory, all samples were stored in a freezer until analysis. Analysis of Telone samples was 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 Appendix 1, Attachment B. "Standard Operating Procedure for the Analysis of Telone (1,3-dichloropropene) in Ambient Air." The laboratory analyzed all samples within two weeks of receipt.

VI. Field Quality Control

The "Quality Assurance Plan for Pesticide Monitoring" (Appendix 1, Attachment C) was followed. Field quality control (QC) for the monitoring included:

1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) prepared by the Quality Management

and Operations Support Branch (QMOSB). The field spikes were exposed to ambient air at the background monitoring site for 24 hour periods at 2 L/minute (collocated with an ambient sample).

2) Four trip spikes prepared by the QMOSB.

3) Replicate (collocated) samples taken for five dates at each sampling location.

4) A trip blank for each week of sampling.

Sampling flow rates were calibrated prior to and after sampling in the field. Samplers were leak checked with the sampling media installed prior to and after each sampling period. As part of the quality assurance program, the Quality Management and Operations Support Branch (QMOSB) independently audited the rotameters (flow rates) before the start of the sampling program.

A field log book was 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 accompanied all samples.

Storage stability and collection efficiency were determined in a previous study (Appendix I, Attachment B).

VII. Laboratory Quality Control

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) were determined in a previous study (Appendix I, Attachment B).

VIII. Ambient Sample Results

Results of the ambient monitoring are listed in Table II. A summary of the results is shown in Table III. The sampling sites were located throughout Kern County: South of Shafter, Rosedale, Bakersfield (urban background), Lamont and Weed Patch. Refer to Table 1 for addresses and contacts at the respective locations. Also refer to Table 1 for the sample identification code for each location as used in Tables II and III.

A wide range of concentrations of Telone were detected: 24-hour values ranged from 0.10 ug/m^3 to a maximum concentration of 13 ug/m^3. Eighty of the 105 samples analyzed were above the limit of detection (0.30 ug/sample or approximately 0.10 ug/m^3). Of these, 28 were 1.0 ug/m^3 or greater.

IX. Quality Assurance Sample Results

The results of the laboratory, trip and field spikes are shown in Table IV. The spikes were prepared by staff of the Quality Management and Operations Support Branch (QMOSB) of the ARB. Refer to Attachment 3 of Appendix III for the procedures used to spike the sample cartridges. The laboratory spikes were placed in the freezer (Testing Section Lab) immediately after preparation and remained there until extraction/analysis. The trip spikes were stored in the freezer until the application test when they were placed in an ice chest on dry ice for transport to the field. The trip spikes remained on dry ice during the entire monitoring period (except for sample log-in and labelling) and transport to the lab after which they were kept in the lab freezer until extraction/analysis. The field spikes were handled the same as the trip spikes except that ambient air was pulled through them at the background sampling location during collection of an ambient sample. The sampling flow rate for the field spikes was 2 l/minute, the same as for the ambient sample.

Field spikes are collocated (same sampling flow rate, duration and environmental conditions) with a background ambient sample. In theory, the mass of pesticide (Telone) found on the field spike cartridge, after ambient air sampling, would be the sum of the mass spiked and the mass collected during the sampling interval. The analyte recovery is calculated by subtracting the amount collected during the sampling interval (background ambient sample result) from the amount found on the field spike cartridge and then dividing by the amount spiked (expected amount). The calculation is based on the assumption that the field spike and ambient sample collection parameters are identical, i.e., collocated sampling. Any deviation from "collocated" sampling conditions could invalidate the results obtained from this type of QA procedure.

Four field spikes were collected during this project, QAT4, QAF2, QAF3 and QAF5. A field blank, QAF4, was also collected. This field blank is effectively a collocated ambient sample. The sampling periods, i.e., start and stop times for the field spikes were supposed to have been identical, as described above, to that of the corresponding ambient samples. However, due to misunderstanding by the field technician, two field spikes, QAF3 and QAF5, had sampling times which were slightly different from that of the corresponding ambient samples. For QAF3 the sample start time was the same as the ambient sample (1315; 8/6/96) but the ambient sample and field spike stop times were 1045 (8/7/96) and 1315 (8/7/96) respectively. Thus, the field spike sample QAF3 was allowed to collect air for 2.5 hours more than the ambient sample. For QAF5, the ambient sample (8/7/96 to 8/8/96) and field spike start times were 1045 and 1315 and the stop times were 1120 and 1320 respectively. The ambient sample ran for 24.5 hours and QAF5 ran for 24 hours. Thus the sampling duration was very close but the sampling periods were not precisely the same. These samples, QAF3 and QAF5, are not valid due to these sample collection discrepancies and so the results are not included in Table IV (but can be found in Appendix III, "Final Telone 1996 QA System Audit Report"). The remaining field spikes, QAT4 and QAF2, were collected according to protocol, i.e., were collocated with the ambient samples, and so the results are included in Table IV.

From Table IV, the average recovery of the laboratory spikes was 75% with a range of 63% to 91%. The average recovery of the trip spikes was 50% with a range of 41% to 59%. The average recovery for the field spikes was 29% with a range of 58% to 0%.

From the November 9, 1995 report "Ambient Air Monitoring in Merced County for Telone (1,3-Dichloropropene) During DowElanco's Commercial Reintroduction, March-

April, 1995," the average reported value for the laboratory spikes was 78% with a range of 72% to 84%. The average recovery of the trip spikes was 43% with a range of 36% to 49%. No field spikes were collected during the March-April, 1995 study.

From the November 8, 1996 report "Ambient Air Monitoring in Kern County for Telone (1,3-Dichloropropene) During DowElanco's Commercial Reintroduction, May-December, 1995", the average reported value for the laboratory spikes was 78% with a range of 39% to 101%. The average recovery of the trip spikes was 61% with a range of 23% to 107%. No field spikes were collected during the May-December, 1995 study.

The results of the QA spikes reported in the two 1995 studies and the results reported in this study (Table IV) indicate that the ambient concentration results for Telone may be under-reported by a factor of approximately 2 or more. No data presented in this report has been "corrected" for field sampling, transport or storage related recovery losses.

The conclusions discussed above regarding the accuracy of ambient concentration results are solely that of the ELB, Testing Section. The QMOSB QA/QC report can be found in Appendix III, "Final Telone 1996 QA System Audit Report". The evaluation of the QA sample results by the QMOSB and subsequent conclusions made regarding the impact on data differ from those of the ELB, as presented above.

TABLE II

KERN COUNTY TELONE DATA, SUMMER 1996

Sample Start Date	Sample I.D.	Sample Volume (m^3)	Mass Per Sample (ug)	Ambient Air Concentration (ug/m^3)
7/1/96	1RB	2.7	0.33	0.12
	1A	2.7	0.35	0.13
	1BF	2.8	1.3	0.46
	1M	3.0	16	5.3
	1V	3.0	28	9.3
7/2/96	2RB	2.7	5.6	2.1
	2RB-D	2.7	5.9	2.2
	2A	2.6	1.6	0.62
	2A-D	2.6	1.4	0.54
	2BF	2.8	1.1	0.39
	2BF-D	2.8	0.97	0.35
	2M	2.8	10	3.6
	2M-D	2.8	11	3.9
	2V	2.8	15	5.4
	2V-D	2.8	15	5.4
	2B (BLANK)	NA	<.30	NA
7/8/96	3RB	3.1	<.30	<.10
	3A	3.0	<.30	<.10
	3BF	2.9	<.30	<.10
	3M	2.7	0.39	0.14
	3V	2.7	5.0	1.9
7/9/96	4RB	2.5	<.30	<.12
	4A	2.5	0.33	0.13
	4BF	2.5	<.30	<.12
	4M	2.7	<.30	<.12
	4V	2.7	2.5	0.93
7/10/96	5RB	2.7	0.44	0.16
	5RB-D	2.7	0.45	0.17
	5A	2.7	<.30	<.11
	5A-D	2.7	<.30	<.11
	5BF	2.6	<.30	<.12
	5BF-D	2.6	<.30	<.12
	5M	2.5	<.30	<.12
	5M-D	2.5	<.30	<.12
	5V	2.4	<.30	<.13
	5V-D	2.4	<.30	<.13

NA = Not Applicable

TABLE II (cont.)

KERN COUNTY TELONE DATA, SUMMER 1996

Sample Start Date	Sample I.D.	Sample Volume (m^3)	Mass Per Sample (ug)	Ambient Air Concentration (ug/m^3)
7/11/96	6B (BLANK)	NA	<.30	NA
	6RB	2.6	<.30	<.12
	6A	2.6	<.30	<.12
	6BF	2.7	0.84	0.31
	6M	2.6	8.1	3.1
	6V	2.6	0.70	0.27
7/15/96	7RB	2.8	0.90	0.32
	7A	2.8	<.30	<.11
	7BF	2.6	<.30	<.12
	7M	2.8	2.3	0.82
	7V	2.8	1.8	0.64
7/16/96	8RB	2.8	1.8	0.64
	8A	2.8	1.7	0.61
	8BF	2.7	0.46	0.17
	8M	2.7	1.9	0.70
	8V	2.7	2.6	0.90
7/17/96	9RB	2.8	1.1	0.39
	9RB-D	2.8	0.97	0.35
	9A	2.8	0.85	0.30
	9A-D	2.8	0.54	0.19
	9BF	2.8	0.44	0.16
	9BF-D	2.8	0.43	0.15
	9M	2.7	0.73	0.27
	9M-D	2.7	0.74	0.27
	9V	2.8	0.89	0.32
	9V-D	2.8	0.80	0.29
7/18/96	10B (BLANK)	NA	<.30	NA
	10RB	2.7	0.58	0.21
	10A	2.7	0.47	0.17
	10BF	2.9	<.30	<.10
	10M	2.8	1.0	0.36
	10V	2.8	<.30	<.11

NA = Not Applicable

TABLE II (cont.)

KERN COUNTY TELONE DATA, SUMMER 1996

Sample Start Date	Sample I.D.	Sample Volume (m^3)	Mass Per Sample (ug)	Ambient Air Concentration (ug/m^3)
7/22/96	11RB	2.7	<.30	<.11
	11A	2.8	1.7	0.61
	11BF	2.6	0.71	0.27
	11M	2.7	1.0	0.37
	11V	2.7	2.3	0.85
7/23/96	12RB	2.9	<.30	<.10
	12A	2.8	2.8	1.0
	12BF	2.8	3.3	1.2
	12M	2.8	2.1	0.75
	12V	2.8	2.5	0.89
7/24/96	13RB	2.7	2.4	0.89
	13RB-D	2.7	2.3	0.85
	13A	2.7	2.4	0.89
	13A-D	2.7	2.3	0.85
	13BF	2.7	6.5	2.4
	13BF-D	2.7	6.5	2.4
	13M	2.6	9.0	3.5
	13M-D	2.6	8.9	3.4
	13V	2.6	22	8.5
	13V-D	2.6	22	8.5
7/25/96	14B (BLANK)	NA	<.30	NA
	14RB	2.7	2.7	1.0
	14A	2.7	1.1	0.41
	14BF	2.8	2.5	0.89
	14M	2.7	1.7	0.63
	14V	2.7	5.2	1.9
7/29/96	15RB	Sample	lost during	analysis
	15A	"	"	"
	15BF	"	"	"
	15M	"	"	"
	15V	"	"	"

NA = Not Applicable

TABLE II (cont.)

KERN COUNTY TELONE DATA, SUMMER 1996

Sample Start Date	Sample I.D.	Sample Volume (m^3)	Mass Per Sample (ug)	Ambient Air Concentration (ug/m^3)
7/30/96	16RB	2.6	0.92	0.35
	16A	2.6	1.2	0.46
	16BF	2.6	1.1	0.42
	16M	2.5	14.	5.6
	16V	2.6	0.26	0.10
7/31/96	17RB	2.7	<.30	<.11
	17RB-D	2.7	<.30	<.11
	17A	2.8	0.54	0.19
	17A-D	2.8	0.53	0.19
	17BF	2.8	0.27	0.10
	17BF-D	2.8	0.43	0.15
	17M	2.8	4.9	1.8
	17M-D	2.8	5.7	2.0
	17V	2.8	<.30	<.11
	17V-D	2.8	<.30	<.11
8/1/96	18B (BLANK)	NA	<.30	NA
	18RB	2.7	0.85	0.31
	18A	2.7	<.30	<.11
	18BF	2.7	0.29	0.11
	18M	2.8	3.1	1.1
	18V	2.7	<.30	<.11
8/5/96	19RB	2.5	<.30	<.12
	19A	2.5	<.30	<.12
	19BF	2.7	1.3	0.48
	19M	2.5	1.2	0.48
	19V	2.5	22	8.8
8/6/96	20RB	2.8	<.30	<.11
	20A	2.8	5.1	1.8
	20BF	2.5	1.2	0.48
	20M	2.8	6.0	2.1
	20V	2.7	13	4.8

NA = Not Applicable

TABLE II (cont.)

KERN COUNTY TELONE DATA, SUMMER 1996

Sample Sample Date	Sample I.D.	Sample Volume (m^3)	Mass Per Sample (ug)	Ambient Air Concentration (ug/m^3)
8/7/96	21RB	2.7	6.0	2.2
	21RB-D	2.7	6.5	2.4
	21A	2.7	4.8	1.8
	21A-D	2.7	5.1	1.9
	21BF	2.8	8.0	2.9
	21BF-D	2.8	8.3	3.0
	21M	2.7	0.65	0.24
	21-M-D	2.7	0.59	0.22
	21V	2.7	0.65	0.24
	21V-D	2.7	0.59	0.22
8/8/96	22B (BLANK)	NA	<.30	NA
	22RB	2.7	4.8	1.8
	22A	2.7	6.7	2.5
	22BF	2.7	2.6	0.96
	22M	2.7	34	13
	22V	2.8	4.9	1.8

NA = Not Applicable

TABLE III

SUMMARY OF TELONE DATA

START DATE	RB TELONE CONC. (ug/m^3)	A TELONE CONC. (ug/m^3)	BF TELONE CONC (ug/m^3)	M TELONE CONC. (ug/m^3)	V TELONE CONC. (ug/m^3)
07/01/96	0.12	0.13	0.46	5.3	9.3
07/02/96	2.1	0.62	0.39	3.6	5.4
07/02/96	2.2	0.54	0.35	3.9	5.4
07/08/96	<.10	<.10	<.10	0.14	1.9
07/09/96	<.12	0.13	<.12	<.12	0.93
07/10/96	0.16	<.11	<.12	<.12	<.13
07/10/96	0.17	<.11	<.12	<.12	<.13
07/11/96	<.12	<.12	0.31	3.1	0.27
07/15/96	0.32	<.11	<.12	0.82	0.64
07/16/96	0.64	0.61	0.17	0.70	0.90
07/17/96	0.39	0.30	0.16	0.27	0.32
07/17/96	0.35	0.19	0.15	0.27	0.29
07/18/96	0.21	0.17	<.10	0.36	<.11
07/22/96	<.11	0.61	0.27	0.37	0.85
07/23/96	<.10	1.0	1.2	0.75	0.89
07/24/96	0.89	0.89	2.4	3.5	8.5
07/24/96	0.85	0.85	2.4	3.4	8.5
07/25/96	1.0	0.41	0.89	0.63	1.9
07/29/96	NR	NR	NR	NR	NR
07/30/96	0.35	0.46	0.42	5.6	0.10
07/31/96	<.11	0.19	0.10	1.8	<.11
07/31/96	<.11	0.19	0.15	2.0	<.11
08/01/96	0.31	<.11	0.11	1.1	<.11
08/05/96	<.12	<.12	0.48	0.48	8.8
08/06/96	<.11	1.8	0.48	2.1	4.8
08/07/96	2.2	1.8	2.9	0.24	0.24
08/07/96	2.4	1.9	3.0	0.22	0.22
08/08/96	1.8	2.5	.96	13	1.8
Maximum	2.4	2.5	3.0	13	9.3
* Mean	.91	.76	.85	2.2	3.0
* # of Samples	18	20	21	24	21

* Only values >LOQ were used to calculate the mean.

TABLE IV

QMOSB QUALITY ASSURANCE
SPIKES and BLANKS
FOR TELONE, SUMMER 1996

Sample Date	Sample I.D.	Sample Volume (m_3)	Uncorrected Mass Per Sample (ug)	Collocated Unspiked Mass Per Sample (ug)	Corrected[1)] Mass Per Sample (ug)	Expected Mass Per Sample (ug)	% Recovery
Held in Freezer 4 days	QAL 1	0	0.95	NA[2]	0.95	1.5	63
	QAL 2	0	0.96	NA[2]	0.96	1.5	64
	QAL 3	0	<.30	NA[2]	<.30	BLANK	NA
	QAL 4	0	8.7	NA[2]	8.7	9.6	91
	QAL 5	0	7.9	NA[2]	7.9	9.6	82
8/5/96	QAT-1A	0	0.67	NA[2]	0.67	1.5	45
8/5/96	QAT-2A	0	<.30	NA[2]	<.30	BLANK	NA
8/5/96	QAT-3A	0	0.61	NA[2]	0.61	1.5	41
8/5/96	QAT-4A	0	5.7	NA[2]	5.7	9.6	59
8/5/96	QAT-5A	0	5.3	NA[2]	5.3	9.6	55
8/5/96	QAT-4	2.7	6.9	1.3	5.6	9.6	58
8/5/96	QAF-2	2.7	1.2	1.3	0.0	1.5	0
8/6/96	QAF-4	2.7	1.4	1.2	.20	BLANK	NA

1) Corrected Mass = Uncorrected Mass - Collocated Unspiked Mass

2) Not Applicable

QAL = lab spikes
QAT = trip spikes (except QAT-4 which was used as a field spike)
QAF = field spikes

APPENDIX I

ELB Telone Monitoring Protocol

Cal/EPA

California
Environmental
Protection
Agency

Air Resources Board

PO Box 2815
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Sacramento, CA
95812-2815

Pete Wilson
Governor

James M. Strock
Secretary for
Environmental
Protection

MEMORANDUM

TO: Dr. John Sanders, Chief
Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulations

FROM: George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division

DATE: July 1, 1996

SUBJECT: 1996 TELONE AMBIENT AIR MONITORING PROGRAM

Attached is the final monitoring protocol, "Protocol for 1996 Ambient Monitoring of Telone in Kern County." If you or your staff have questions or need further information, please contact me at (916) 263-1630 or Kevin Mongar at (916) 263-2063.

Attachment

cc: Genevieve Shiroma, SSD

bcc: Bill Oslund, MLD
Jeff Cook, MLD

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Protocol for 1996 Ambient Monitoring of Telone in Kern County

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. C96-045

Date: June 26, 1996

APPROVED:

Kevin Mongar, Project Engineer

Cynthia L. Castronovo, Manager
Testing Section

George Lew, Chief
Engineering and Laboratory Branch

Protocol for the 1996 Ambient Monitoring
of Telone in Kern County

I. Introduction

At the request of the Department of Pesticide Regulation (April 9, 1996 memo from John Sanders to Genevieve Shiroma, and May 14, 1996 memo from Genevieve Shiroma to George Lew), the Air Resources Board (ARB) Monitoring and Laboratory Branch (MLD) staff will conduct ambient air monitoring for the pesticide Telone (1,3-dichloropropene). ARB staff conducted monitoring last year, the first year of Telone's reintroduction since 1990 (final report pending). The purpose the 1996 summer monitoring program is to determine ambient air concentrations during the use of Telone under Department of Pesticide Regulation's (DPR) 1996 revised Telone permit conditions.

The heaviest use of Telone is anticipated to be in Kern County during the period of mid-June through August 1996. The DPR's request specified that the monitoring be similar to that of the 1995 Telone air monitoring study. The Stationary Source Division (SSD) of ARB suggested that "the MLD monitor within the highest usage period in Kern County for either two days a week over a duration of two months, or for four days a week for one month." The SSD also suggested that "MLD use the same five monitoring sites as last year, and include an additional site in the southern area of Kern County near Mettler, if a suitable sampling site can be found," and "Depending on the use pattern, and if an additional monitor is not available, MLD might consider moving the sampler from the Almondale School site to the Mettler area." As an additional monitor is not available, we are looking for another site in the Mettler area. If no such site is found then Almondale School site will be used again for the summer 1996 monitoring program. Sampling sites have been chosen based on the above recommendations as well as from consultation with Trical Incorporated, the Telone applicator.

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 two liters per minute (lpm).

Four sampling sites plus an urban background site were selected by ARB personnel from the areas of Kern County where Telone use is predominant. Sites were selected for their proximity to the fields with the expected highest Telone usage and with considerations for both accessibility and security of the sampling equipment. Planned monitoring sites are in: Weed Patch, Lamont, Bakersfield, and Mettler (if a suitable site can be found) areas in Kern County. Four samples, plus one collocated sample, will be taken at each site per week, for five weeks. Sample collection will be approximately 24 hours in duration at approximately two lpm. All samples in the field will be stored in an ice chest containing dry ice. No meteorological data will be collected on site. These samples will be collected over a five week period from July 1, 1996 to August 8, 1996. Addresses for the sites are listed in Table 1.

Table 1. Ambient Sampling Sites	
Rio Bravo Union School 6601 Enos Lane Bakersfield, CA 93112 (Highway 43 and Kratzmeyer Road)	Gerald Higbey, Superintendent (805) 589-2696
Almondale School 10510 Chippewa Road Bakersfield, CA 93312 (Chippewa and Verdugo Roads)	Diane Dalton, Principal (805) 588-6060
Air Resources Board Ambient Air Monitoring Site 5558 California Avenue, Suite 460 Bakersfield, CA 93309 (California Avenue and Stockdale Highway)	Peter Ouchida (916) 322-3719
Mt. View School 8201 Palm Avenue Lamont, CA 93241 (Highway 184 and Mt. View Road)	John Chavez, Superintendent (805) 845-0751
Vineland School Superintendent 14327 Vineland Road Weed Patch, CA 93307 (Vineland and Sunset Roads)	Steven Greenfield, (805) 845-3713
Possible site in Mettler	

III. Analysis

Upon arrival at the ARB Northgate Laboratory, all samples will be stored in a freezer until analysis. Analysis of Telone samples will be performed by MLD 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 instrument 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 and at least one blank per week will be provided.

As part of the quality assurance program, the ARB Quality Management and Operating 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.

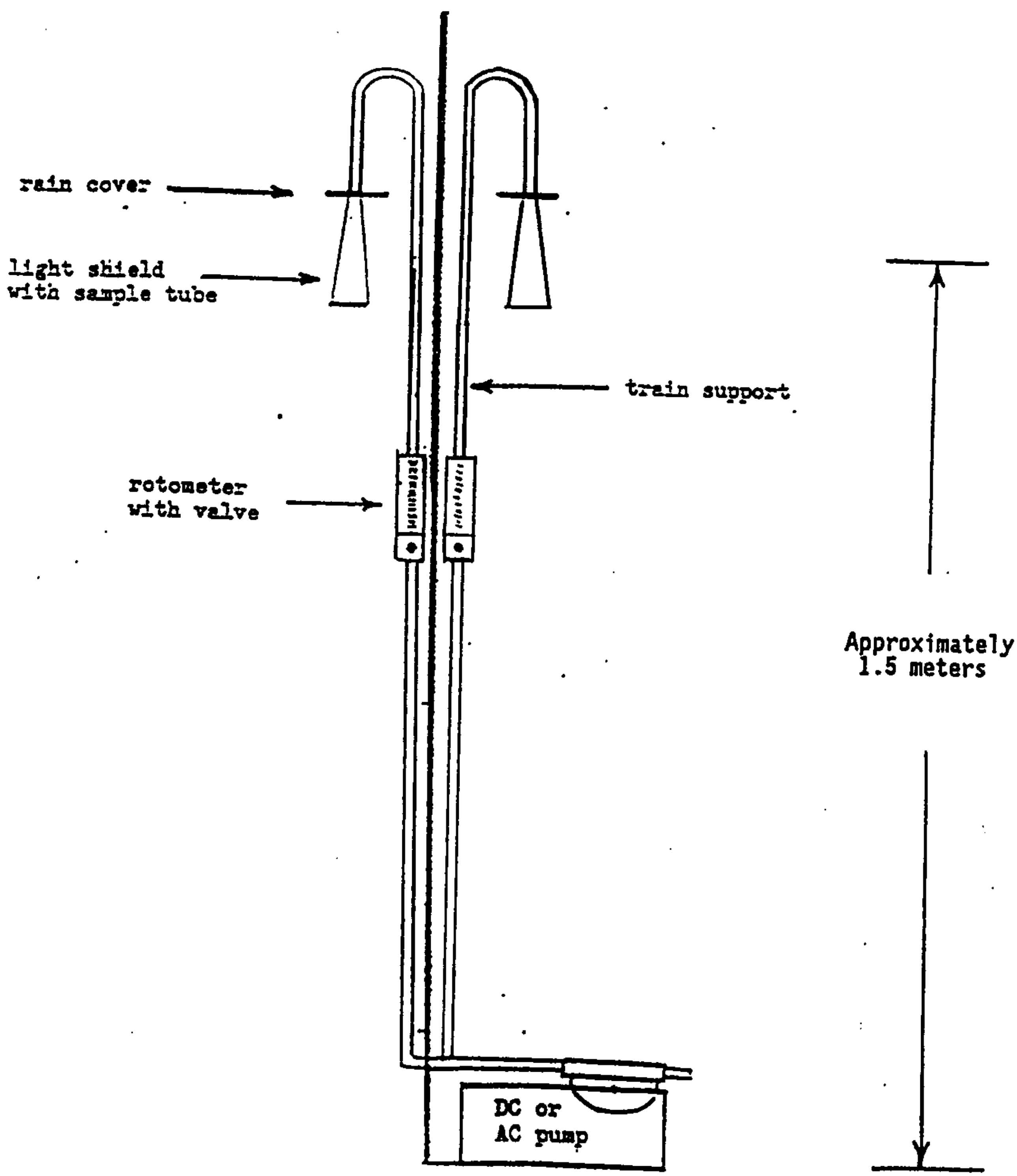
Field Quality Control (QC) for the monitoring will include; 1) five field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) will be prepared by the QMOSB and spiked at five different levels. The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 2 L/minute. 2) Five trip spikes will be prepared by the AMOSB and spiked at five different levels. 3) Replicate samples will be taken for five dates at each sampling location. 4) Trip blanks will be obtained at each of the five sampling locations.

V. <u>Personnel</u>

ARB Monitoring personnel will consist of Kevin Mongar (Project Engineer) and Instrument Technicians from the ARB Air Quality Surveillance Branch's Air Monitoring-Central Section.

ATTACHMENT A

Pesticide Monitoring Apparatus


rain cover
light shield
with sample tube
train support
rotometer
with valve
Approximately
1.5 meters
DC or
AC pump

ATTACHMENT B

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

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

Standard Operating Procedure for the Analysis of
Telone (1,3-dichloropropene) in Ambient Air
(Revised with breakthrough data Sept. 8, 1994)
(Revised with additional stability data January 18, 1996)

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 ul. 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°C
Injector: 250°C
Column: J&W Scientific DB-624, 30 meter, 0.32 mm i.d., 1.0 um film thickness.

Program: Initial 40°C, hold 1 min.; to 70°C @ 50 C/min., hold 1 min.; to 82°C @ 1°C/min., hold 0.0 min.; to 225°C @ 50°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.
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 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:

Conc., ug/m^3 = (Extract Conc., ug/ml X 3 ml) / Air Volume Sampled, m^3

6. QUALITY ASSURANCE

A. Instrument Reproducibility

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

TABLE 1. INSTRUMENT REPRODUCIBILITY

AMOUNT INJECTED (ug/ml)		INTEGRETATION 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:

total (cis + trans) $y = 3.173 \times 10^{-6}X + 0.0650$ 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:

$$MDL = |I| + 3(s.d._{low})$$

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

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

lowest concentration used = 0.05 + 0.001 ug/ml

MDL = |0.0650| + 3(0.001) = 0.068 ug/ml

Using 3 ml extraction volume and an average of 4.3 m^3 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^3 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)	2.2	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 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

Additional stability studies were conducted as part of the quality assurance program during a lengthy Telone monitoring program in Kern County during 1995. The results are included on the next page.

In-house Stability Study 10-11/95			
Day	Level (ug)	Recovered	Percent
0 (neat)	1.5	1.7	113
2	1.5	1.4	93
14	1.5	1.2	80
14	7.5	8.8	117
14	15.0	16.0	107
22	1.5	1.2	80
22	7.5	8.1	108
22	15.0	16.0	107
34	1.5	0.90	60

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

APPROVED:

_____________________, Chief
Toxic Air Contaminant
Identification Branch

_____________________, Chief
Quality Management and Operations
Support Branch

_____________________, Chief
Engineering Evaluation Branch

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

APPENDIX

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	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. 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 ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

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

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

A. Ambient Reports

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

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

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

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

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

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: ______________ Date: ____/____/______
Sample/Run #: ______________ Time: ______________
Job name: ______________________________
Sample Location: ______________________________
Type of Sample: ______________________________
Log #'s: ____________

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

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: ______________________________

APPLICATION CHECKLIST

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

APPENDIX II

Request for Telone Monitoring

Cal/EPA

California Environmental Protection Agency

Air Resources Board

P.O. Box 2815
2020 L Street
Sacramento, CA
95812-2815

Pete Wilson
Governor

James M. Strock
Secretary for Environmental Protection

MEMORANDUM

TO: George
George Lew, Chief
Engineering and Laboratory Branch
Bill
Bill Oslund, Chief
Air Quality Surveillance Branch

FROM: Genevieve Shiroma
Genevieve A. Shiroma, Chief
Air Quality Measures Branch

DATE: May 14, 1996

SUBJECT: REQUEST FOR TELONE MONITORING IN 1996

The Department of Pesticide Regulation (DPR) recently requested that the Air Resources Board (ARB) conduct additional air monitoring for Telone in 1996 (Enclosure), similar to that of the 1995 Telone air monitoring study. At this time, we request that the Monitoring and Laboratory Division (MLD) conduct this monitoring in 1996, during the period of Telone's highest usage. This request is due, in part, to revisions the DPR made in their 1996 permit conditions which allow increased Telone usage, and because the monitoring data from 1995 was not representative of expected Telone usage. DPR's changes to the Telone permit conditions include:

- an increased injection rate from 12 gallons/acre to 35 gallons/acre;
- allowing statewide usage instead of only in 13 counties;
- changing the injection depth from 18 inches to 14 inches for flat broadcast injections, and from 18 inches to 12 inches for row crop injections;
- a field can receive a treatment every year, instead of once every 3 years; and
- addition of a township usage cap of 5,000 gallons/township.

We suggest the MLD monitor within the highest usage period in Kern County for either two days a week over a duration of two months, or for four days a week for one month. Although it is difficult to predict the months of highest usage in advance, historically, one of the peak usage periods is in the summer months. At this point, we suggest the monitoring occur during the period of mid-June through August 1996. After comparing specific application sites from 1995 with the placement of the ARB monitors, we suggest that:

1. MLD use the same five monitoring sites as last year, and include an additional site in the southern area of Kern County near Mettler, if a suitable sampling site can be found.

2. MLD discuss the recent usage and placement of Telone applications in Kern County with Paul Niday of Trical Inc. (the applicator of Telone), to help determine the expected month(s) of highest usage, and where the majority of applications are expected to occur.

3. Depending on the use pattern, and if an additional monitor is not available, MLD might consider moving the sampler from the Almondale School site to the Mettler area.

We understand that it is hard to gauge the maximum usage and sampler placement for 1996 based on 1995 data. Discussions with Trical Inc., nearer to the time of maximum applications, should assist you in planning for the best monitoring program for 1996.

Thank you again for your continued help on this project. If you have any questions please call me at (916) 322-7072, or have your staff call Ms. Cara Roderick, at (916) 322-3943.

Enclosure

cc: Bryan Stuart, Ph.D.
DowElanco
3835 North Freeway Boulevard, No. 240
Sacramento, California 95834

Mr. Paul Niday
Trical Incorporated
P.O. Box 1327
Hollister, California 95024

Mr. Paul Gosselin
Assistant Director, Division of Enforcement,
Environmental Monitoring, and Data Management
Department of Pesticide Regulation
1020 N Street, Room 100
Sacramento, California 95814

Mr. John Sanders
Chief, Environmental Monitoring
and Pest Management Branch
Department of Pesticide Regulation
1020 N Street
Sacramento, California 95814

Richard Becker, Ph.D., D.A.B.T.
Deputy Director of Scientific Affairs
Office of Environmental Health Hazard Assessment
P.O. Box 942732
Sacramento, California 94234

Mr. Cliff Calderwood
Manager of Compliance, Southern Region
San Joaquin Valley Unified Air Pollution Control District
2700 M Street, Suite 275
Bakersfield, California 93301

Ms. Cara Roderick
Substance Evaluation Section
Stationary Source Division

State of California

Memorandum

ENCLOSURE

To : Genevieve Shiroma, Chief
Air Quality Measures Branch
Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Date : April 9,

Place :

From : **Department of Pesticide Regulation** — 1020 N Street, Room 161
Sacramento, California 95814-5624

Subject : AIR MONITORING FOR 1,3-DICHLOROPROPENE

As you know, all permits for the use of pesticides containing 1,3-dichloropropene (1,3-D) were suspended in 1990 following its detection in air at levels of concern. DowElanco, the principal manufacturer of 1,3-D, conducted field tests to determine if the use of 1,3-D can be modified to reduce residues in air to acceptable levels. In 1994, the Department of Pesticide Regulation (DPR) approved a limited commercial re-entry of Telone® (1,3-D) in California, and the Air Resources Board (ARB) conducted air monitoring in conjunction with this limited resumption of use.

DPR requests that ARB once again conduct air monitoring in conjunction with Telone® use, similar to the 1995 Telone® air monitoring study. Please consult with DowElanco, once again, to determine the location, dates, and specific details of the planned use.

If you have any questions, please feel free to call me.

for

John Sanders, Chief
Environmental Monitoring and
Pest Management Branch
(916) 324-4100

cc: Paul Gosselin
Kevin Kelley
George Lew, ARB

Printed on Recycled Paper

SURNAME

APPENDIX III

Audit Report

Cal/EPA

California Environmental Protection Agency

Air Resources Board

P.O. Box 2815
2020 L Street
Sacramento, CA
95812-2815

Pete Wilson
Governor

Secretary for Environmental Protection

MEMORANDUM

TO: George Lew, Chief
Engineering and Laboratory Branch

THROUGH: Jeff Cook, Chief
Quality Management and Operations
Support Branch

FROM: Alice Westerinen, Manager
Quality Assurance Section

DATE: July 17, 1997

SUBJECT: FINAL TELONE 1996 QA SYSTEM AUDIT REPORT

Attached is the final quality assurance system audit report on the Telone monitoring project conducted during the months of July through August, 1996, by the Engineering and Laboratory Branch (ELB) of the Air Resources Board.

Thank you for participating in this audit. If you have any questions, please contact Russell Grace at 322-7317.

Attachment

cc: Kevin Mongar
Russell Grace

T10N1978-7/97-RDG

STATE OF CALIFORNIA AIR RESOURCES BOARD

MONITORING AND LABORATORY DIVISION

QUALITY ASSURANCE SECTION

SYSTEM AUDIT REPORT

1996 AMBIENT MONITORING OF TELONE

IN

KERN COUNTY

JULY 1997

TABLE OF CONTENTS

TELONE MONITORING IN KERN COUNTY

ATTACHMENTS

I. EXECUTIVE SUMMARY

During the months of July and August 1996, the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) began conducting ambient air sampling in Kern County, California, to document the airborne emissions for the pesticide Telone in the vicinity of treated fields during and after an application. The purpose of the monitoring program was to determine the ambient air concentrations during the use of Telone under the Department of Pesticide Regulation's (DPR) 1996 revised Telone permit conditions.

The Quality Assurance Section (QAS) of the ARB's Monitoring and Laboratory Division (MLD) conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

Additionally, QAS staff conducted performance audits of the ambient air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The flow rate audit was conducted on May 30, 1996. The difference between the reported and assigned flow rates averaged -4.4% with a range of -7.8% to -0.5%.

To determine the effectiveness of the analytical procedure, laboratory performance audits were conducted during the study from August 1, 1996, through August 19, 1996. On August 1, 1996, a total of 15 audit samples were spiked with known amounts of QAS's standard solution of Telone in hexane. The 15 quality assurance (QA) audit samples were designated as QA field spikes, QA trip spikes, and QA laboratory spikes.

Telone is a volatile compound. The ELB's stability study analytical results indicate the difference between the assigned and the reported total mass of Telone ranged from approximately -7% after two days of storage to -20% after 14 and 22 days of storage at the 1.5 micrograms (μg) level. The difference between the assigned and reported mass of Telone at the 7.5μg and 15.0 μg levels ranged from +17% after 14 days to +8% after 22 days, and +7% after 14 and 22 days, respectively.

The laboratory spikes were stored in ELB's freezer for four days before extraction and analysis on August 5, 1996. The results of the analyses indicate the difference between the assigned and the reported total mass of Telone averaged -25.0% with a range of -36.7% to -9.4%. After review and discussions with ELB staff, the data were determined to be reasonable. Considering the results of the Telone stability study, the QA laboratory audit results could be slightly under-reported at the 1.5 μg mass level and slightly over-reported at the 9.6 μg mass level.

The QA trip spikes were exposed to the same handling and storage conditions as those occurring at the time of ambient monitoring. The trip spikes were shipped, in an ice chest containing dry ice, from the ELB laboratory to the Bakersfield ambient air monitoring station. At the Bakersfield site, the trip spikes were stored for four days in a refrigerator at 4° Celsius, packaged in an ice chest containing dry ice, and returned to the ELB laboratory for analysis. The QA trip spikes were analyzed on August 15, 1996 and August 19, 1996. The results of the trip spike analyses indicate the difference between the assigned and the reported total mass of Telone averaged -50.0% with a range of -59.3% to -40.6%. Considering the results of the Telone stability studies, the QA trip audit results could be slightly under-reported at the 1.5 μg mass level and slightly over-reported at the 9.6 μg mass levels.

The QA field spikes were transported in an ice chest containing dry ice to the ARB ambient air monitoring station in Bakersfield. After exposure to approximately 24 hours of ambient air sampling conditions, the samples were packaged, stored, and shipped, along with the QA trip spikes, in an ice chest containing dry ice to ELB's laboratory for analysis. The QA field spikes were analyzed by ELB on August 19, 1996. After correcting for the background ambient air concentrations, the analytical results indicate the difference between the assigned and the reported total mass of Telone for the QA field spikes averaged 15.2% with a range of -100% to 226.7%.

After reviewing and discussing the QA trip and field spike results with ELB staff, it has been determined that the QA trip results reported low recovery rates and the QA field results were erratic.

The investigation to determine the cause of the low and erratic recovery rates during the QAS analytical performance audit for the field and trip spikes was conducted by reviewing QAS's spiking standard solution handling, storage, and shipping records, along with the records for the analyses of the QA spikes and ambient samples at ELB's laboratory. The following paragraphs summarize the findings of the investigation.

The QAS's Telone standard and ELB's Telone standard were procured from Chem Service. The standards were from the same Telone lot number and have the same expiration date of September 1998. No spiking or calculation errors were found when reviewing the QA spiking logbook.

The QAS's standard solution was analyzed by ELB on December 2, 1996. The ELB staff determined QAS's standard solution to be within acceptable limits (95% of the expected value) of the 150 µg/ml value assigned to it.

The ambient air samples and the QA laboratory, trip, and field spiked samples were transported, stored, and analyzed within 21 days; this time period was within the range of the stability study conducted by ELB.

The Varian 3400 Gas Chromatograph was calibrated daily during the analysis of the ambient air samples and the QA spiked samples. Four Telone standard concentration levels were used to calibrate the gas chromatograph (using a single injection per level). The coefficient of correlation of each set of daily calibration standards indicated a high linear relationship, correlation averaged 0.9997 with a range of 0.9994 to 0.99999. Review of the chromatograms and the sample analyses data showed no data transfer or calculation errors.

Each QA spiked sample and ambient sample was analyzed using a single injection. Therefore, no precision data could be established. While ELB did include internal laboratory blanks and spikes, ELB did not utilize internal field and trip spikes to verify that no interferences were introduced by the field storage and handling conditions during the ambient air monitoring process.

The QA field spikes and the corresponding collocated ambient samples, in some cases, were run for different time periods. One of the QA field spikes (QA-F5), while exposed for the same length of time (24 hours) as the collocated background sample, had start and end times that were 2.5 hours before the respective background sample. The shift in run times could contribute to the erratic results, but the full impact on the ambient data cannot be determined at this time. Based on the results of the ELB stability study, the level of Telone detected could be slightly higher than reported for some of the ambient data at lower mass levels (approximately 1.5µg).

II. CONCLUSION

Operations

The records for field operations, sample handling procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring.

Field Flow Rates

The results of the reported flow rates were in good agreement with the actual flow rates measured by QAS staff.

Laboratory Accuracy

The results for the QA laboratory spike analyses indicate the difference between the assigned and the reported total mass of Telone averaged -25.0% with a range of -36.7% to -9.4%. After review and discussions with ELB staff, the data were determined to be reasonable.

The results of the Telone stability study are factored in by adjusting the reported masses according to the respective recovery rates at the various concentration levels. By dividing the reported masses at the 1.5 μg level by .93 (93% recovery rate after two days for 1.5 μg) and at the 9.6 μg level by 1.07 (107% recovery rate after 14 days for 15 μg), the QA laboratory audit reported masses are adjusted to 1.02, 1.03, 8.1, and 7.4 μg for samples QA-L1, QA-L2, QA-L4, and QA-L5, respectively. This results in an under-reporting at the 1.5 μg mass level by approximately 7% and over-reporting at the 9.6 μg level by approximately 7% of the original reported masses.

The results for the QA trip spike analyses indicate the difference between the assigned and the reported total mass of Telone averaged -50.0% with a range of -59.3% to -40.6%. The results of the Telone stability study are factored by dividing the reported masses at the 1.5 μg and 9.6 μg levels by .80 (80% recovery at 1.5 μg after 14 days) and by 1.17 (117% recovery at 7.5 μg after 14 days), respectively. The QA trip audit results then become 0.84, 0.76, 4.9, and 4.5 μg for samples QA-T1A, QA-T3A, QA-T4A, and QA-T5A, respectively. The adjusted reported masses reflect an approximate 20% under-reporting at 1.5 μg and an approximate 17% over-reporting at 9.6 μg of the original reported masses. The audit results for the QA field spike analyses indicate the difference between the assigned and the reported total mass of Telone averaged 15.2% with a range of -100% to 226.7%. Our investigation of the QA field spike results indicate the erratic results could have been partially caused by differences in the run times for the spikes and the blank and the corresponding background ambient samples.

Impact on Data

The total impact of the erratic QA field spikes, possibly caused by differing run times, on the ambient data cannot be determined at this time. When the results of the stability study are considered, the level of Telone detected in the QA laboratory and trip spikes could be up to 20% higher for the lower concentrations (around 1.5 μg) and up to 17% lower for higher concentrations. This does not mean that QAS advocates the application of a correction factor to ambient data, only that the QA sampling results indicate a potential variation from the reported values.

III. RECOMMENDATIONS AND ELB COMMENTS

NOTE: The ELB's comments, where received, on these recommendations are listed below followed by our responses in parenthesis and bold.

1. The QAS and ELB should develop the quality assurance pesticide monitoring process (specifically the field and trip spikes acceptance limits) prior to the start of ambient and application monitoring. This would include validation of QA standard solution and validation of spiked laboratory, trip and field samples prior to and after air monitoring.

2. The ELB should perform four injections of each sample to determine the precision of the sample injection. **(The QAS agrees with the ELB response that for capillary column chromatography 10% of the samples should be run in duplicate, with the remainder run only once.)**

3. The ELB should establish and perform an internal audit program. In addition to ELB's use of the ELB laboratory spikes, ELB should add internal field and trip spikes to verify that no interferences were introduced by the field storage and handling conditions during the air monitoring process.

   The ELB staff indicated that the QAS trip and field spikes were intended for these purposes and ELB trip and field spikes would be redundant. **(The QA trip and field spikes, along with the laboratory spikes, constituted the QAS performance audit with the intention of verifying the integrity of the QA spikes during handling and storage. The QA spikes were not intended to establish the data necessary for verifying that no interferences were introduced by the field storage and handling conditions. The QA trip and field spike analytical results, however, could be used to augment ELB findings. It is also noted that in previous Telone system audits, ELB and the contract laboratories have included their own blanks and spikes.)**

4. The QAS should use protective containers when shipping the QA trip and field spikes.

5. The ELB should run the background ambient samples and the QA field spikes on the same schedule and run times.

IV. INTRODUCTION

During the months of July and August 1996, ELB of ARB began conducting ambient air sampling in Kern County, California, to document the airborne emissions for the pesticide Telone in the vicinity of treated fields during and after an application. The purpose of the monitoring program was to determine the ambient air concentrations during the use of Telone under the Department of Pesticide Regulations' (DPR) 1996 revised Telone permit conditions. The samples were collected and analyzed by ELB. The QAS staff conducted a system audit of the field and laboratory operations, performance flow audits of the air samplers, and a laboratory performance audit.

V. AUDIT OBJECTIVE

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

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in July 1996, through a questionnaire submitted to ELB staff. Additionally, the protocol for 1996 ambient air monitoring of Telone and the laboratory's standard operating procedure for the analysis of Telone were reviewed by QAS staff. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

<u>Site Locations</u>

The DPR's request specified that monitoring be similar to that of the 1995 Telone air monitoring study. ARB selected the same 1995 Telone air monitoring sites. The ambient air monitoring was conducted at the Rio Bravo School (Shafter), Almondale School (Rosedale), ARB ambient air monitoring station (Bakersfield), Mt. View School (Lamont), and the Vineland School (Weed Patch).

Each site was selected on the basis of meeting the criteria listed in the ARB QA Plan for Pesticide Monitoring.

<u>Ambient Air Sampling, Sample Handling and Storage</u>

Samples were collected by drawing ambient air at measured rates through glass tubes containing 600 mg of charcoal. An air sampler consisted of two sampling tubes, each connected with Teflon tubing to an in-line rotameter, which in turn was connected to an air pump. The sampling tubes were protected from the direct sunlight and the sampling assembly was supported by a two-meter section of galvanized steel tube (Attachment 1). The samplers' rotameters were set to an indicated flow rate of 2.0 liters per minute (LPM).

The sampling was conducted following the schedule specified in the sampling protocol. The samples were stored in culture tubes on dry ice and held in the field for up to four days prior to shipment to the laboratory. Upon receipt at the ELB laboratory, the samples were stored in a freezer until extraction and analyses were conducted. All samples were analyzed within two weeks of receipt by ELB.

Sample Analysis

The analytical method was developed by ELB and described in a document titled "Standard Operating Procedure for the Analysis of Telone (1,3-dichloropropene) in Ambient Air". The method calls for the charcoal to be desorbed with 3 mL of carbon disulfide. The analysis was performed using a Varian 3400 Gas Chromatograph. Four levels of Telone standard concentrations (using a single injection per level) were used to establish the instrument standard calibration curve.

Quality control activities performed to monitor and document the quality of the data included analysis of a field control blank with every sample shipment, laboratory blanks, and field duplicates from collocated sites once per sampling period. A calibration standard was interdispersed between samples during each batch of ten samples. During analysis, each sample was injected once. Precision checks were not performed.

Method Validation

The minimum detection limit (MDL) was calculated as 0.07 μg/mL. Trapping efficiency was determined as 86% to 98%. During the 1995 Telone monitoring program, a sample storage stability study was conducted to determine the percent recovery of Telone spikes stored at 4° Celsius. The stability study results indicated that a 1.5 μg sample stored for two days had a 93% recovery rate. The percent of Telone recovered at the 1.5 μg level after 14 days and 22 days of storage were 80%. After 34 days at the 1.5 μg level the recovery was 60%. The recovery rates for the 7.5 μg and 15 μg mass levels ranged between 117% and 108% after 14 and 22 days, and 107% after 14 and 22 days of storage, respectively. The ELB staff determined that the samples were stable for at least 21 days.

No breakthrough mass load was detected in the secondary section sampling tubes during the trapping efficiency study.

Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were retained by ELB. The information recorded in the field data sheets included sampler ID, sampling date, start and stop times, flow rate, and comments about unusual conditions.

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

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

VII. PERFORMANCE AUDITS

Flow Rate Audit

The flow rate of each sampler used for the monitoring was audited on May 30, 1996, following the procedures outlined in Attachment 2. The audit was conducted with a 0 to 3 LPM mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates averaged -4.4% and ranged from -7.8% to -0.5% (Table 1).

Table 1
Results of the Flow Audit Conducted on the Samplers Used in the Monitoring of Telone

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1A	1.9	2.03	-6.4
1B	1.9	2.06	-7.8
2A	1.9	1.91	-0.5
2B	1.9	2.00	-5.0
3A	1.9	1.98	-4.0
3B	1.9	2.01	-5.5
4A	1.9	2.01	-5.5
4B	1.9	1.98	-4.0
5A	1.9	1.98	-4.0
5B	1.9	1.95	-2.6
6A	1.9	1.98	-4.0
6B	1.9	1.96	-3.1

NOTE: The percent difference is calculated using the following equation:

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

Laboratory Performance Audit

On August 1, 1996, a total of 15 audit samples were spiked with known amounts of the QAS's standard solution of Telone in hexane following the procedures outlined in Attachment 3. The 15 audit samples were designated as QA field spikes, QA trip spikes, and QA laboratory spikes.

During shipment of the QA field and trip spikes, three trip spikes and one field spike were damaged. The QA trip spike identified as QA-T4 was used to replace the damaged field sample (QA-F1). On August 5, 1996, a set of five additional QA audit samples were spiked with known amounts of Telone in hexane. These audit samples were designated as the replacement set of QA trip spikes.

The ELB's stability study results indicate the difference between the assigned and the reported total mass of Telone ranged from -7% after two days of storage to -20% after 22 days of storage at the 1.5 μg level, from +17% after 14 days to +8% after 22 days at the 7.5 μg level, and +7% after 14 and 22 days of storage at the 15 μg level (Table 5).

The laboratory spikes were stored in ELB's freezer for four days before extraction and analysis on August 5, 1996. The results of the analyses indicate the difference between the assigned and the reported total mass of Telone averaged -25.0% with a range of -36.7% to -9.4% (Table 2). The data were compared to the 1995 QA laboratory audit results. The comparison shows the 1996 data to have a slightly lower recovery rate, up to 11.4% less. The results of the 11 laboratory spikes from the 1995 QA audit ranged from -25.3% to 1.3%. After review and discussions with ELB staff, this data were determined to be reasonable.

When the results of the Telone stability study are factored, the QA laboratory audit reported masses are adjusted to 1.02, 1.03, 8.1, and 7.4 μg for samples QA-L1, QA-L2, QA-L4, and QA-L5, respectively. This results in an under-reporting at the 1.5 μg mass level of approximately 7% and over-reporting at the 9.6 μg level by approximately 7% of the original reported masses.

Table 2
Results of Analyses of the QA Laboratory Spikes
Telone in Hexane Samples

Sample ID	Assigned Mass (μg)	Reported Mass (μg)	Percent Difference
QA-L1	1.5	0.95	-36.7
QA-L2	1.5	0.96	-36.0
QA-L3	0.0	0.0	-
QA-L4	9.6	8.7	- 9.4
QA-L5	9.6	7.9	-17.7

NOTE: The percent difference is calculated by using the following equation:

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

The QA trip spikes were exposed to the same handling and storage conditions as those occurring at the time of ambient monitoring. The trip spikes were shipped, in an ice chest containing dry ice, from the ELB laboratory to the Bakersfield ambient air monitoring station. At the Bakersfield site, the trip spikes were stored for four days in a refrigerator at 4° Celsius, packaged in an ice chest containing dry ice, and returned to the ELB laboratory for analysis.

The QA trip spikes were analyzed on two separate dates. The QA trip spike samples identified as QA-T1A, QA-T2A, QA-T3A, and QA-T4A were analyzed by ELB on August 15, 1996. The QA trip spike sample identified as QA-T5A was analyzed by ELB on August 19, 1996. The results of the trip spike analyses indicate the difference between the assigned and the reported total mass of Telone averaged -50.0% with a range of -59.3% to -40.6% (Table 3). When the results of the Telone stability study are considered, the QA trip audit results would become 0.84, 0.76, 4.9, and 4.5 μg for samples QA-T1A, QA-T3A, QA-T4A, and QA-T5A, respectively. The adjusted reported masses then reflect an approximate 20% under-reporting at 1.5 μg and approximate 17% over-reporting at 9.6 μg of the original reported masses.

The data for the 1996 QA trip results were compared to the 1995 QA "field" audit results. The 1995 QA "field" audit samples followed the same handling and storage conditions of the ambient samples (the 1995 "field" audit samples were not exposed to the environmental or monitoring conditions that occurred at the time of ambient sampling and are, therefore, trip spikes not field spikes). The comparison shows the percent difference between the assigned and the reported total mass of Telone for the 1995 "field" spikes (which included 14 samples) ranged from -33.3% to 7.2%, while the 1996 trip spikes (five samples) ranged from

-59.3% to -40.6% without consideration of the Telone stability study results. After review and discussions with the ELB staff, it has been determined that the 1996 QA trip results have low recovery rates.

Table 3
Results of Analyses of the QA Trip Spikes
Telone in Hexane Samples

Sample ID	Assigned Mass (μg)	Reported Mass (μg)	Percent Difference
QA-T1A	1.5	0.67	-55.3
QA-T2A	0.0	0.0	-
QA-T3A	1.5	0.61	-59.3
QA-T4A	9.6	5.7	-40.6
QA-T5A	9.6	5.3	-44.8

NOTE: The percent difference is calculated by using the following equation:

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

The QA field spikes were transported in an ice chest containing dry ice to the ARB ambient air monitoring station in Bakersfield. The spiked samples were installed into the pesticide air monitor at this station and exposed to 24 hours of ambient air sampling through the tube samples at a rate of 2 LPM. A replicate air sampler (collocated) was used to collect and determine the background ambient air concentrations. After exposure to the field conditions, the samples were packaged, stored, and shipped, along with the QA trip spikes, in an ice chest containing dry ice to ELB's laboratory for analysis.

The QA field spikes were analyzed by ELB on August 19, 1996. After correcting for the background ambient air concentrations, the analytical results indicate the difference between the assigned and the reported total mass of Telone for the QA field spikes averaged 15.2% with a range of -100.0% to 226.7% (Table 4).

Table 4
Results of Analyses of the QA Field Spikes
Telone in Hexane Samples

Sample ID	Assigned Mass (μg)	Reported Mass (μg)	Background Mass (μg)	Corrected Mass (μg)	Percent Difference
QA-F2	1.50	1.2	1.2	0.0	-100.0
QA-F3	9.60	8.5	1.2	7.3	-24.0
QA-F4	0.00	1.4	1:2	0.2	-
QA-F5	1.50	13.0	8.1	4.9	226.7
QA-T4	9.60	6.9	1.3	5.6	-41.7

NOTE: The percent difference is calculated by using the following equation:

$$\frac{\text{Corrected Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

NOTE: The corrected mass is calculated by using the following equation:

Corrected Mass = Reported Mass - Background Mass

The data for the 1996 QA field audit results could not be compared to the 1995 QA "field" audit results because the 1995 QA "field" spikes were not exposed to the actual ambient air monitoring conditions.

An investigation to determine the cause of the low and variable recovery rates during the QAS analytical performance audit for the field and trip spikes was conducted by reviewing QAS's spiking standard solution handling, storage, and shipping records, along with the records for the analyses of the QA spikes and ambient samples at ELB's laboratory. The following are the results of the investigation.

The QAS's Telone standard and the ELB's Telone standard were procured from Chem Service. The standards were from the same Telone lot number and have the same expiration date of September 1998. No spiking or calculation errors were found when reviewing the QA spiking logbook.

The QAS's standard solution was analyzed by ELB on December 2, 1996. The ELB determined QAS's standard solution to be within acceptable limits (95% of the expected value) of the 150 µg/mL value assigned to it.

Telone is a volatile compound. The stability study analyses conducted by ELB indicate the difference between the assigned and the reported total mass of Telone ranged from approximately -7% after two days of storage to -20% after 22 days of storage at the 1.5 µg level, from +17% after 14 days to +8% after 22 days at the 7.5 µg level, and +7% after 14 and 22 days of storage at the 15 µg level. The ambient air samples and the QA laboratory, trip, and field spiked samples were transported, stored, and analyzed within 21 days, which was within the range of the stability study conducted by ELB.

The Varian 3400 Gas Chromatograph was calibrated daily during the analysis of the ambient air samples and the QA spiked samples. Four Telone standard concentration levels were used to calibrate the gas chromatograph (using a single injection per level). The coefficient of correlation of each set of daily calibration standards indicated a high linear relationship - the correlation averaged 0.9997 with a range of 0.9994 to 0.99999. Review of the chromatograms and the sample analyses data showed no data transfer or calculation errors.

Each spiked sample and ambient sample was analyzed using a single injection. Therefore, no precision data could be established. The ELB did not use internal field and trip spikes to verify that no interferences were introduced by field storage and handling conditions during the ambient air monitoring process.

The Telone background data collected from the collocated air monitors were compared with the ambient Telone values collected during the ambient air monitoring program. The statistical data for the ambient Telone values were calculated to have an average of 4.1 μg, standard deviation of 5.7 μg, and the range was from 0 μg to 34 μg. The five QA field reported masses were within the ambient Telone values. However, when comparing the background samples and QA field samples exposure times, the exposure times for the QA field samples identified as QA-F3, QA-F4, and QA-F5 were different from the collocated background samples.

The QA-F3 and QA-F4 samples were exposed to the ambient conditions for a total of 26.5 hours, an additional 2.5 hours over the collocated background samples. This may explain why the QA field blank (QA-F4) had a value of 0.2 μg of Telone after the sample was corrected for background Telone levels. The QA-F5 sample and the collocated background sample were exposed for the same length of time, but different time periods. The QA-F5 sample start and end times were 2.5 hours before the background sample. The different run times could account for the increased mass collected on this QA field spike. The impact on the ambient data of these differences in run times cannot be determined at this time. However, the differences in run times for QA-F3, QA-F4 and QA-F5 field samples indicate that the field protocol for ambient monitoring may not have followed the approved plan.

If only the results of QA-F2 and QA-T4 are considered due to the uncertainty introduced by the different sampling times of samples QA-F3, QA-F4 and QA-F5, the reported masses would shift to 1.5 and 5.9 μg for samples QA-F2 and QA-T4, respectively, based upon the stability study results. The corrected masses are then adjusted which results in the level of Telone detected being up to 20% higher at the 1.5 μg level and up to 17% lower at the 9.6 μg level. Since the QA trip audit results indicate a low recovery rate, the QA field samples could reflect an under-reporting of Telone mass.

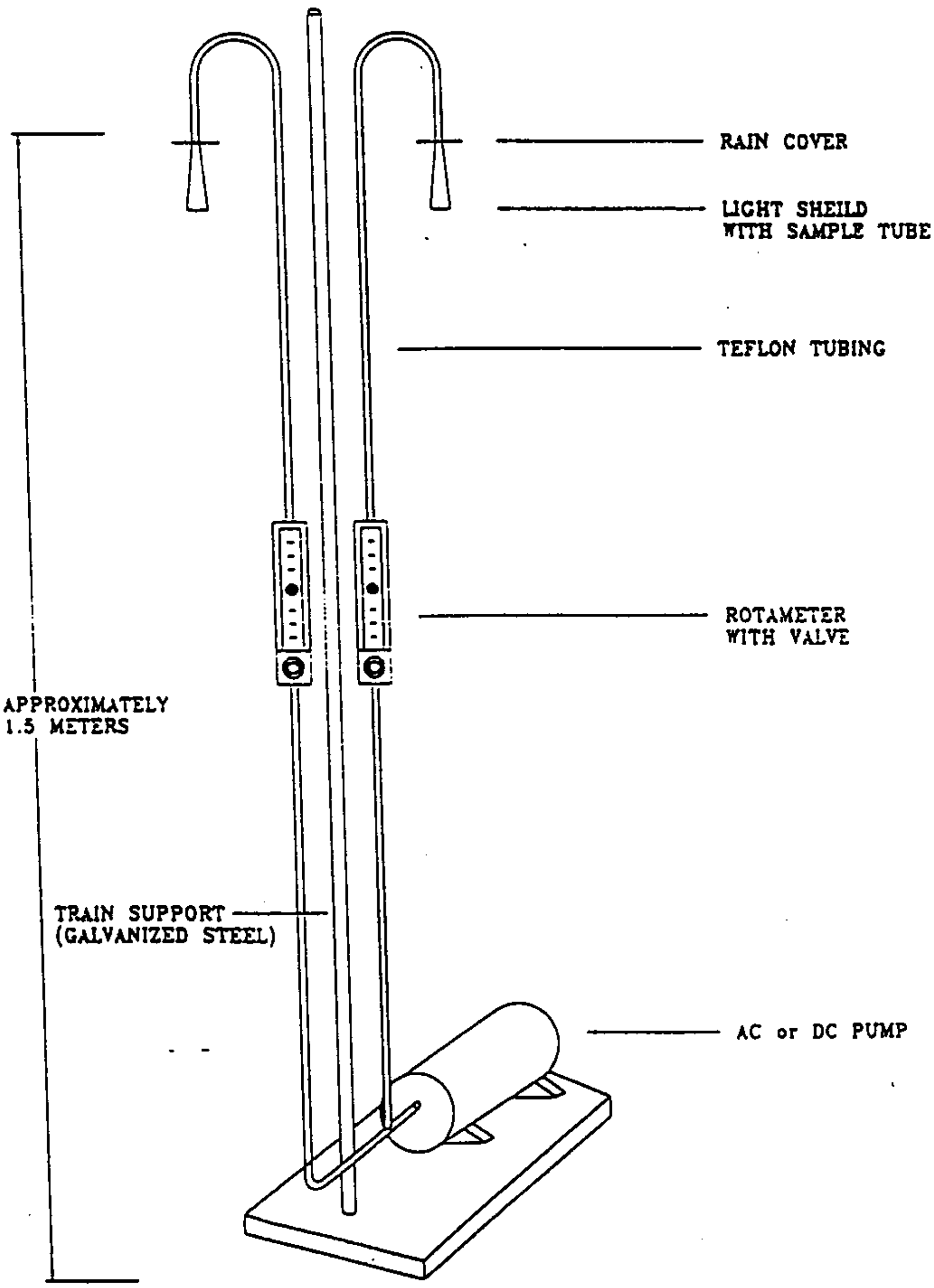
The adjustments discussed are based upon the stability study results for Telone presented in Table 5.

Table 5
Results of the 1995 Telone Stability Study

Day	Level (μg)	Recovered (μg)	Percent
0	1.5	1.7	113
2	1.5	1.4	93
14	1.5	1.2	80
14	7.5	8.8	117
14	15.0	16.0	107
22	1.5	1.2	80
22	7.5	8.1	108
22	15.0	16.0	107
34	1.5	0.9	60

ATTACHMENT 1

AIR SAMPLER USED IN THE MONITORING OF TELONE



FLOW RATE AUDIT PROCEDURES FOR AIR SAMPLERS USED IN PESTICIDE MONITORING

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a National Institute of Standards and Technology (NIST) traceable flow calibrator. The audit device is connected in series with the sampler's flow meter. 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 is compared to the true flow and a percent difference is determined.

Equipment

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

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

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a five-foot section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another five-foot section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least one to two minutes and record the flow rate indicated by the sampler and 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.

   The percent difference is calculated by using the following equation:

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

PERFORMANCE AUDIT PROCEDURES FOR THE LABORATORY ANALYSIS OF TELONE

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical method used by the laboratory to measure the ambient concentrations of Telone. The audit is conducted by submitting audit samples spiked with known concentrations of Telone. The analytical laboratory reports the results to the Quality Assurance Section. The difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Telone, 0.15 $\mu g/\mu l$ in Hexane, Chem Service, Lot #151-70A
2. Charcoal tubes, SKC, 600 mg, Lot #120

Safety Precautions

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

Preparation of Audit Samples

Prepare five trip samples, five field samples, and five laboratory audit samples by spiking the XAD-2 adsorbent tubes with the volume of Telone spiking solution indicated in Table 1, Table 2, and Table 3 below. Using a microsyringe, insert the needle into the primary section of the XAD-2 tube, and push the plunger slowly while rotating the tube. Avoid contact of the spiking solution with the tube walls.

Table 1
Volume of Telone in Hexane Used to
Spike trip Audit Samples

Sample ID	Telone Spiking Solution Volume (μl)
QA-T1	10
QA-T2	0
QA-T3	10
QA-T4	64
QA-T5	64

Table 2
Volume of Telone in Hexane Used to
Spike Field Samples

Sample ID	Telone Spiking Solution Volume (μl)
QA-F1	64
QA-F2	10
QA-F3	64
QA-F4	0
QA-F5	10

Table 3
Volume of Telone in Hexane Used to Spike
Laboratory Audit Samples

Sample ID	Telone Spiking Solution Volume (μl)
QA-L1	10
QA-L2	10
QA-L3	0
QA-L4	64
QA-L5	64

Using the above procedure, prepare five new field samples by spiking the XAD-2 adsorbent tubes with the volume of QAS's standard solution indicated in Table 4 below. The five field spikes will be used to replace the broken field spikes (Table 2).

Table 4
Volume of Telone in Hexane Used to
Spike Field Sample

Sample ID	Telone Spiking Solution Volume (μl)
QA-T1A	10
QA-T2A	0
QA-T3A	10
QA-T4A	64
QA-T5A	64