California Environmental Protection Agency

Air Resources Board

Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Kern County – Summer 2001

Prepared by
Operations Planning and Assessment Section
Quality Management Branch
Monitoring and Laboratory Division

Project No. P01-004

Date: June 20, 2002

Monitoring Report Approval

Title: Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Kern County – Summer 2001

Approval: The following monitoring report has been reviewed and approved by the Monitoring and Laboratory Division.

Signatures:

Jeffrey P. Cook, Chief
Quality Management Branch
6.19.02
DATE

Kenneth R. Stroud, Chief
Air Quality Surveillance Branch
6/19/02
DATE

Michael Poore, Chief
Northern Laboratory Branch
6/19/02
DATE

Janette Brooks, Chief
Air Quality Measures Branch
Stationary Source Division
6/19/02
DATE

William V. Loscutoff, Chief
Monitoring and Laboratory Division
6.20.02
DATE

Executive Summary

Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Kern County - Summer 2001

In June 2000, the California Department of Pesticide Regulation (DPR) requested that the Air Resources Board (ARB) conduct ambient air monitoring during 2001 for the soil fumigants methyl bromide and 1,3-dichloropropene (also known as Telone II or Telone). Monitoring was conducted in Kern County from June 30, 2001, through August 31, 2001, to coincide with the use of the two soil fumigants prior to planting of a variety of crops. The sampling site selection specifically focused on the use of 1,3-dichloropropene prior to planting carrots. In one case, a site was selected for monitoring based on its proximity to use of methyl bromide on roses. Coincident monitoring conducted during 2001 for the fumigant chloropicrin and the metam sodium breakdown products methyl-isocyanate and methyl-isothiocyanate will be described in a separate report. Additional monitoring for these fumigants conducted during 2001 in Monterey and Santa Cruz Counties will be described in separate reports to the DPR. Similar monitoring studies for methyl bromide and 1,3-dichloropropene were conducted in Kern, Monterey, and Santa Cruz Counties during 2000. The DPR will use the 2001 monitoring results to document the impact of additional regulatory measures implemented to mitigate the 2000 air monitoring levels.

Ambient air samples were collected at 5 sites throughout the rose and carrot growing regions of Kern County; urban background samples were also collected in Bakersfield. The Fall 2000 network was modified slightly for the 2001 sampling season for both methyl bromide and 1,3-dichloropropene, with new information becoming available. A site was relocated from Shafter to the Arvin High School in Arvin. Samples of 24 hours in duration were collected randomly over the full 7-day week during the sampling period (usually 4 sample periods/week).

Air samples for methyl bromide and 1,3-dichloropropene were collected using evacuated 6 liter Silcosteel® canisters (i.e., each canister sample was analyzed for both compounds). Canister samples were analyzed using gas chromatography with a mass selective detector operated in single ion monitoring mode. The monitoring study included 198 individual sampling periods (6 sites x 33 sampling days). Results for 27 of the sampling periods were invalidated due to a sampling flow rate problem.

Prior to the monitoring, at the request of the methyl bromide industry, DPR released ARB's draft monitoring protocol, which listed the locations of the monitoring sites and the schedule of sampling days.

Methyl Bromide Results

Concentrations of methyl bromide were measured as high as 98.3 micrograms per cubic meter of sampled air (µg/m^3) at the University of California's Cotton Research Station (CRS) near the town of Shafter. Methyl bromide was used north and northwest of the CRS site associated with growing roses. The prevailing wind in the CRS area is from the northwest. No methyl bromide was used at the CRS during 2001. The highest average concentration for the 8-week canister monitoring period was 11 µg/m^3, also measured at the CRS site. Of the 198 ambient canister samples, 171 contained concentrations of methyl bromide above the estimated quantitation limit (reporting limit) of 0.036 µg/m^3, and 27 samples were invalidated due to a sampling problem.

For comparison, during the Summer of 2000 monitoring, the highest 24-hour concentration of methyl bromide was 55 µg/m^3 , while the highest average concentration at any of the monitoring sites during the 7-week monitoring period was 9 µg/m^3.

1,3-Dichloropropene Results

Concentrations of 1,3-dichloropropene were measured as high as 96 ug/m^3. This concentration was measured at the Arvin High School (ARV) site. The highest average concentration for the 8-week monitoring period was 4.9 ug/m^3, also measured at the ARV site. Of the 198 ambient canister samples, 97 contained concentrations of 1,3-dichloropropene above the estimated quantitation limit of about 0.05 ug/m^3 , 46 were found to have results of "detected", 28 were below the MDL, and 27 were invalidated due to sampling problems.

For comparison, during the Summer of 2000 monitoring, the highest 24-hour concentration of 1,3-dichloropropene was 135 µg/m^3 , while the highest average concentration at any of the monitoring sites during the 8-week monitoring period was 8.5 µg/m^3.

Acknowledgments

Assistance in sampling site selection was provided by Mr. Robert Wegis of the Kern County Agricultural Commissioner's Office. Staff of the Air Resources Board (ARB) Air Quality Surveillance Branch collected the ambient samples. Mr. Steve Rider of the AQSB coordinated the field work. Mr. Jim Omand and Mr. Mike Orbanosky of the ARB Special Analysis Section laboratory performed the method development and chemical analyses. Mr. Lynn Baker of the ARB Stationary Source Division provided helpful advice and comments in regard to project planning and the monitoring protocol and report.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Ambient Air Monitoring
for Methyl Bromide and 1,3-Dichloropropene
in Kern County – Summer 2001

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (June 28, 2000, memorandum, Helliker to Lloyd and July 25, 2001, memorandum, Sanders to Cook), the Air Resources Board (ARB) staff determined airborne concentrations of the pesticides methyl bromide (bromomethane) and 1,3-dichloropropene (also referred to as Telone II or Telone). Monitoring was conducted in Kern County from June 30, 2001, through August 31, 2001, to coincide with the use of the two soil fumigants prior to planting of a variety of crops. The sampling site selection specifically focused on the use of 1,3-dichloropropene prior to planting carrots. In one case, a site was selected for monitoring based on its proximity to use of methyl bromide on roses. This monitoring was done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), which requires the ARB "to document the level of airborne emissions... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The ARB Special Analysis Section laboratory conducted the method development and sample analyses. The ARB Air Quality Surveillance Branch staff conducted sample collection for the ambient study. Coincident monitoring conducted during 2001 for the fumigant chloropicrin and the metam sodium breakdown products methyl-isocyanate and methyl-isothiocyanate will be described in a separate report. Additional monitoring for these fumigants conducted during 2001 in Monterey and Santa Cruz Counties will be described in separate reports to the DPR. Similar monitoring studies for methyl bromide and 1,3-dichloropropene were conducted in Kern, Monterey, and Santa Cruz Counties during 2000. The DPR will use the 2001 monitoring results to document the impact of additional regulatory measures implemented to mitigate the 2000 air monitoring levels.

The protocol for the ambient air monitoring for methyl bromide and 1,3-dichloropropene is enclosed separately as Appendix I (page 1 of a separate volume of appendices to this report). The protocol Attachments have not been included in Appendix I, but are available upon request. The protocol Attachments included standard operating procedures which are not relevant to this report (i.e., for chloropicrin, MIC, and MITC sampling) or which are reproduced in the laboratory report (i.e., for methyl bromide and 1,3-dichloropropene in Appendix II). The protocol Attachments also included the "Quality Assurance Plan for Pesticide Air Monitoring", the "Pesticide Ambient Sampling Procedures for Canisters", and the "Canister Field Log Sheet and Canister Field Data Sheet".

The laboratory report, "Bromomethane and 1,3-Dichloropropene Method Development and Analytical Results for Kern County Ambient Monitoring Samples Collected in Six- liter Silco™ Canisters", is enclosed separately as Appendix II (page 13 of the

separate volume of appendices to this report). The canister sampling/analysis Standard Operating Procedures (SOP) are also enclosed in Appendix II (page 45 of the separate volume of appendices to this report).

The DPR's July 25, 2001 memorandum, "Use Information and Air Monitoring Recommendations for Field Fumigations with the Pesticide Active Ingredients 1,3-Dichloropropene, Chloropicrin, Metam Sodium, and Methyl Bromide", is enclosed separately as Appendix III (page 62 of the separate volume of appendices to this report).

The canister ambient field log sheets are enclosed separately as Appendix IV (page 108 of the separate volume of appendices to this report).

II. Chemical Properties of Methyl Bromide and 1,3-dichloropropene

Information regarding the chemical properties of methyl bromide and 1,3-dichloropropene is summarized in the DPR's July 25, 2001, memorandum, "Use Information and Air Monitoring Recommendations for Field Fumigations with the Pesticide Active Ingredients 1,3-Dichloropropene, Chloropicrin, Metam Sodium, and Methyl Bromide" (page 62 of appendices). The technical product for 1,3-dichloropropene (e.g., Telone II) is a mixture of approximately equal quantities of the cis (z) and trans (e) isomers, of which the cis-isomer is more nematicidally active.

III. Sampling

The monitoring study in Kern County was conducted from June 30, 2001, through August 31, 2001. The monitoring of methyl bromide and 1,3-dichloropropene involved Silcosteel® canister sampling. Individual samples were collected for 24-hour periods. For ambient fumigant monitoring conducted in 2000, 24-hour samples were collected 4 days per week, Monday through Friday. However, for the 2001 monitoring, the DPR had requested that, "At each site, 4 samples per week should be collected randomly over the full 7-day week during the sampling period". To accommodate this request, the sampling schedule was arranged, generally in groups of 4 consecutive sampling periods separated by 1, 2, or 3 off-days, to add sampling days during most of the weekends during the 8-week monitoring study.

The canister monitoring study included 198 individual sampling periods (6 sites x 33 sampling days). Results for 27 of the sampling periods were invalidated due to a sampling flow rate problem described below.

Collocated (duplicate) samples were collected for one day/week at each sampling location. Trip blanks were submitted once per week.

A. Canisters: Methyl Bromide and 1,3-Dichloropropene

Integrated ambient air samples were collected using passive air sampling into evacuated 6-liter Silcosteel® treated canisters obtained from Restek Corporation. The flow rate of 3 standard cubic centimeters per minute (sccpm) was set and measured using a calibrated, mass flow meter. The battery operated mass flow meter (MFM) was calibrated to standard conditions (1 atm and 25 °C). On-site meteorological data was not collected. The sampling system operated continuously for 24 hours with the exact operating interval recorded in the log sheets (see Appendices, page 108). The target duration for the sampling periods was 24 hours, but sampling times often deviated slightly from this target. The passive samplers are not automated and must be turned on and off manually by the sampling technician. The daily sample collection schedule required some flexibility in order to deal with sampler problems, sampler maintenance, traffic problems, etc. At the end of each sampling period, the canisters were placed in shipping containers with a sample identification/chain of custody sheet and transported as soon as reasonably possible to the ARB Sacramento laboratory for analysis. The samples were stored at ambient laboratory temperature prior to analysis. The canister samples were at sub-atmospheric pressure when delivered to the laboratory, where they were pressurized (by addition of clean nitrogen gas) to approximately 5 pounds per square inch gauge (psig) before analysis.

Silcosteel® passive air sampling kits were obtained from Restek Corporation. The critical orifice flow controllers (Silcosteel® treated Veriflo SC423XL, Restek Corporation) are attached to the valve fitting on the canister with a Silcosteel® treated swagelock connector (see Figure 2). A 6-foot section of 1/8 inch O.D., Silcosteel® treated copper tubing is attached to the inlet end of an in-line, 5 micron filter, which is attached to the inlet end of the flow controller. The inlet end of the tubing is bent into a U shape to prevent rain from entering and is supported about 5 1/2 feet above the building roof tops for the ambient monitoring.

Silcosteel® treated canisters and sampling kits were selected to conduct the monitoring for fumigants. The Silcosteel® treatment adds a fused silica lining to the interior surfaces of the canisters and sampling kits, which increases inertness to improve analyses of many 'difficult compounds' (polar and sulfur-containing volatile organic compounds). The DPR had requested that the ARB attempt to develop a single method that could sample and analyze for the fumigants methyl bromide,
1,3-dichloroprpene, chloropicrin, and the metam sodium breakdown products methyl isocyanate, methyl isothiocyanate, hydrogen sulfide, and carbon disulfide. The use of the Silcosteel® treated canisters offered the best possibility of developing a single method, which included the polar and sulfur-containing compounds. Also, due to the increased inertness, the SilcoCans™ offered potential increased stability of non-polar compounds (e.g., methyl bromide and 1,3-dichloropropene) at the very low levels requested by DPR.

When using a critical orifice flow restrictor for passive integrated canister sampling, the

potential decrease in flow rate as the vacuum in the canister changes must be taken into account. The flow control device used for the study (Veriflo SC423XL, Restek Corporation) was designed to regulate and maintain a constant flow as the vacuum in the canister decreases. The manufacturer specifications indicate that the controller is capable of maintaining a continuous low flow with vacuum ranges from -29.9 to -5 inHg. The in-line filter helps prevent particles from entering the critical orifice of the flow controller, which could clog the critical orifice and affect the flow through the controller. The manufacturer specifications indicate that the outside temperature can have a slight effect on the flow rate. For example, there could be an approximately 6% flow drop when the temperature changes from 80 °F to 125 °F.

Canister vacuum readings were measured by the laboratory staff before and after transport of each canister to/from the field. The laboratory vacuum readings were used to calculate the sample volumes collected. The canister vacuum readings were also recorded in the field at the start and end of each sampling period using the –30 to 0 inHg gauge on the passive samplers. At a flow rate of 3.0 sccpm, the expected start and end canister vacuum readings would be –29.9 inHg and -8 inHg, respectively. However, referring to the field log sheets (page 108 of appendices), the sampling period end vacuum readings were different than expected for some samples. Also, the start flow rate was set to 3.0 sccpm for all samples, but the sampling period end flow rate for a number of samples deviated from 3.0 sccpm. Sample results were flagged if the end flow rate deviated from 3.0 sccpm by greater than 25% (i.e., less than 2.2 sccpm or greater than 3.8 sccpm). This criteria, based on a review by the ARB Quality Management Branch, was applied to ensure the representativeness of the integrated samples. Forty-six samples have been flagged due to unacceptable deviation in the flow rate. This number included 15 samples that were one of a pair of collocated samples where the other was valid and four pairs of collocated samples where both samples were flagged. Thus the results of 27 sampling periods were affected by this problem.

The canister sampling field log sheets are enclosed as Appendix IX (page 108 of appendices). These forms were used to record start and stop times, start and stop vacuum readings, sample identifications, weather conditions, sampler's initials, and any other significant data.

B. Sampling Site Selection

The historical use patterns for methyl bromide and 1,3-dichloropropene suggested that monitoring should occur in Kern County during the months of July and August to coincide with the use of the two soil fumigants prior to the planting of a variety of crops. Monitoring was conducted in Kern County from June 30, 2001, through August 31, 2001. The site selection specifically focused on the use of 1,3-dichloropropene prior to planting carrots. In one case, a site (CRS) was selected for monitoring based on its proximity to use of methyl bromide on roses. Five sampling sites were selected by ARB personnel "in populated areas or in areas frequented by people" (DPR's July 25, 2001 memorandum). Site

selection was based upon considerations for accessibility, security of the sampling equipment, and compliance with technical siting requirements. Urban background samples were collected at the ARB air monitoring site in Bakersfield. Five of the sampling sites were the same as for the monitoring conducted during 2000 and the sixth site was relocated from the lowest 1,3-dichloropropene site from the 2000 monitoring (Shafter) to Arvin (the ARV site). The six sites are presented in Figure 1 and listed in Table 1. Although the sampling sites are near areas of historical use of methyl bromide and 1,3-dichloropropene, it is understood that DPR staff will verify and quantify the actual use of methyl bromide and 1,3-dichloropropene that occurred during the study when the information becomes available.

Table 1
Ambient Sampling Sites

ARB	ARB Ambient Air Monitoring Station 5558 California Avenue, Suite 460 Bakersfield, CA 93309 Section/Township/Range: S.34/T.29S/R.27E GPS Coordinates: N. 35° 21.40' W. 119°03.76'	(661) 334-3991 Phil Powers, Air Pollution Specialist
CRS	Cotton Research Station 17053 Shafter Avenue Shafter, CA 93263 Section/Township/Range: S.33/T.27S/R.25E GPS Coordinates: N. 35° 31.96' W. 119°16.91'	(661) 868-6210 Dr. Brian Marsh, Superintendent
MVS	Mountain View School 8001 Weedpatch Highway Lamont, CA 93241 Section/Township/Range: S.30/T.30S/R.29E GPS Coordinates: N. 35° 16.90' W. 118°54.83'	(661) 845-6518 Dave Beckman, Director of Maintenance
VSD	Vineland School District – Sunset School (661) 8301 Sunset Boulevard Bakersfield, CA 93307 Section/Township/Range: S.19/T.31S/R.29E GPS Coordinates: N. 35° 13.25' W. 118°54.77'	845-3713 Steve Greenfield, District Superintendent
ARV	Arvin High School 900 Varsity Avenue Arvin, CA 93203 Section/Township/Range: S.NW23/T.31S/R.29E GPS Coordinates: N. 35° 13.02' W. 118°50.24'	(661) 827-3181 Janet Shell, Director of Business Services

MET	Mettler Fire Station 1801 Mettler Frontage Road Mettler, CA 93381 Section/Township/Range: S.1/T.11N/R.20W GPS Coordinates: N. 35° 03.83' W. 118°58.25'	(661) 391-7025 LeCostel Hailey, Deputy Chief

ARB

The background site was located at the ARB's ambient air monitoring station in the city of Bakersfield. This station monitors concentrations and collects samples of most criteria gas and particulate pollutants, as well as toxics and meteorological data. The site is located in an area having a mix of suburban, business offices, and strip malls. Bakersfield has an approximate population of over 222,000. The pesticide samplers were operated on the roof, and their inlets were about 17 feet above ground level. No obstructions were present, and the site met all technical siting requirements. Elevation of the site is $\leq$ 446 feet above mean sea level (MSL). No carrot fields were noted within a 3-mile radius.

CRS

The Cotton Research Station is a part of the University of California Agricultural Research Center, which is located in an agricultural area approximately 2 miles north of the city of Shafter, which has a population of less than 12,000. The pesticide samplers were operated just off the ground on a pallet west of the station's buildings alongside the station's meteorological site. Sampler intakes were about 5.5 feet above ground level. No obstructions were present, and the site met all technical siting requirements. Elevation of the site is $\leq$ 475 feet above MSL. The nearest carrot field noted was 2.1 miles to the east southeast. The nearest rose fields are approximately 1 mile to the north and northwest. No methyl bromide was used at the CRS during 2001. 1,3-dichloropropene was applied once during 2001, on March 19, at the CRS.

MVS

The Mountain View School site is located on State Highway 184 in the city of Lamont, which is approximately 8 miles southeast of Bakersfield. The sampling site is in a rural, residential/agricultural mixed area on the north side of Lamont, which has a population of less than 12,000. The pesticide samplers were operated on the roof of one of the school buildings, and their inlets were about 23 feet above ground level. No obstructions were present and the site met all technical siting requirements. Elevation of the site is $\leq$ 440 feet above MSL. No carrot fields were noted within a 3-mile radius.

VSD

The Vineland School District Site is located on the grounds of Sunset School, which is in the area of Weedpatch, an unincorporated area of the city of Bakersfield. This site is 2 miles south of the Mountain View site, just off Highway 184, and approximately 10 miles from central Bakersfield. This sampling site is located in a rural, agricultural/residential mixed area. The pesticide samplers were operated on the roof of one of the school buildings, and their inlets were about 20 feet above ground level. No obstructions were present, and the site met all technical siting requirements. Elevation of the site is $\leq$ 414 feet above MSL. Carrot fields were

noted at 335 feet north and 692 feet east of samplers. Neither field was planted until mid-August.

ARV

The Arvin High School site is located in an agricultural/residential mixed area at the north end of the city of Arvin, which has a population of less than 12,000. The pesticide samplers were operated on the roof of one of the school buildings, and their inlets were about 20 feet above ground level. No obstructions were present, and the site met all technical siting requirements. Elevation of the site is $\leq$ 512 feet above MSL. A small carrot field was noted 0.7 miles north of the samplers.

MET

The Mettler Fire Station site was located in a rural, residential/agricultural mixed area in the town of Mettler, which has a population of $\leq$ 2,000. Mettler is situated near the intersection of State Highways 99, 166, and Interstate 5. The pesticide samplers were operated on the roof of a carport and their inlets were about 18 feet above ground level. The site did not meet all technical siting requirements. A tree stood 18 feet north of the samplers and was about 35 feet above the sample inlet. Trees blocked approximately 75% of the NW quadrant. Elevation of the site is $\leq$ 554 feet above MSL. Carrot fields were noted 3.0 miles north and 0.2 miles to east across highway from samplers.

IV. Analytical Methodology

The standard operating procedures for sampling and analysis of methyl bromide and 1,3-dichloropropene in Silcosteel® canisters are enclosed in Appendix II (page 45 of appendices). The procedures specify that ambient air is collected into evacuated 6-liter Silcosteel® canisters, and field sampling is conducted with passive integrated samplers. A gas chromatograph/ quadrapole mass spectrometer (GC/MS) with a cryogenic preconcentrator is used for analysis. The MS detector is operated in selected ion monitoring (SIM) mode using deuterated bromomethane and deuterated 1,2-dichloropropane as internal standards. The field samples are delivered to the lab at sub-ambient pressure, and are pressurized to approximately 5 psig before analysis. The target estimated quantitation limits (EQLs) requested by DPR for methyl bromide and dichloropropene were 0.4 micrograms/m^3 and 0.01 micrograms/m^3, respectively. To maintain consistency with the laboratory reports, units of nanograms (ng), rather than micrograms (ug), will be used for the remainder of this report. Thus, the DPR target EQLs were 400 ng/m^3 and 10 ng/m^3, respectively, for methyl bromide and dichloropropene. The EQLs achieved by the laboratory staff, based on a 400 ml analytical sample size, were 36 ng/m^3 for methyl bromide, 44 ng/m^3 for cis 1,3-dichloropropene, and 64 ng/m^3 for trans 1,3-dichloropropene. The maximum sample size was set at 400 ml, based on the increased probability of matrix interferences from high levels of sample moisture with larger sample volumes. The GC/MS instruments were run using selected ion monitoring mode to achieve the highest level of instrument

sensitivity. Given the sample size and instrument parameters, the EQLs reported are the best that could be achieved. Two GC/MS instruments were used for the analyses. One instrument, MSD-4, was used for the low concentration range and the other instrument, MSD-3, was used for the higher concentration samples.

V. Monitoring Results

Table 2 presents the results of ambient air monitoring for methyl bromide and 1,3-dichloropropene in units of nanograms per cubic meter (ng/m^3) and parts per trillion by volume (pptv). Summaries of the ambient results for methyl bromide and 1,3-dichloropropene are presented in Tables 3 and 4, respectively. The monitoring period included 198 individual sampling periods (6 sites x 33 sampling days).

A number of sample results have been flagged due to unacceptable deviation in the sampling flow rate. Sample results were flagged if the end flow rate deviated from 3.0 sccpm by > 25% (i.e., <2.2 sccpm or >3.8 sccpm). This criteria, based on a review by the ARB Quality Management Branch, was applied to ensure the representativeness of the integrated samples. In order to collect a representative integrated sample, the flow rate should remain constant over the duration of the sampling period, producing an accurate (representative) average result for a 24-hour sampling period. This is important, because there is no information about the variation of pesticide air concentration during the sampling period. Also, there is no way to know when the flow alteration occurred during the sampling period. Samples with a flow deviation of >25% may not produce an accurate average that is representative of the 24-hour sampled period. The results of samples, where the end flow rate deviated from 3.0 sccpm by > 25%, are included and flagged in Table 2. However, these sample results have not been included in the results summary Tables 3 and 4 and have not been included in the calculation of average concentrations. Forty-six samples have been flagged (**) in Table 2 for this problem. Fifteen of the flagged samples were one of a pair of collocated samples where the other sample was valid. In 4 additional cases, both samples in a collocated pair were flagged due to this problem. Thus, the results of 27 sampling periods were affected by this flow rate problem.

The Special Analysis Section laboratory determined the analytical MDL as (3.14)(s), where s is the standard deviation calculated for the results of 7 replicate canister spikes (near the estimated detection limit). The MDL was 7.1 ng/m^3 for methyl bromide. The MDLs were 8.7 ng/m^3 and 12.8 ng/m^3 for cis and trans 1,3-dichloropropene, respectively. The estimated quantitation limit (EQL), calculated as 5 times the MDL, for MeBr was 36 ng/m^3 and the EQLs for cis and trans 1,3-dichloropropene were 44 and 64 ng/m3, respectively. Results equal to or above the MDL but below the EQL are reported as detected (Det). Laboratory results, in units of ng/m^3, equal to or above the EQL were reported to 3 significant figures. The 1,3-dichloropropene results are reported separately for the cis and trans isomers and are also reported as total

(cis + trans) 1,3-dichloropropene. Only values greater than the EQLs for the cis and trans isomers were used to calculate the total 1,3-dichloropropene.

The equation used to convert methyl bromide air concentration results from units of ng/m^3 to parts per trillion by volume (pptv) units at 1 atmosphere and 25°C is shown below:

$$\text{pptv} = (\text{ng/m}^3) \times \frac{(0.0820575 \text{ liter-atm/mole-°K})(298\text{°K})}{(1 \text{ atm})(94.9 \text{ gram/mole})} = (0.2577) \times (\text{ng/m}^3)$$

The equation used to convert 1,3-dichloropropene (total) air concentration results from units of ng/m^3 to pptv units at 1 atmosphere and 25°C is shown below:

$$\text{pptv} = (\text{ng/m}^3) \times \frac{(0.0820575 \text{ liter-atm/mole-°K})(298\text{°K})}{(1 \text{ atm})(111.0 \text{ gram/mole})} = (0.2203) \times (\text{ng/m}^3)$$

For methyl bromide, of the 198 ambient canister samples collected (spikes, blanks, and the lower value of collocated sample sets excluded), 171 were found to be above the EQL, none were found to have results of "detected", none were found to be below the MDL, and 27 were flagged due to sampling problems. The highest methyl bromide concentration, 98,300 ng/m^3 (25,000 pptv), was observed at the Cotton Research Station (CRS) sampling site on August 6, 2001. Methyl bromide was used to the north and northwest of the CRS as associated with rose farming. The prevailing breezes in the CRS area are from the northwest. The UC Agricultural Extension Center at the CRS maintains and operates a meteorological station, which was located directly adjacent to the canister air sampler.

For 1,3-dichloropropene, of the 198 ambient canister samples collected (spikes, blanks, and the lower value of collocated sample sets excluded), 97 were found to be above the EQL, 46 were found to have results of "detected", 28 were below the MDL, and 27 were flagged due to sampling problems. The highest 1,3-dichloropropene (total) concentration, 95,800 ng/m^3 (21,100 pptv), was observed at the Arvin High School (ARV) sampling site on July 7, 2001.

No sample results have been adjusted or corrected for recoveries of quality assurance spike samples.

VI. Quality Assurance

Field QC for the ambient monitoring included the following:

1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) prepared by the Special Analysis Section staff; the field spikes were obtained by sampling ambient air at the

background monitoring site for 24-hour periods (collocated with an ambient sample);
2) four trip spikes;
3) collocated (duplicate) samples taken once per week at each sampling location; and
4) 1 trip blank submitted per week;
5) The battery operated mass flow meters used to set and check the sampling flow rate were calibrated by the ARB Program Evaluation and Standards Section.

For the canister samplers, the flow rates were set at the start of every sampling period (every sample) using a calibrated, battery operated digital mass flow meter. The flow rates were also checked and recorded at the end of each sampling period using the mass flow meter.

VII. Quality Assurance Results

A. Method Development

Refer to Appendix II (page 13 of the appendices) for discussion and results of method development studies. The canister storage stability study results (page 18 of appendices) show that methyl bromide and 1,3-dichloropropene are stable for at least 35 days under laboratory conditions. All of the canister samples were analyzed within 16 days of receipt.

B. Trip Blanks

Referring to page 101 of the appendices, all 8 of the canister trip blanks were <MDL for methyl bromide and 1,3-dichloropropene.

C. Collocated Sample Results

Referring to Table 5, 23 collocated pairs of samples had both methyl bromide results above the EQL. The relative percent difference, RPD = (| difference | /average) x 100 of the methyl bromide (canister) data pairs averaged 7.4% and ranged from 0.8% to 42.3%.

Referring to Table 5, nine collocated pairs of samples had both 1,3-dichloropropene (total) results above the EQL. The relative percent difference, RPD = (| difference | /average) x 100 of the 1,3-dichloropropene (canister) data pairs averaged 18% and ranged from 2.1% to 70.3%.

D. Laboratory, Trip, and Field Spikes

Laboratory, trip, and field canister spikes were prepared and collected 4 times during the study, approximately every other week. To prepare the spike samples, laboratory staff added a small volume (about 100 ml) of a gas standard, with a certified concentration of methyl bromide and 1,3-dichloropropene, to an evacuated canister. The laboratory canister spikes were kept in the laboratory at room temperature until analysis. The trip spike samples were kept in the vehicle (the same one used for samples) during transport to and from the field and at all times while in the field. The field spikes were collected by sampling ambient air into the previously spiked cans and were collocated with an ambient sample (same location, flow rate, and sampling time). The collocated (unspiked) sample result is subtracted from the field spike sample result before calculation of percent recovery of the analytes. The laboratory, trip, and field spikes are pressurized before analysis to approximately 5 psig. The analysis of laboratory, trip, and field spikes normally occurs at the same time. Laboratory, trip, and field canister spikes were prepared by the Special Analysis Section staff from a stock standard separate from those used for the analysis method calibration and laboratory control samples. Two instruments, MSD-3 and MSD-4, were used in the laboratory for analysis of the samples; therefore, two sets of spike results were presented in the laboratory report.

1) Canister Laboratory Spikes: The laboratory canister spike results for MSD-3 and MSD-4 are listed in Tables 6 and 9, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-3 were 139%, 95%, and 83%, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-4 were 117%, 77%, and 65%, respectively.

2) Canister Trip Spikes: The canister field spike results for MSD-3 and MSD-4 are listed in Tables 7 and 10, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-3 were 143%, 101%, and 93%, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-4 were 121%, 80%, and 70%, respectively. These results are consistent with the lab spike results and indicate that the sample transport, storage, and analytical procedures used in this study produce acceptable results for methyl bromide and 1,3-dichloropropene.

3) Canister Field Spikes: The canister field spike results for MSD-3 and MSD-4 are listed in Tables 8 and 11, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-3 were 132%, 90%, and 82%, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-4 were 114%, 75%, and 60%, respectively. These results are consistent with the lab and trip spike results and indicate that the sampling, sample transport, storage, and analytical procedures used in this study produce acceptable results for methyl bromide and 1,3-dichloropropene.

The spike results for methyl bromide were consistently on the high side. As described in the laboratory report, the stock standard (cylinder standard) used to prepare the lab, trip, and field spikes was different from the cylinders used for preparation of the calibration standard and laboratory control samples (LCS). The use of a standard containing higher levels of the two compounds was necessary to minimize the volume of standard added to the field spike samples (otherwise the 24-hour ambient sampling could not be conducted correctly). The laboratory report states:

> "Both instruments had spike recoveries that averaged above 100% (119% for MSD-4 and 144% for MSD-3). This indicates that the standard used for spikes gave results higher than those from the standard used for calibration, irrespective of the instrument. Even though the standard assignments do not match exactly, each is within its certified concentration criteria, based on the average spike recovery from MSD-4.
>
> The sample concentrations were quantified based upon the calibration standard and were not corrected for recovery results from either the LCS or spikes. The values for the spikes are an independent result and are not necessarily reflective of the results obtained from the unspiked samples".

Thus, the high spike recovery results for methyl bromide are likely due to the inherent inaccuracy ($\pm$ 20%) of the individual standard cylinder assignments. The difference in spike recovery results between the 2 instruments may have been due to the relatively high concentration of the spike samples which were over 10 times above the upper calibration range on MSD-4. The higher level spike samples were analyzed on MSD-4 by concentrating a much smaller (15 ml) than normal (400 ml) volume of sample for analysis. The laboratory report states:

> "It is difficult to identify the factor or factors that contributed to this difference in results between MSD-4 and MSD-3. It could be that there indeed is a positive bias in the performance of MSD-3 relative to MSD-4. It could be a number of small contributing factors. One such possibility is that the spike levels (about 10.5 ug/m^3), which required running a 15-ml sample aliquot (dilution) on MSD-4 to be within the calibration range (upper level 0.847 ug/m^3), may have introduced another level of error".

The purpose of the field spikes is to provide an estimate of the sampling efficiency and analyte recovery under the "same environmental and experimental conditions as those occurring at the time of ambient sampling". The percent recovery of field spikes can then be used, at the discretion of the data user (DPR), to adjust ambient concentrations for exposure assessment. However, in this case, due to the issues described above, the spike results should not be used to correct or adjust the ambient sample results.

Figure 1. Ambient Monitoring Area
(use map provided by DPR)

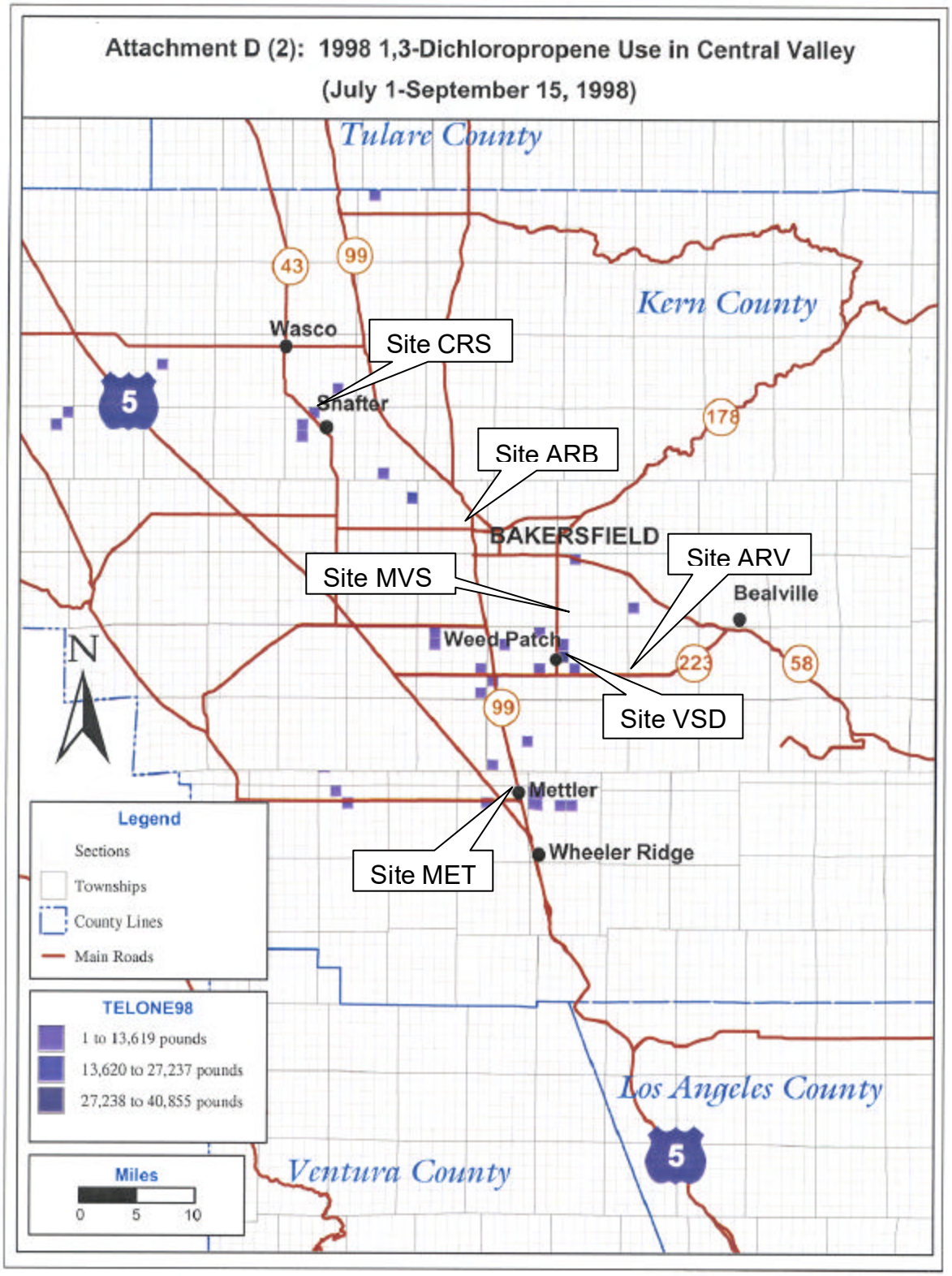

Figure 2

Passive Canister Sampling Train