California Environmental Protection Agency

Air Resources Board

Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Monterey and Santa Cruz Counties

Fall 2001

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Executive Summary

Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Monterey and Santa Cruz Counties - Fall 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 Monterey and Santa Cruz Counties from September 8, 2001, through November 8, 2001, to coincide with the use of the two soil fumigants prior to the planting of a variety of crops. The sampling site selection specifically focused on areas of historical use of methyl bromide prior to planting strawberries. 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 Kern County will be described in separate reports to the DPR. Similar monitoring studies for methyl bromide and 1,3-dichloropropene were conducted in Monterey, Santa Cruz, and Kern Counties during 2000. The DPR will use the 2001 methyl bromide monitoring results to document the impact of additional regulatory measures implemented to mitigate the 2000 air monitoring levels.

Ambient air samples were collected at 4 sites in Monterey County and 2 sites in Santa Cruz County. Samples of 24 hours in duration were collected randomly over the full 7-day week during the sampling period (usually 4-sample periods/week). The canister monitoring study included 192 individual sampling periods (6 sites x 32 sampling days). Results for 19 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 five of the six monitoring sites and the schedule of sampling days. ARB staff subsequently made a slight modification to the sampling schedule.

Samples were also collected for a one-week period in an area relatively distant to the use of methyl bromide. A site in Santa Cruz was chosen through consultation with the Santa Cruz County Agricultural Commissioner. Four samples were collected at this site between September 24, 2001, and September 29, 2001. The Santa Cruz County Agricultural Commissioner's office has verified that there was no methyl bromide used within a five-mile radius of the sampling site during the sampling period.

Air samples for methyl bromide and 1,3-dichloropropene were collected using evacuated six-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.

Methyl Bromide Results

Concentrations of methyl bromide in canister samples were measured as high as 142 micrograms per cubic meter of sampled air ($\mu g/m^3$). This concentration was measured at the MacQuiddy Elementary School in the town of Watsonville. Methyl bromide was used in the Watsonville area as associated with growing strawberries.

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 Greenfield to the MacQuiddy Elementary School in Watsonville. A background site in Santa Cruz was also added.

The highest average concentration for the eight-week canister monitoring period in 2001 was 23.8 $\mu g/m^3$, also measured at the MacQuiddy Elementary School site. All of the ambient canister samples reported contained concentrations of methyl bromide above the estimated quantitation limit (reporting limit) of 0.036 $\mu g/m^3$.

For comparison, during the Fall of 2000 monitoring, the highest 24-hour concentration of methyl bromide was 119 $\mu g/m^3$, while the highest average concentration at any of the monitoring sites during the 8-week monitoring period was 28.9 $\mu g/m^3$.

1,3-Dichloropropene Results

Concentrations of 1,3-dichloropropene (total) were measured as high as 18.9 $\mu g/m^3$. This concentration was measured at the MacQuiddy Elementary School site in Watsonville. The highest average concentration for the 8-week monitoring period was 1.74 $\mu g/m^3$, also measured at the MacQuiddy Elementary School site. Of the 192 ambient canister samples collected, 118 (61%) were found to be above the EQL (0.108 $\mu g/m^3$), 35 (18%) were found to have detectable results (Det), 22 (11%) were below the MDL, and 19 (10%) were flagged due to sampling problems.

For comparison, during the Fall of 2000 monitoring, the highest 24-hour concentration of 1,3-dichloropropene was 4.3 $\mu g/m^3$, while the highest average concentration at any of the monitoring sites during the 8-week monitoring period was 0.4 $\mu g/m^3$.

Background Sample Results

The highest methyl bromide concentration observed in the four samples collected from the Santa Cruz background site was 2.88 $\mu g/m^3$ and the four-day average methyl bromide concentration was 1.74 $\mu g/m^3$. Detectable levels (Det) of 1,3-dichloropropene were found in all four samples.

Acknowledgments

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

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I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (June 28, 2000, memorandum, Helliker to Lloyd), 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 Monterey/Santa Cruz Counties from September 8, 2001, through November 8, 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 areas of historical use of methyl bromide prior to planting strawberries. This monitoring was done to fulfill the requirements of Assembly Bill 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 (MIC) and methyl-isothiocyanate (MITC) will be described in a separate report. Additional monitoring for these fumigants conducted during 2001 in Kern County will be described in separate reports to the DPR. Similar monitoring studies for methyl bromide and 1,3-dichloropropene were conducted in Monterey, Santa Cruz, and Kern 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 Monterey and Santa Cruz Counties Ambient Air Monitoring Samples Collected in 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) for methyl bromide and 1,3-dichloropropene 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 63 of the separate volume of appendices to this report).

The canister ambient field log sheets are enclosed separately as Appendix IV (page 109 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 63 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 procedure used for the fumigant monitoring involved canister sampling. Both methyl bromide and 1,3-dichloropropene were analyzed from each canister sample. Canister samples were collected for the fumigants from September 8, 2001, through November 8, 2001. 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 four 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 192 individual sampling periods (6 sites x 32 sampling days). Results for 19 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 (one week was missed).

Samples were also collected for a one-week period in an area relatively distant to the use of methyl bromide and 1,3-dichloropropene. A site in Santa Cruz was chosen through consultation with the Santa Cruz County Agricultural Commissioner. Four samples were collected at this site between September 24, 2001, and September 29, 2001. The Santa Cruz County Agricultural Commissioner's office has verified that there was no methyl bromide used within a five-mile radius of the sampling site during the sampling period.

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

Integrated 24-hour ambient air samples were collected using passive air sampling into evacuated 6-liter Silcosteel® treated canisters (obtained from Restek Corporation). The flow rate of 3.0 standard cubic centimeters per minute (sccpm) was set and measured using a calibrated mass flow meter (battery operated). The 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 approximately 24 hours with the exact operating interval recorded on the log sheets (see Appendices, page 106). 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, from 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 very low levels (as 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, from 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. If all sampling parameters function correctly at a flow rate of 3.0 sccpm, the expected start and end canister vacuum readings will be –29.9 inHg and -8 inHg, respectively. However, referring to the field log sheets (page 109 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. Twenty-one samples (including two individual collocated samples) have been flagged due to unacceptable deviation in the flow rate. 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.

The canister sampling field log sheets are enclosed as Appendix IV (page 109 of appendices). These forms were used to record start and stop times, start and stop flow rates and vacuum readings, sample identifications, weather conditions, operator'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 Monterey/Santa Cruz Counties during September and

October to coincide with the use of these two soil fumigants prior to the planting of a variety of crops. ARB staff selected a total of six sampling sites, four in Monterey County and two in Santa Cruz County. Five of the sampling sites were the same as for the monitoring conducted during 2000, and the sixth site was relocated from the lowest methyl bromide site from the 2000 monitoring (Greenfield) to Watsonville (the MES site).

The sampling site selection specifically focused on areas of historical use of methyl bromide prior to planting strawberries. Sampling sites were selected in accordance with the DPR's "Monitoring Recommendations for 2001", which indicates that sampling sites will be selected "in populated areas or in areas frequented by people." Site selection was also based upon considerations for accessibility, security of the sampling equipment, and compliance with technical siting requirements. The six sites are shown 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. Samples were also collected for one week at a site in Santa Cruz. The Santa Cruz site was intended as a regional background site for methyl bromide (i.e., relatively distant to methyl bromide use).

Table 1
Ambient Sampling Sites

SAL	MBUAPCD Ambient Monitoring Station 867 E. Laurel Drive Salinas, CA 95905 Section/Township/Range: S.22/T.14S/R.3E GPS Coordinates: N. 36° 41.63' W. 121°37.39'	(831) 647-9411 Tony Sotello Station Operator
MES	MacQuiddy Elementary School 331 Martinelly Street Watsonville, CA 95076 Section/Township/Range: S.33/T.11E/R.2E GPS Coordinates: N. 36° 18.92' W. 121° 15.10'	(831) 728-6248 ext. 291 John McCann Env. Health & Safety Officer
CHU	Chualar School 24285 Lincoln Street Chualar, CA 93925-0188 Section/Township/Range: S.3/T.16S/R.4E GPS Coordinates: N. 36° 34.37' W. 121° 31.00'	(831) 679-2504 Nancy Torres Business Manager

Table 1
Ambient Sampling Sites (cont.)

LJE	La Joya Elementary 55 Rogge Road Salinas, CA 93906 Section/Township/Range: S.10/T.14S/R.3E GPS Coordinates: N. 36° 43.97' W. 121° 38.05'	(831) 443-7216 Mary Stefan Principal
PMS	Pajaro Middle School 250 Salinas Road Watsonville, CA 95076 Section/Township/Range: S.9/T.12S/R.2E GPS Coordinates: N. 36° 53.91' W. 121° 43.95'	(831) 728-6238 Jackie Defendis Principal
SES	Salsepuedes Elementary School 115 Casserly Road Watsonville, CA 95076 Section/Township/Range: S.22/T.11S/R.2E GPS Coordinates: N. 36° 57.67' W. 121° 43.88'	(831) 728-6830 Rebecca Salinas Principal
SCF	Santa Cruz Fire Station #3 335 Younglove Avenue Santa Cruz, CA 95060 Section/Township/Range: S.NE23/T.11S/R.2W GPS Coordinates: N. 36° 57.691' W. 122° 02.606'	(831) 420-5281 Paul Horvath Safety Officer

SAL
The urban background site was located at Monterey Bay Unified APCD's ambient air monitoring station in the city of Salinas. This station monitors concentrations and collects samples of most criteria gas and particulate pollutants, as well as meteorological data. The site is located in an area that has a mix of business offices, parks, agriculture, and residences. Salinas has a population of approximately 130,000. The pesticide samplers were operated on a raised platform, and their inlets were 11 feet above ground level. The site met all technical siting requirements. Elevation of the site is $\leq$ 140 feet (43 meters) above mean sea level (MSL). No strawberry fields were noted within a 3-mile radius.

CHU
The Chualar School site was located in a rural agricultural/residential mixed area on the east edge of the town of Chualar, which has a population of approximately 1,000. 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 ≤ 177 feet (54 meters) above MSL. No strawberry fields were noted within a 3-mile radius. This site was selected based on historical use of 1,3-dichloropropene.

LJE

The La Joya Elementary School site was located in a rural, residential/agricultural mixed area north of Salinas. The pesticide samplers were operated on the roof of one of the school buildings, and their inlets were about 15 feet above ground level. The site met all technical siting requirements. Elevation of the site is ≤ 176 feet (54 meters) above MSL. Strawberry fields were noted 500 feet to the north and 1.3 miles to the west southwest.

PMS

The Pajaro Middle School site was located in an urban, commercial/residential/agricultural mixed area on the west-side of the town of Pajaro, which has a population of approximately 3,500. The pesticide samplers were operated on the roof of one of the school buildings and their inlets were about 21 feet above ground level. The site met all technical siting requirements. Elevation of the site is ≤ 104 feet (32 meters) above MSL. Strawberry fields were noted at 1.0 mile to the northwest and 1.5 miles to the east.

MES

The MacQuiddy Elementary School site was located in an urban, residential/agricultural mixed area at the east-end of the city of Watsonville, which has a population of approximately 38,000. The pesticide samplers were operated on the roof of one of the school buildings, and their inlets were about 19 feet above ground level. The site met all technical siting requirements. Elevation of the site is ≤ 100 feet (31 meters) above MSL. Strawberry fields were noted 360 feet to the northeast and 0.6 miles to the west southwest.

SES

The Salsipuedes Elementary School was located in a rural, agricultural/residential mixed area 3.5 miles to the north northeast of Watsonville. The pesticide samplers were operated on the roof of one of the school buildings, and their inlets were about 19 feet above ground level. No obstructions were present, and the site met all technical siting requirements. Elevation of the site is ≤ 217 feet (66 meters) above MSL. No strawberry fields were noted within a 3-mile radius.

SCF

The Santa Cruz City Fire Station site was located in an urban, residential/commercial mixed area in the northwest quadrant of downtown Santa Cruz, which has a population of approximately 55,000. The pesticide sampler was operated on the roof of a shipping container and its inlet was 13.8 feet above ground level. No obstructions were present and the site met all technical siting requirements. Elevation of the site is ≤ 118 feet (36 meters) above MSL. No strawberry fields were noted within a 3-mile radius.

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 (pages 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 1,3-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 (μg), 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 1,3-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 instrument was 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.

V. Canister Monitoring Results

Table 2 presents the results of ambient air monitoring for methyl bromide and 1,3-dichloropropene (cis, trans, and total) in units of nanograms per cubic meter (ng/m^3) and parts per trillion by volume (pptv). Summaries of the ambient canister results (in units of ng/m^3) for methyl bromide and 1,3-dichloropropene (total) are presented in Tables 3 and 4, respectively. Samples were collected for 192 individual sampling periods (6 sites x 32 sampling days each). Results for 19 of the sampling periods were invalidated due to a sampling flow rate problem. Table 12 presents the results of the 4 background samples collected in Santa Cruz.

A number of samples 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 flow alteration occurred during the sampling period. Samples with a flow deviation >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 summaries in Tables 3 and 4, and the results have not been included in the calculation of average concentrations also listed in Table 3 and 4. Twenty-one samples were flagged (**) in Table 2 for flow rate deviations. Two of these flagged samples were one of the samples in a collocated pair for which the other sample was valid. Thus, flow rate deviations affected the results of 19 sampled periods.

The Special Analysis Section laboratory determined the method detection limit (MDL) as 3.14 x s (from 40 CFR 136, Appendix B); where s is the standard deviation calculated for the results of seven 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 methyl bromide was 36 ng/m^3 and the EQLs for cis and trans 1,3-dichloropropene were 44 and 64 ng/m^3, 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 192 ambient canister samples collected (spikes, blanks and the lower value of collocated sample sets excluded), 173 (90%) were found to be above the EQL, none (0%) were found to have results of "detected", none (0%) were below the MDL, and 19 (19)(10%) were flagged due to sampling problems. The highest methyl bromide concentration, 142,000 ng/m^3 (36,600 pptv), was observed at the MacQuiddy Elementary School (MES) sampling site on October 6, 2001. The highest 8-week average, 23,800 ng/m^3 (6,133 pptv) was also at the MacQuiddy Elementary School.

For 1,3-dichloropropene, of the 192 ambient canister samples collected (spikes, blanks and the lower value of collocated sample sets excluded), 118 (61%) were found to be above the EQL, 35 (18%) were found to have results of "detected", 22 (11%) were below the MDL, and 19 (10%) were flagged due to sampling problems. The highest 1,3-dichloropropene (total) concentration, 18,900 ng/m^3 (4163 pptv), was observed at the MacQuiddy Elementary School (MES) sampling site on September 25, 2001. The highest 8-week average, 1740 ng/m^3 (383 pptv), was also at the MacQuiddy Elementary School.

Results for 1,3-dichloropropene in all four samples collected from the Santa Cruz background site were detected (Det). The highest methyl bromide concentration observed was 2,880 ng/m^3 (742 pptv). The four-day average methyl bromide concentration was 1,740 ng/m^3 (448 pptv).

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

VI. Quality Assurance

Field QC for the canister 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 were taken once per week at each sampling location; and
4) 7 trip blanks;
5) The battery operated mass flow meters used to set and check the sampling flow rate (for canisters and charcoal tubes) 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 17 days of receipt.

B. Trip Blanks

Referring to page 43 of the appendices, 7 trip blank samples were analyzed. Six of the 7 blank samples were <MDL and one contained detectable levels (Det) for methyl bromide. All 7 blank sample results were <MDL for 1,3-dichloropropene.

C. Collocated Sample Results

Referring to Table 5, 40 collocated pairs of canister samples had both methyl bromide results above the EQL. The relative percent differences (100 x difference/average) of the methyl bromide (canister) data pairs averaged 7.0% and ranged from 0.0% to 27%.

Referring to Table 5, 21 collocated pairs of canister samples had both 1,3-dichloropropene (total) results above the EQL. The relative differences (100 x difference/average) of the 1,3-dichloropropene (canister) data pairs averaged 20% and ranged from 0% to 90%.

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 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-4 were 123%, 95%, and 94%, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-3 were 152%, 102%, and 90%, respectively.

2) Canister Trip Spikes: The canister field 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-4 were 125%, 96%, and 91%, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-3 were 149%, 101%, and 93%, 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 6 and 9, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-4 were 122%, 90%, and 82%, respectively. The average recoveries for methyl bromide and cis and trans 1,3-dichloropropene for MSD-3 were 156%, 95%, and 87%, 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% (124% for MSD-4 and 152% 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 (± 20%) of the individual standard cylinder assignments. 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)

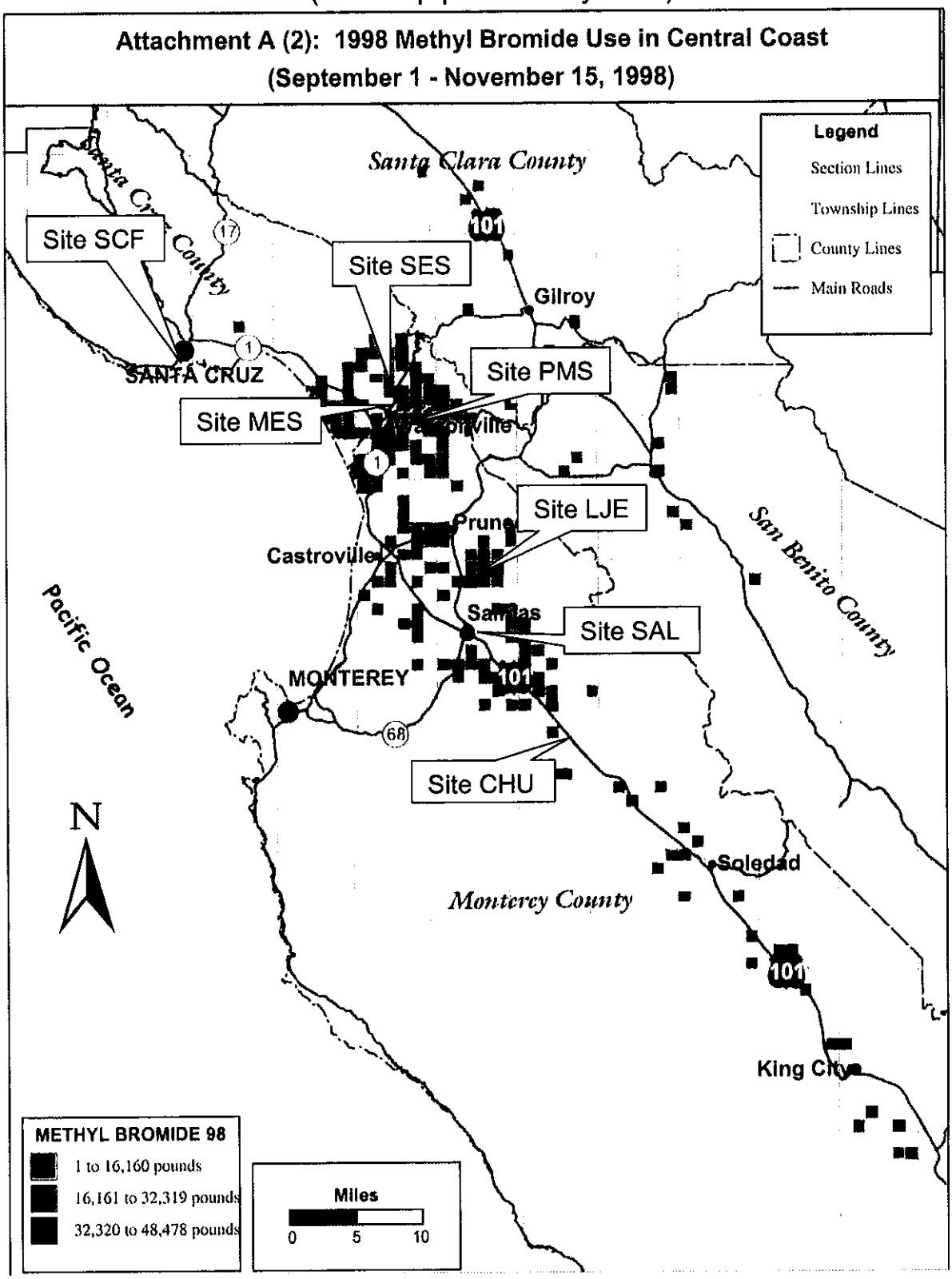

Figure 2

Passive Canister Sampling Train