Summary and Analysis of 2001 Ambient Air Monitoring Data for Methyl Bromide

NOTE: This summary and analysis is based on a combination of preliminary and final data submitted by the Air Resources Board and the Alliance of the Methyl Bromide Industry, as well as preliminary pesticide use data. Some of the data is known to contain errors. Several air concentration values will change slightly, but the overall conclusions will remain the same.

Summary and Analysis of Monitoring Conducted by the

California Environmental Protection Agency - Air Resources Board
and
Alliance of the Methyl Bromide Industry

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EXECUTIVE SUMMARY

Methyl bromide is one of the most widely used pesticides in California. It is a gaseous fumigant that kills insects, mites, rodents, nematodes, termites, weeds, and organisms that cause plant diseases. Farmers use methyl bromide to treat soil before planting vegetable, fruit and nut crops, and flower and forest nurseries. Depending on the crop, field applications may occur annually, or once every several years. Methyl bromide is injected into the soil with specialized application equipment. The fumigant is also used for termite eradication in homes and other structures, and to control insects in mills, ships, railroad cars and other transportation vehicles.

DPR has monitored applications of methyl bromide since 1993 and has imposed the nation's most stringent restrictions on the fumigant, the most recent of which were regulations that went into effect in January 2001, intended to better protect workers and others from short-term (acute) exposures.

Monitoring was conducted in 2001 as a follow-up to studies monitoring done the previous year. The intent has been to determine the effectiveness of restrictions in reducing potential health risk posed by overexposure to methyl bromide in ambient air, particularly exposure concentrations averaged over longer, seasonal periods of up to eight weeks. Monitoring studies conducted in 2000 in areas of high methyl bromide use found levels higher than DPR's seasonal reference concentration (0.001 to 0.002 parts per million, that is, 1 to 2 parts per billion). Although these are not levels that pose an immediate health concern, DPR believed and continues to believe that exposure levels over the long term should be reduced.

DPR asked the State Air Resources Board (ARB) to conduct further methyl bromide monitoring in 2001, and at the same time, broadened the scope of its evaluation effort by requiring the Alliance of the Methyl Bromide Industry (AMBI) to conduct monitoring studies in other high-use areas of the state. Both monitoring projects were part of DPR's ongoing effort to evaluate seasonal exposures to methyl bromide and determine if current restrictions provide adequate safety for people who live and work in areas where fumigations occur to multiple fields. This document summarizes the 2001 monitoring results, estimates exposure and risk, compares air concentrations with pesticide use patterns, and compares 2001 to 2000 results.

Monitoring results in 2001 confirmed trends and findings seen in 2000 monitoring. In brief:

- Methyl bromide use continues to decline. DPR's restrictions—which include larger buffer zones and limitations on acreage--make it more difficult to treat large acreage and prohibit treating some fields close to populated areas. In addition, the impending federal phaseout of methyl bromide in 2005, accompanied by a staged phasedown, has curtailed supplies and correspondingly increased costs of treatment.

- Ten of the 12 ARB sites had also been monitored in 2000. Eight of the ten sites had lower air concentrations in 2001 compared to 2000. The eight-week average air concentrations at the ten sites declined by an average of 22 percent. The overall decrease is consistent with the decrease in methyl bromide use. DPR found a correlation between 2001 methyl bromide use and air concentration in Kern and Monterey/Santa Cruz. This correlation agreed with the analysis of 2000 data. The correlation indicates that the decrease in air concentrations detected from 2000 to 2001 is due to a decrease in use of methyl bromide. Methyl bromide use and air concentration did not demonstrate a correlation for Santa Barbara and Ventura counties. The 2001 pesticide use data indicates that the monitoring occurred in areas of high methyl bromide use and during periods of peak agricultural use, except for Ventura County. Peak use of methyl bromide in Ventura County occurred several weeks before the start of monitoring.

- All one-day and one-week concentrations detected were less than the reference concentrations. The eight or nine-week average air concentrations exceeded the 1 ppb reference concentration for children at seven of the 20 monitoring sites, including five sites in the Monterey/Santa Cruz area. The highest eight-week average concentration detected was 5.5 ppb.

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BACKGROUND

Methyl bromide is one of the most widely used pesticides in California. In 2000, the most recent year for which use reports have been fully compiled, there were about 11 million pounds applied annually in the state. Methyl bromide is a gaseous fumigant that kills insects, mites, rodents, nematodes, termites, weeds, and organisms that cause plant diseases. Because it is a colorless, odorless gas, methyl bromide is normally mixed with chloropicrin, a tear gas with a noticeable odor.

Farmers use methyl bromide to treat soil before planting vegetable, fruit and nut crops, and flower and forest nurseries. Depending on the crop, field applications may occur annually, or once every several years. Methyl bromide is injected into the soil with specialized application equipment. After harvest, methyl bromide fumigation protects crops from pest damage during storage and transportation. The fumigant is also used for termite eradication in homes and other structures, and to control insects in mills, ships, railroad cars and other transportation vehicles.

The Department of Pesticide Regulation (DPR) and the County Agricultural Commissioners have implemented extensive restrictions on the use of methyl bromide, such as buffer zones surrounding treated fields, prescribed equipment and procedures for application, worker safety requirements, and notification to people near fumigated fields.

As required by state law, DPR evaluates, identifies, and controls pesticides as toxic air contaminants. Under this program, methyl bromide was identified as a toxic air contaminant in 1996. As part of the toxic air contaminant program, the Air Resources Board (ARB) monitors for pesticides under the direction of DPR. ARB conducted ambient air monitoring for methyl bromide in 2000 and 2001. Additional monitoring was conducted by the Alliance of the Methyl Bromide Industry (AMBI) at DPR's request in 2001. Both monitoring projects were part of DPR's ongoing effort to evaluate seasonal exposures to methyl bromide and determine if current restrictions provide adequate safety for people who live and work in areas where fumigations occur to multiple fields. ARB monitoring will also be used to evaluate the impact of additional regulatory measures implemented to reduce the ambient air levels found in 2000 air monitoring. This document summarizes the 2001 monitoring results, estimates exposure and risk, compares air concentrations with pesticide use patterns, and compares 2001 to 2000 results.

MONITORING PLAN

This section summarizes the monitoring plans. Complete descriptions can be found in ARB (2002a, 2002b) and AMBI (2002), all available on DPR's Web site.

Monitoring was designed to be conducted within the areas and during periods of highest use. ARB monitored six locations in Kern County from June 30 to August 30, 2001 (Figure 1) and six locations in the Monterey and Santa Cruz area from September 9 to November 7, 2001 (Figure 2). In Kern County, methyl bromide is primarily used on land to be planted with carrots or flower crops. In the coastal counties, it is used primarily to prepare land for strawberry plantings. At each location, one-day samples were collected four days per week for eight weeks. Additional samples were collected for quality control, including duplicate samples taken once per week at each site. The averaged results of the duplicate samples are reported in this summary.

AMBI monitored four locations in the Oxnard/Camarillo area of Ventura County from August 15 to October 10, 2001 (Figure 3) and four locations in the Santa Maria area of Santa Barbara County from August 23 to October 9, 2001 (Figure 4). At each location, daily samples were collected four days per week for nine weeks in Ventura County and eight weeks in Santa Barbara County. One site in Ventura County had two excluded sampling periods from September 6 to September 9 and from September 27 to September 30 due to methyl bromide fumigations closer than 1200 feet to the sampling site. Additional samples were collected for quality control, including duplicate samples. The averaged results of the duplicate samples are reported in this summary.

Both ARB and AMBI collected background samples at locations several miles from historical use areas. ARB collected its background samples for a four-day period (September 24 - 29, 2001) in the city of Santa Cruz. AMBI collected its background samples concurrently with the Santa Barbara County monitoring (August 15 - October 10, 2001) in the city of San Luis Obispo.

Both ARB and AMBI collected 24-hour air samples using evacuated 6-liter stainless steel canisters. ARB used Silcosteel® canisters and AMBI used SUMMA® canisters. Air flow rates for both were approximately three milliliters per minute, and the flow rates and canister pressure were checked at the beginning and end of each sampling period. The flow controllers used to maintain a constant airflow into the canisters malfunctioned in many cases, causing the ending flow rate to be significantly different from the starting the flow rate. These samples were considered invalid. ARB's Northern Laboratory Branch in Sacramento analyzed the ARB samples. Environmental Analytical Service in San Luis Obispo analyzed the AMBI samples. Both laboratories analyzed the samples by pressurizing the canisters to remove a subsample of air and using a cryogenic trap to concentrate the subsample. The subsamples were injected into a gas chromatograph equipped with a mass selective detector to identify and quantify the amount of methyl bromide. Quality control included the analysis of blank samples and samples containing known amounts of methyl bromide (spikes). ARB reported air concentrations in nanograms per cubic meter. AMBI reported air concentrations in parts per billion (ppb) on a volume basis. For this report, the ARB results are converted to ppb on a volume basis, the same unit as AMBI. ARB's and AMBI's 2001 methods are consistent with the ones used by ARB for the 2000 monitoring.

MONITORING RESULTS

This section summarizes the results presented in the monitoring reports ARB (2002a, 2002b) and AMBI (2002), both available on DPR's Web site.

Table 1 summarizes the results of the ARB monitoring and Table 2 the AMBI monitoring; the results are presented in more detail in Appendix A. All of the 344 ARB samples and 214

AMBI samples contained a detectable and quantifiable amount of methyl bromide. (The detection limit for the ARB samples was 0.002 ppb, the quantitation limit 0.01 ppb; for the AMBI samples the detection limit was 0.003 ppb, the quantitation limit 0.009 ppb). For the ARB monitoring the highest daily concentration detected was 36.6 ppb; highest one-week average concentration was 13.4 ppb; and the highest average concentration for the study period (8 weeks) was 5.5 ppb. For the AMBI monitoring, the highest one-day concentration detected was 11.2 ppb; highest one-week average concentration was 6.5 ppb; and the highest average concentration for the study period (8 or 9 weeks) was 1.3 ppb. Review of the AMBI report shows discrepancies in the identification of valid and invalid samples. Once these discrepancies are resolved, some of the AMBI concentrations may be slightly higher or lower than reported here. See the *Evaluation of Quality Control Data* for more details on the discrepancies of valid and invalid samples.

Higher air concentrations were detected in areas with higher methyl bromide use (Figures 5 - 8). The highest air concentrations were detected in the Watsonville area of Monterey and Santa Cruz counties (MacQuiddy Elementary School, Pajaro Middle School, and La Joya Elementary School). A detailed discussion of the correlation between methyl bromide use and air concentrations is given below.

Ten of the 12 ARB sites had also been monitored in 2000. Differences between levels of methyl bromide detected in 2001 compared to 2000 for the eight-week average concentrations ranged from an increase of 18 percent at the Cotton Research Station in Kern County to a decrease of 61 percent at Pajaro Middle School in Monterey County (Table 3). Eight of the ten sites had lower air concentrations in 2001 compared to 2000. The eight-week average air concentrations at the ten sites declined by an average of 22 percent. The overall decrease is consistent with the decrease in methyl bromide use as discussed below.

All background samples contained detectable and quantifiable concentrations of methyl bromide. ARB's four background samples in Santa Cruz ranged from 0.2 - 0.7 ppb. AMBI's 32 background samples in San Luis Obispo ranged from 0.01 to 1.1 ppb. The nearest reported methyl bromide fumigations occurred at least eight miles from the background monitoring locations (Figures 6 and 7). Several factors may account for the positive background concentrations, including long-distance transport of methyl bromide, unreported applications near the background sites, structural or post-harvest fumigations near the background sites (these uses are reported only as total amount for the county without location-specific information), natural sources of methyl bromide, or sampling/laboratory error.

EVALUATION OF HEALTH RISKS

Methyl bromide causes a variety of adverse health effects in experimental animals and humans. Since exposure can occur without toxicity (when the specified period of exposure does not exceed the threshold of injury), margins of exposure must be defined in terms of the specific type of toxicity or adverse effect and the dose/time threshold values for these effects. This is determined by comparing the actual level of exposure to a chemical to the level of exposure that is not expected to cause any adverse effects, even in the most susceptible people. Levels of exposure at which no adverse health effects are expected are called “health reference levels,”(in this document called a “reference concentration”), and they generally are based on the results of animal studies. However, scientists usually set health reference levels much lower than the levels of exposure that were found to have no adverse effects in the animals tested. This approach helps to ensure that real health risks are not underestimated by adjusting for possible differences in a chemical’s effects on laboratory animals and humans; the possibility that some humans, such as children and the elderly, may be particularly sensitive to a chemical; and possible deficiencies in data from the animal studies. As a general guideline when working with animal-test based data, a factor of 100 is used, reflecting a possible 10-fold application factor for extrapolating from animals to humans, and a 10-fold factor for human variability in response to a chemical. Exposures above the health reference level are not necessarily hazardous, but the risk of toxic effects increases as the dose increases. If an assessment determines that human exposure to a chemical exceeds the reference concentration, the values do not necessarily dictate regulatory action, but further investigation is warranted.

For a one-day average exposure to methyl bromide, DPR's reference concentration is 250 ppb for children and 210 ppb for adults (the reference concentration for a child is higher than an adult in this case). For a one-week average exposure, the reference concentration is 70 ppb for children and 120 ppb for adults. For an eight-week average exposure, the reference concentration is 1 ppb for children and 2 ppb for adults.

These studies (as do most environmental studies) detected a wide range of concentrations. To estimate the health risk of the range or distribution of air concentrations, DPR characterizes the distribution statistically. The average air concentration represents what people would be exposed to over an extended period of time. While the average concentration is a useful measure of long-term (e.g., seasonal or annual) inhalation exposure, DPR uses an upper-bound value for short-term (e.g, one-day and one-week) inhalation exposures. The 95th percentile is DPR’s target upper-bound value. A 95th percentile one-day air concentration of 50 ppb means that 95 percent of one-day air concentrations are less than 50 ppb and 5 percent of one-day air concentrations are greater than 50 ppb. A 95th percentile one-week average concentration of 10 ppb means that 95 percent of one-week average air concentrations are less and 5 percent are greater than 10 ppb. As with all measurements, there is uncertainty in these values. To incorporate the uncertainty in the estimate of the 95th percentile, tolerance limits are computed instead of the percentiles. DPR uses 90 percent tolerance limits for the 95th percentiles of one-day and one-week methyl bromide exposures. A tolerance limit expresses the confidence in the percentile estimate. For example, if the 90 percent tolerance limit for the 95th percentile weekly average concentration is 20 ppb, it means that, with 90 percent confidence, we can predict that 95 percent of all future one-week air concentrations will be less and 5 percent will be greater than 20 ppb. The greater the variability in air concentration, the greater the tolerance limit. Some tolerance limits are greater than the highest concentration detected and some are lower. All one-day and one-week tolerance limits as well as highest concentrations detected are less than the reference concentrations (Tables 1 and 2).

To estimate the eight-week or nine-week exposure risk, DPR uses the arithmetic average of the weekly average concentrations. The eight-week or nine-week average air concentrations exceeded the 1 ppb reference concentration for children at seven of the 20 monitoring sites, including five sites in the Monterey/Santa Cruz area (Tables 1 and 2). The highest eight-week average concentration detected was 5.5 ppb.

While the eight-week reference concentration was exceeded in several locations, these would still be considered low-risk exposure situations unlikely to cause harm because the reference concentrations are set 100 times lower than a level that caused no adverse health effects in animals. A complete description of the health evaluation is given in Appendix B.

METHYL BROMIDE USE IN THE MONITORING AREAS

The following is based on preliminary 2001 pesticide use reports. This data may contain errors and may be incomplete.

Methyl bromide use near each monitoring site during the monitoring periods is shown in Figures 5 - 8. DPR compiles data for agricultural applications of pesticides, including methyl bromide. Reports of pesticide applications to production agricultural fields (including methyl bromide) contain information on the product applied, the amount applied, the number of acres treated, the date of application, and location referenced by the Public Land Survey System. The Public Land Survey System locates fields within a one square mile area, according to meridian, township, range, and section. Figures 5 - 8 show the methyl bromide use in each one-mile section during the monitoring period. Methyl bromide used for structural or post-harvest fumigations are not shown in Figures 5 - 8 because these uses are reported only as total amount for the county. Figures 5 - 8 indicate that monitoring occurred near areas of high agricultural use. Figure 9 shows that monitoring occurred in the four counties with the highest agricultural use for 2001 (Monterey, Santa Barbara, Santa Cruz, and Ventura).

Figures 10 - 14 show methyl bromide use over time in the counties of monitoring. These figures indicate that monitoring occurred during periods of peak agricultural use, except for Ventura County. Peak use of methyl bromide in Ventura County occurred several weeks before the start of monitoring.

Methyl bromide use in the counties of monitoring as well as statewide declined between 2000 and 2001 (Table 4). This is consistent with the phaseout of methyl bromide under the federal Clean Air Act, and is paralleled by a decrease in air concentrations. *[Note: Pesticide use reports appear complete for all monitored counties, except Kern. Reports for Kern and other counties not monitored appear incomplete.]* During the monitoring periods, methyl bromide use declined in all five counties where monitoring occurred, ranging from a 10 percent decrease in Santa Cruz County to a 34 percent decrease in Ventura County. The average decrease between 2000 and 2001 was 18 percent for the five counties during the monitoring periods.

CORRELATION OF METHYL BROMIDE USE AND AIR CONCENTRATIONS

Ambient air concentrations from multiple fumigations are affected by proximity to the fumigation, the number of fumigations, and the period over which they occur. In 2000, DPR found a high correlation between air concentrations detected by ARB and pesticide use (DPR 2001). DPR used similar methodology to analyze the 2001 data. To determine the effect of proximity, pesticide use report data was tabulated for concentric areas surrounding each monitoring site, during the monitoring period. To determine correlation, DPR aggregated the amount of methyl bromide reported over various combinations of time and areas surrounding the monitoring sites. Measured air concentrations were regressed on methyl bromide use for 24 different combinations of time and area size. The ARB 2001 monitoring data agreed with the empirical relationships established using the monitoring data of 2000. Regression models derived separately from 2000 data and 2001 data of ARB air monitoring were not substantially different (Appendix C). For 2001, the methyl bromide use during the eight-week monitoring period within a three-by-three mile area surrounding each monitoring site gave the best correlation to detected air concentrations (Tables 5 and 6, Figures 15 - 17). Combining the 2000 and 2001 ARB data, the following equation gives the highest correlation between methyl bromide use and eight-week air concentration.

$$\text{air concentration [ppb]} = 0.414 + 0.000539(\text{use in } 9\ \text{mi}^2\ [\text{pounds/week}])$$

DPR found higher correlation when various weighting factors were used to account for distance of fumigations, wind direction, and dates of application relative to the locations and dates of the ARB monitoring. However, DPR does not plan to modify the above equation based on these factors because scientific judgment was used to select most of the weighting factors. DPR will investigate methods to objectively determine the weighting factors and other approaches to improve the ability of pesticide use and other data to estimate air concentrations.

The AMBI air monitoring data did not support a linear relationship between the use and air concentration over an eight-week period (Tables 7 and 8, Figures 18 and 19). Lack of correlation using the AMBI data may be due to several factors such as discrepancies in the data, high proportion of missing and invalid monitoring data, errors in the sampling or analysis, or incomplete or erroneous use report data. A complete description of this analysis is given in Appendix C.

EVALUATION OF QUALITY CONTROL DATA

ARB and AMBI analyzed quality control samples within each laboratory as well as between the laboratories. Quality control samples included blank samples, spike samples, duplicate samples, collocated samples, and a standard comparison. The results are summarized in Table 9.

Both ARB and AMBI had high recoveries of spike samples. ARB analyzed the canister samples using two different instruments, one for high concentrations (MSD-3) and one for low concentrations (MSD-4). Recovery of ARB laboratory, trip, and field spikes using

MSD-3 were 152 percent, 149 percent, and 156 percent, respectively. Recovery of ARB laboratory, trip and field spikes using MSD-4 were 123 percent, 125 percent, and 122 percent, respectively. Recoveries of AMBI laboratory and trip spikes were 121 percent and 122 percent, respectively. Problems with the AMBI field spikes make the data unrepresentative. The high recoveries for ARB, particularly for instrument MSD-3, are likely due to differences between the standards used for calibration and spiking, and may not indicate the true performance of the method. According to ARB's report, "the stock standard (cylinder standard) used to prepare the lab, trip, and field spikes was different from the cylinders used for the preparation of the calibration standard and laboratory control samples." "The high spike recovery results for methyl bromide are likely due to the inherent inaccuracy (±20 percent) of the individual standard cylinder assignments." If the recoveries of the ARB and/or AMBI spikes are actually high, the air concentrations may be overestimated.

None of ARB's trip blank or laboratory blank samples contained a detectable amount of methyl bromide. In contrast, all 12 of AMBI's trip blank samples contained a detectable amount of methyl bromide, and five of these contained a quantifiable amount (Table 9). This may indicate contamination of the samples. It is unclear if any of AMBI's laboratory blank samples contained detectable amounts of methyl bromide. If the samples were contaminated, the AMBI air concentrations may be overestimated.

ARB duplicate field samples had a relative percent difference of 7 percent. AMBI duplicate field samples had a relative percent difference of 24 percent (Table 9).

ARB and AMBI exchanged standards for comparison. ARB and AMBI showed agreement for the ARB standard, but differences for the AMBI standard (Table 9).

DPR collected collocated canister samples with AMBI, and had them analyzed by ARB. Results of these collocated samples are inconsistent. All of the DPR/ARB samples from Ventura County were higher than the AMBI samples, while all of the DPR/ARB samples from Santa Barbara County were lower than the AMBI samples (Table 10).

There were other issues regarding the quality of the AMBI monitoring (Segawa, 2002). First, AMBI did not monitor during two four-day periods at one site because they were concerned that methyl bromide applications had occurred within 1200 feet of the monitoring site. DPR disagrees that these samples should have been excluded. In addition, AMBI has not documented that methyl bromide fumigations occurred on the specified dates, and pesticide use report records submitted to DPR do not show any applications. Secondly, this study may not meet the standard for completeness, depending on the standard chosen for completeness, the standard chosen for valid samples, and the correct identification of valid samples. Most of the invalid samples are due to deviations in airflow rate of the samplers. However, AMBI's standard for flow deviation differs from ARB's. Additionally, some samples appear to have been misidentified as valid, but are actually invalid and vice versa. Three samples were identified as "lost" with little or no explanation. Ventura County may have as many as 30 percent invalid samples.

CONCLUSIONS FROM MONITORING DATA

Monitoring was conducted during the high methyl bromide use period of June 30 to August 30 in Kern County, September 9 to November 7 in Monterey and Santa Cruz counties, and August 23 to October 9 in Santa Barbara County. Monitoring was conducted August 15 to October 10 in Ventura County, several weeks after the high methyl bromide use period.

Monitoring was conducted in four areas of the highest methyl bromide use.

The one-day air concentrations of methyl bromide met DPR's goal (i.e., they were lower than the one-day reference concentration) at all locations.

The one-week air concentrations of methyl bromide met DPR's goal (i.e., they were lower than the one-week reference concentration) at all locations.

The average air concentrations of methyl bromide for the eight or nine-week study period did not meet DPR's goal (i.e., they were greater than the eight-week reference concentration). Seven of the 20 monitoring sites exceeded the 1 ppb child reference concentration: five in Monterey/Santa Cruz area, one in Kern County, and one in Santa Barbara County. Four sites exceeded the 2 ppb adult target level: three in Monterey/Santa Cruz area and one in Kern County. The highest average concentration at any of these seven sites was 5.5 ppb.

Eight of the ten sites monitored in 2000 had lower air concentrations in 2001. The eight-week concentration declined by an average of 22 percent at the ten sites.

All background samples contained methyl bromide. The positive background samples may be due to a variety of factors.

The correlation of 2001 methyl bromide use and air concentration in Kern and Monterey/Santa Cruz agreed with the analysis of 2000 data. Methyl bromide use and air concentration did not demonstrate a correlation for Santa Barbara and Ventura counties.

Discrepancies in the AMBI report may cause some air concentrations to be slightly lower or higher than currently documented.

REFERENCES

AMBI, 2002. Final report: Methyl bromide ambient air monitoring in Oxnard/Camarillo and Santa Maria, August-October, 2001. Report dated April 4, 2002. Sacramento, CA: Alliance of the Methyl Bromide Industry.

ARB, 2002a. Draft Report for the 2001 Methyl Bromide and 1,3-Dichloropropene Air Monitoring in Kern County. California Air Resources Board, Sacramento, CA.

ARB, 2002b. Final Report for the 2001 Methyl Bromide and 1,3-Dichloropropene Air Monitoring in Monterey and Santa Cruz Counties. California Air Resources Board, Sacramento, CA.

DPR, 2001. Methyl bromide risk management plan for seasonal community exposures. Letter from Paul Helliker to Interested Parties, June 26, 2001. California Department of Pesticide Regulation, Sacramento, CA.

Segawa, 2002. Review of Registrant Revised Report on Methyl Bromide Air Monitoring. Memorandum from Randy Segawa to John Sanders, May 29, 2002. California Department of Pesticide Regulation, Sacramento, CA.

Table 1. Summary of 2001 ARB methyl bromide air monitoring results. Study period concentrations are the averages of the eight or nine weekly average concentrations.

Location	Highest 1-Day Concentration (ppb)	1-Day 95% Tolerance Limit (ppb)	Highest 1-Week Concentration (ppb)	1-Week 95% Tolerance Limit (ppb)	Average Concentration for Study Period (ppb)
Monterey and Santa Cruz Counties, Sep 8 – Nov 7, 2001					
CHU-Chualar School, Chualar	1.84	2.08	1.16	1.40	0.56
LJE-La Joya Elem School, Salinas	14.49	21.72	8.99	11.29	2.82
MES-MacQuiddy Elem Sch, Watsonville	36.64	59.28	13.43	18.76	5.51
PMS-Pajaro Middle School, Watsonville	21.08	21.10	10.47	12.50	2.99
SAL-Air Monitoring Station, Salinas	9.25	7.61	6.16	6.91	1.38
SES-Salsepuedes Elem Sch, Watsonville	5.31	7.53	2.04	3.32	1.22
SCF-Santa Cruz Fire Station, Santa Cruz	0.74	Not applicable	0.45	Not applicable	Not sampled
Kern County, Jun 30 – Aug 30, 2001					
ARB-Air Monitoring Station, Bakersfield	0.31	0.47	0.19	0.26	0.12
ARV-Arvin High School, Arvin	0.22	0.28	0.13	0.18	0.08
CRS-Cotton Research Station, Shafter	25.34	23.98	10.04	11.86	2.54
MET-Mettler Fire Station, Mettler	0.25	0.23	0.13	0.17	0.07
MVS-Mountain View School, Lamont	0.23	0.30	0.14	0.18	0.08
VSD-Vineland School Dist, Bakersfield	0.23	0.29	0.15	0.19	0.08
Reference concentrations [a]					
Child	*250*	*250*	*70*	*70*	*1*
Adult	*210*	*210*	*120*	*120*	*2*

[a] DPR scientists refer to reference concentrations identified in risk assessments. Reference concentrations indicate when further investigation of monitoring data is warranted; the values do not necessarily dictate regulatory action.

Table 2. Summary of 2001 AMBI methyl bromide air monitoring results. Study period concentrations are the averages of the eight or nine weekly average concentrations.

Location	Highest 1-Day Concentration (ppb)	1-Day 95% Tolerance Limit (ppb)	Highest 1-Week Concentration (ppb)	1-Week 95% Tolerance Limit (ppb)	Average Concentration for Study Period (ppb)
Oxnard/Camarillo, Ventura County, Aug 15 – Oct 10, 2001					
PVW-Pleasant Valley Water Station	3.17	2.56	2.01	2.59	0.56
UWC-United Water Conservation Station	4.35	8.77	2.08	3.48	0.82
SHA-Sharps Automotive	2.94	2.43	2.30	2.55	0.50
ABD-Abandoned Building	0.44	0.44	0.44	0.58	0.18
Santa Maria, Santa Barbara County, Aug 23 – Oct 9, 2001					
BLO-Blosser Road	4.55	4.85	1.89	2.25	0.73
AGC-Agricultural Commissioners Office	1.16	1.28	0.85	1.00	0.28
EDW-Edwards Community Center	11.15	10.57	6.49	7.10	1.32
PNT-Plantell Greenhouse	2.69	4.62	1.75	2.26	0.93
BACKGROUND-San Luis Obispo	1.12		0.30		0.08
Reference concentrations [a]					
Child	*250*	*250*	*70*	*70*	*1*
Adult	*210*	*210*	*120*	*120*	*2*

[a] DPR scientists refer to reference concentrations identified in risk assessments. Reference concentrations indicate when further investigation of monitoring data is warranted; the values do not necessarily dictate regulatory action.

Table 3. Comparison of 2000 and 2001 ARB average concentration for the study periods. Concentrations are the averages of the seven to nine weekly average concentrations.

Location	2000 Average Concentration (ppb)	2001 Average Concentration (ppb)	% Change from 2000 to 2001
CHU-Chualar School, Chualar	0.64	0.56	-12.5
LJE-La Joya Elem School, Salinas	3.79	2.82	-25.6
MES-MacQuiddy Elem Sch, Watsonville	Not sampled	5.51	
OAS-Oak Ave School, Greenfield	0.39	Not Sampled	
PMS-Pajaro Middle School, Watsonville	7.68	2.99	-61.1
SAL-Air Monitoring Station, Salinas	1.29	1.38	7.0
SES-Salsepuedes Elem Sch, Watsonville	2.60	1.22	-53.1
ARB-Air Monitoring Station, Bakersfield	0.19	0.12	-36.8
ARV-Arvin High School, Arvin	Not sampled	0.075	
CRS-Cotton Research Station, Shafter	2.16	2.54	17.6
MET-Mettler Fire Station, Mettler	0.084	0.065	-22.6
MVS-Mountain View School, Lamont	0.092	0.081	-12.0
SHA-Air Monitoring Station, Shafter	0.79	Not sampled	
VSD-Vineland School Dist, Bakersfield	0.099	0.078	-21.2
Reference concentrations [a]			
Child	*1*	*1*	
Adult	*2*	*2*	

[a] DPR scientists refer to reference concentrations identified in risk assessments. Reference concentrations indicate when further investigation of monitoring data is warranted; the values do not necessarily dictate regulatory action.

Table 4. Reported methyl bromide use in the monitored counties and statewide

County	2000 Use (lbs)	2001 Use (lbs)	Change from 2000 to 2001 (lbs)	% Change from 2000 to 2001
Use for Entire Year				
Kern	613,832	260,848	-352,984	-57.5
Monterey	1,877,182	1,501,293	-375,890	-20.0
Santa Cruz	662,195	557,698	-104,496	-15.8
Santa Barbara	680,852	425,062	-255,790	-37.6
Ventura	1,728,696	1,430,515	-298,181	-17.2
Statewide	10,862,836	5,916,935	-4,945,901	-45.5
Use During Monitoring Months				
Kern (Jul - Aug)	136,757	119,281	-17,476	-12.8
Monterey (Sep - Oct)	1,168,348	945,787	-222,562	-19.0
Santa Cruz (Sep - Oct)	384,989	345,477	-39,512	-10.3
Santa Barbara (Aug - Oct)	518,499	345,081	-173,417	-33.5
Ventura (Aug - Oct)	847,030	746,576	-100,454	-11.9

Note: Pesticide use reports appear complete for all monitored counties, except Kern. Reports for Kern and other counties not monitored appear incomplete for 2001.

Table 5. Eight-week average air concentrations and methyl bromide use over various spatial scales centered on ARB monitoring sites

			Weekly Methyl Bromide Use (lb/week)							
County	**Site**	**Concentration (ppb)**	**1x1 (mi)**	**3X3 (mi)**	**5X5 (mi)**	**7X7 (mi)**	**9X9 (mi)**	**11X11 (mi)**	**13X13 (mi)**	**15X15 (mi)**
Monterey	SAL	1.41	0	1417	7806	10872	23476	36672	46794	51452
Santa Cruz	MES	6.14	3034	7224	16181	28872	39391	52252	55096	58744
Monterey	CHU	0.58	0	561	1317	3475	6912	13551	18529	21538
Monterey	LJE	2.86	0	3150	7518	13820	23889	31082	40790	46707
Monterey	PMS	3.31	0	4458	17439	38231	57111	63801	66301	67926
Santa Cruz	SES	1.14	0	5452	12275	19429	27580	41171	44346	53127
Kern	ARB	0.12	0	0	0	0	0	0	0	0
Kern	ARV	0.08	0	0	0	0	0	0	0	0
Kern	CRS	2.76	0	2737	4059	4059	7452	7452	9438	9438
Kern	MVS	0.08	0	0	0	0	1570	1570	1570	1570
Kern	VSD	0.08	0	0	0	0	0	0	0	0

NOTE: Some of the average air concentrations shown here differ from those shown in Table 1 due to different averaging methods.

Table 6. Correlation (R^2 and EMS)[a] between average air concentration (ppb) and average methyl bromide usage (lb/week) over various areas and periods using ARB 2001 monitoring data

	Time period					
	1 week (n = 93)[b]		4 weeks (n = 22)		8 weeks (n = 11)	
Area Size	**R^2**	**EMS**	**R^2**	**EMS**	**R^2**	**EMS**
1x1 mi	0.147	8.04	0.394	2.39	0.593	1.67
3x3 mi	0.288	6.71	0.322	2.68	0.742	1.05
5x5 mi	0.197	7.57	0.325	2.67	0.644	1.45
7x7 mi	0.178	7.75	0.326	2.67	0.590	1.68
9x9 mi	0.158	7.93	0.305	2.75	0.558	1.81
11x11 mi	0.163	7.89	0.298	2.77	0.542	1.87
13x13 mi	0.164	7.87	0.294	2.79	0.521	1.96
15x15 mi	0.146	8.05	0.265	2.90	0.488	2.09
Significant R^2 values						
$R^2_{0.10}$	0.018		0.081		0.176	
$R^2_{0.05}$	0.030		0.130		0.271	

[a] R^2 is the coefficient of determination, representing the decimal fraction of variation of air concentration that is explained by the regression model. EMS is the Error Mean Square or average squared residuals not explained by the model.

[b] n is the number of samples for the regression.

Table 7. Eight-week average air concentrations and methyl bromide use over various spatial scales centered on AMBI monitoring sites

			Weekly Methyl Bromide Use (lb/week)							
County	**Site**	**Concentration (ppb)**	**1x1 (mi)**	**3X3 (mi)**	**5X5 (mi)**	**7X7 (mi)**	**9X9 (mi)**	**11X11 (mi)**	**13X13 (mi)**	**15X15 (mi)**
Santa Barb	PLN	0.90	156	4394	17365	17899	22195	24389	31280	36642
Santa Barb	EDW	1.51	3828	4159	10708	21727	28773	34334	36437	36642
Santa Barb	AGC	0.28	0	526	4922	19356	22889	29296	35687	35778
Santa Barb	BLO	0.80	0	7484	11256	27100	29323	32848	36528	36731
Ventura	SHA	0.51	0	2089	9137	12761	27899	35841	37300	40658
Ventura	ABD	0.18	0	4549	10672	27009	36628	41553	44901	44928
Ventura	UWC	0.82	0	3814	10091	23899	40930	49955	52006	57849
Ventura	PVW	0.56	0	0	9549	19280	29076	46804	48215	51166

NOTE: Some of the average air concentrations shown here differ from those shown in Table 2 due to different averaging methods.

Table 8. Correlation (R^2 and EMS)[a] between average air concentration (ppb) and average methyl bromide usage (lb/week) over various areas and periods using AMBI 2001 monitoring data

	Time period					
	1 week (n = 63)[b]		4 weeks (n = 16)		8 weeks (n = 8)	
Area Size	**R^2**	**EMS**	**R^2**	**EMS**	**R^2**	**EMS**
1x1 mi	0.657	0.331	0.474	0.140	0.653	0.071
3x3 mi	0.454	0.527	0.020	0.260	0.127	0.178
5x5 mi	0.453	0.527	0.056	0.250	0.210	0.161
7x7 mi	0.385	0.593	0.109	0.236	0.025	0.198
9x9 mi	0.297	0.678	0.150	0.225	0.005	0.202
11x11 mi	0.236	0.737	0.242	0.201	0.022	0.199
13x13 mi	0.227	0.746	0.158	0.223	0.054	0.192
15x15 mi	0.227	0.746	0.158	0.224	0.027	0.198
Significant R^2 values						
$R^2_{0.10}$	0.026		0.114		0.257	
$R^2_{0.05}$	0.043		0.181		0.386	

[a] R^2 is the coefficient of determination, representing the decimal fraction of variation of air concentration that is explained by the regression model. EMS is the Error Mean Square or average squared residuals not explained by the model.

[b] n is the number of samples for the regression.

Table 9. Summary of ARB and AMBI quality control samples

Quality Control Type	ARB[a]	AMBI
Laboratory Spike (% recovery)	152 (MSD-3); 123 (MSD-4)	121
Trip Spike (% recovery)	149 (MSD-3); 125 (MSD-4)	122
Field Spike (% recovery)	156 (MSD-3); 122 (MSD-4)	Invalid
Laboratory Blank (% positive)	0	Unknown
Trip Blank (% positive)	0	100
Field Duplicate (relative % difference)	7.0	23.7
ARB 0.50 ppb Standard (% recovery)	87 (MSD-3); 105 (MSD-4)	83
AMBI 0.63 ppb Standard (% recovery)	148 (MSD-3); 147 (MSD-4)	105

[a] ARB used two different instruments to analyze the samples. MSD-3 was used for samples with high methyl bromide concentrations. MSD-4 was used for samples with low methyl bromide concentrations.

Table 10. Results of AMBI and DPR/ARB collocated samples

Sample Site	Sampling Date	Concentration (ppb) AMBI	Concentration (ppb) DPR/ARB	% Difference from AMBI
Ventura				
SHA	8/24/01	2.86	*6.96 (invalid)*[a]	
PVW	8/24/01	*1.44 (invalid)*	5.64	
UWC	8/24/01	2.01	2.87	42
SHA	8/25/01	1.09	*1.58 (invalid)*	
PVW	8/25/01	0.81	1.97	142
UWC	8/25/01	0.25	1.74	595
Santa Barbara				
BLO	9/26/01	0.34	0.083	-75
AGC	9/26/01	0.42	0.25	-40
PNT	9/26/01	0.55	0.27	-51
EDW	9/26/01	*11.15 (invalid)*	4.03	
BLO	9/27/01	1.20	0.77	-35
AGC	9/27/01	0.71	0.37	-48
PNT	9/27/01	0.83	0.48	-42
EDW	9/27/01	4.05	0.26	-93

[a] Four samples were invalid due to flow deviations.