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# Department of Pesticide Regulation



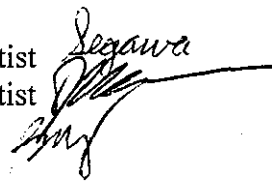
Gray Davis  
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Secretary, California  
Environmental  
Protection Agency

## MEMORANDUM

*Attachment 1*

TO: John S. Sanders  
Branch Chief

FROM: Randy Segawa, Senior Environmental Research Scientist  
Bruce Johnson, Senior Environmental Research Scientist  
Terri Barry, Senior Environmental Research Scientist 

DATE: January 21, 2000

SUBJECT: SUMMARY OF OFF-SITE AIR MONITORING FOR METHYL BROMIDE  
FIELD FUMIGATIONS

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### BACKGROUND

The preliminary risk characterization by the Department of Pesticide Regulation (DPR) for methyl bromide indicated toxic effects at doses lower than those previously documented, and that there was unacceptable exposure for several uses (Nelson, 1992). Subsequently, DPR and others conducted off-site and worker air monitoring for methyl bromide field fumigations. In 1993, DPR issued recommendations (including buffer zones) to mitigate unacceptable methyl bromide exposure, based on initial monitoring data. DPR has updated its buffer zone and other mitigation recommendations as additional monitoring data was collected. Current buffer zones are set so that air concentrations measured at the specified distance are not likely to exceed 0.21 parts per million (ppm). This concentration is a 24-hour time-weighted average and provides a 100-fold margin of exposure (100 times less than the no observed effect level in animal tests). This document summarizes the off-site air monitoring data for field fumigations used to determine the buffer zone and related regulatory requirements.

### METHYL BROMIDE PROPERTIES, USES, AND APPLICATION METHODS

Methyl bromide (other names: bromomethane, monobromomethane, CAS 74-83-9) is a natural product, as well as manufactured synthetically. With a vapor pressure of approximately 2000 torr at 25 degrees Celsius, methyl bromide is a gas at normal pressure and temperature and a liquid under high pressure or at low temperature. It is colorless (a dye is sometimes added) and odorless except at high concentrations. Methyl bromide is primarily used as a pesticide. It is also used as a chemical intermediate, solvent, and degreaser.

Methyl bromide is one of the most widely used pesticides, with approximately 15 million pounds applied annually in California over the last few years. It is registered as a soil fumigant, as a fumigant for harvested food and non-food commodities, and for pest control in buildings. Methyl bromide is used throughout the year and in almost every county of California. The largest quantity of methyl bromide is used as a fumigant of bare soil prior to planting in agricultural fields.



There are a number of methods of applying methyl bromide to agricultural fields, depending on the crop and target pest. Most involve injection beneath the soil surface with tractor-mounted chisels. Several different types of chisels are used and injection depth varies from 6 to 30 inches. Many, but not all, of these application methods also cover the field with a plastic tarpaulin during the injection process. Methyl bromide can be applied to flat fields (broadcast) or to fields with preformed beds. Tarpaulins used for broadcast applications are normally removed several days after fumigation. Tarpaulins used for bed applications normally stay in place throughout the growing season.

#### DESCRIPTION OF SAMPLING AND LABORATORY ANALYSIS METHODS

Most of the monitoring studies used to develop DPR's methyl bromide restrictions were designed to determine the distance and time at which 0.21 ppm (24-hour time-weighted average) occurred downwind from a fumigated field. The studies monitored a variety of application methods, locations, seasons, application rates, and acres. Off-site air concentrations were determined by sampling at fixed locations with absorbent tubes. In general, 8 to 24 locations were sampled for monitoring an individual application. Normally, several distances were sampled for each application. Distances varied from the edge of the field to 1000 feet. In general, sampling was initiated with the start of an application and continued for two to seven days. Individual sampling intervals were 4 to 24 hours. The individual reports for each study describe the sampling methods in more detail.

Air samples were collected using absorbent tubes attached to portable suction pumps. In this method, air is drawn through the tubes by the pumps at a known flow rate. The absorbent tubes filter or trap any methyl bromide contained in the air. The amount of methyl bromide trapped in the tubes is determined by a laboratory analysis. The air concentration is calculated by dividing the amount of methyl bromide detected by the volume of air drawn through the tubes. Activated charcoal was used as the trapping media. Normally, each sample consisted of two tubes, connected in series. The second or backup tube traps any methyl bromide that escapes the primary tube. As long as most of the methyl bromide is detected in the primary tube, it is assumed that the sample (primary + backup) is valid. A number of different laboratory methods were used to analyze the charcoal tubes. Most involve either extraction of the charcoal with organic solvent and analysis of the extract, or a headspace analysis. Most analyses were conducted with a gas chromatograph equipped with an electron capture detector. Laboratory quality control samples were analyzed with each study. The individual reports for each study describe the analytical methods in more detail. A recent study by DPR indicates that the absorbent tube method may underestimate methyl bromide air concentrations. The results from this study are discussed in the next section.

The tarpaulins used for the monitored fumigations were tested for methyl bromide permeability using a method developed by Kolbezen and Abu-El-Haj (1977). With the exceptions discussed later, the tarpaulin permeability ranged from 6 to 8 milliliters of methyl bromide per hour per square meter per 1000 ppm at 30 degrees Celsius.

## ESTIMATES OF SAMPLING AND LABORATORY METHOD PERFORMANCE

Laboratory quality control samples (spikes) indicate that the charcoal tube sampling and analytical methodology used for the monitoring recovers 69 to 82%. However, results from a DPR study show different recovery rates (Biermann and Barry 1999). The DPR recovery study used a custom-made apparatus to introduce gaseous methyl bromide on to the charcoal sampling tubes. The standard laboratory spikes are prepared by dissolving methyl bromide in a solvent and adding the liquid solvent to charcoal tubes. DPR's recovery study more closely replicates the sampling conditions in the field. The performance of two sampling methods for ambient methyl bromide concentrations, charcoal tubes and SUMMA canisters, was determined in a laboratory using simulated field sampling procedures. A gas mixing and handling system was set up to generate controlled flows of air with known amounts of methyl bromide and moisture content. Samples were taken from the air flow inside the system using regular field sampling equipment with typical operating parameters. Initial tests with the charcoal tubes showed breakthrough at very high relative humidity (RH > 90%) and recoveries near zero for extremely dry air (RH < 10%). Most of the data were limited to a humidity range of 20% to 80% and concentrations between 20 parts per billion (ppb) and 2000 ppb. Within this range, no major effects of either humidity or concentration were found. The average recovery was  $49\% \pm 7\%$  (standard deviation) for the charcoal tubes and  $78\% \pm 12\%$  (standard deviation) for the SUMMA canisters.

This study also examined field data about the relative performance of collocated charcoal tubes and SUMMA canisters. A linear regression of the log-transformed concentrations of the two methods indicated that at the 200 ppb level the charcoal tube results were 71% of the SUMMA canister data. This was not significantly different from the same regression done on the laboratory data, where the charcoal tubes yielded 63% of the SUMMA canisters. Adjusting the relative performance of 71% in the field by the laboratory measured recovery of the SUMMA canisters of 78%, gives a net recovery of 55% for the charcoal tubes under field conditions. This net recovery of the field samples is consistent with the laboratory-measured recovery of 49%.

While DPR's best estimate of method performance indicates that the charcoal tube method used for the monitoring recovers approximately 50%, other data conflicts with this estimate. The conflicting data and DPR's adjustment for recovery are discussed in the data summary section below.

## DESCRIPTION OF DATA ANALYSIS METHODS

One of the major drawbacks to field monitoring is that it can only determine air concentrations at specific locations at specific times. Extrapolating these data to other locations and times is usually very difficult due to variability in field size, amount of methyl bromide applied, weather, and other factors. To overcome this drawback, DPR uses methyl bromide monitoring data in conjunction with a computer model, the Industrial Source Complex (ISC) model to simulate air concentrations at different locations and under a variety of conditions (USEPA 1995). For the analysis of methyl bromide monitoring data, DPR uses the ISC model for two primary purposes. 1) DPR uses the ISC model to estimate the flux rate, or the mass of methyl bromide volatilizing from the field over time (e.g., number of pounds per acre per day). To compare fumigations, DPR expresses the flux rate over the peak 24-hour period as a proportion of the application rate, or "emission ratio." DPR compares and contrasts monitored fumigations using the flux rate-based emission ratio rather than air concentrations. Air concentrations are influenced by numerous factors such as field size, field shape, application rate, wind speed, wind direction, and distance from the field. DPR uses the ISC model to adjust for many of these factors. This adjustment produces a flux estimate that is not biased by many of the factors influencing air concentrations, such as field size, application rate, and distance from the field. 2) DPR also uses the ISC model to estimate air concentrations at all points surrounding a monitored field. Since a limited number of samplers are deployed, the plume or area of highest concentration may miss the samplers. The ISC model is used to determine the location of the plume, as well as the furthest distance from the field at which the 0.21 ppm target level occurs.

The ISC model simulates air concentrations based on three main factors: 1) characteristics of the pollution source, such as flux rate and dimensions of the field; 2) weather conditions at the time of emission, such as wind speed and wind direction; and 3) terrain over the downwind area, such as urban or rural geography. It employs the standard gaussian equation for estimating downwind air concentration:

$$C(x, y, z) = \frac{Qf(\sigma_y(x), \sigma_z(x))}{3.14u\sigma_y(x)\sigma_z(x)}$$

where  $C(x,y,z)$  is the air concentration in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) at downwind distance  $x$  in meters (m), centerline offset  $y$  (m) and height  $z$  (m);  $Q$  is the emission rate for the field in micrograms per second ( $\mu\text{g}/\text{s}$ , when normalized by area, the units are  $\mu\text{g}/\text{m}^2\text{s}$  and the term flux is used);  $f$  is an empirical adjustment factor, a function of  $x,y,z$  and the standard deviation of lateral ( $\sigma_y$ , meters, a function of  $x$ ) and vertical plume concentration spatial distribution ( $\sigma_z$ , meters, a function of  $x$ ); and  $u$  is the wind speed (m/s). An important feature in

the gaussian equation is the proportional relationship between flux and air concentration. Assuming the ISC model provides estimates of offsite air concentrations that are correlated to measured offsite air concentrations, regression or "back-calculation" can be used to adjust an assumed flux rate in order to estimate the actual flux rate. This procedure is described in detail in Johnson et al. 1999a. In a test of this procedure, measured flux rates were compared to back-calculated flux values and found to be within a factor of two (Ross et al. 1996).

This back-calculation may not estimate the true flux rate under all conditions. The ISC model does not account for all factors that influence air concentrations, such as diffusion that may be a dominant process during low wind conditions. In addition, the back calculation procedure attempts to eliminate monitoring differences due to wind direction, field shape, field size, application rate, distance from the field, etc. However, the ISC model cannot account for nor simulate processes that directly affect flux rate. Such processes may be soil moisture, soil texture, depth of application, tarpaulin type, etc. DPR has assumed that application rate has a direct proportional effect on flux.

#### SUMMARY OF MONITORING RESULTS

As discussed previously, DPR estimates that the charcoal tube method recovers approximately 50%. However, in seven cases, this value conflicts with DPR's estimate of the mass of methyl bromide volatilizing from fumigated fields. For seven fields, DPR estimates that at least 50% of the applied methyl bromide volatilized in a 24-hour period. If the monitoring method recovers 49%, the mass of methyl bromide volatilizing from the field exceeds the amount applied. There are three possible sources of error in these estimates. 1) The mass of methyl bromide applied to the field was measured incorrectly. A significant error in this value is unlikely since it depends on a simple weight measurement. 2) There are unaccounted factors in the back-calculated flux estimate. As discussed above, it is possible for unaccounted factors to cause inaccuracies in the flux estimate, but these cannot be quantified. 3) There are unaccounted factors in the recovery estimate. Other environmental factors such as temperature are known to cause variability in methyl bromide absorption and desorption from charcoal. In addition, it is most appropriate to use an adjustment factor specific to each sample or study, associated with the laboratory that conducted the analyses. However, DPR has the appropriate data only for the studies it conducted.

Since DPR is uncertain as to the source of error, the following adjustment will be used until a more reliable estimate is determined. DPR will adjust the back-calculated flux rates assuming that 50% is recovered (i.e. flux rates are doubled). However, the 24-hour flux rate will be limited to a value that does not exceed the amount applied. This adjustment will apply to all studies, assuming that all laboratories conducting the analyses have similar recoveries.

Table 1 shows that 47 applications have been monitored to date. The data indicate that methyl bromide air concentrations exceed 0.21 ppm (peak 24-hour concentration) outside the field for many of the applications monitored. Air concentrations are highly variable, with measured concentrations 30 feet from the field ranging from 0.042 – 1.1 ppm, plus 1.7 ppm detected 330 feet from the field for one application. Air concentrations vary with numerous factors such as distance from the field, wind speed, wind direction, application rate, field size and dimensions, and method of application. Field to field comparisons of air concentrations are problematic due to the many confounding factors.

Flux rates or emission ratios are more useful to compare and summarize because the ISC model accounts for many factors that effect air concentrations. Comparison of emission ratios shows that fumigations with no tarpaulin have higher flux rates than fumigations with tarpaulins. Bed fumigations have higher flux rates than broadcast fumigations. Injection depth does not have a statistically significant effect on flux rates (Attachment 1). There is insufficient information to determine if other factors such as season or location effect flux rates.

Studies conducted under controlled conditions show that flux rates correlate with temperature, soil bulk density, soil moisture content, and soil organic content (Rice, et al. 1996; Gan, et al. 1996). The higher the temperature, bulk density, moisture, or organic content, the lower the flux rates. However, these correlations cannot be confirmed with field data, possibly due to other confounding factors.

The tarpaulins used for broadcast applications are usually removed five to ten days following application (tarpaulins for bed applications normally remain in place all season). Air concentrations and flux rates are higher during tarpaulin removal, in comparison to concentrations on the previous day. However, the air concentrations and flux rates during tarpaulin removal are less than the peak 24-hour period on the day of application, or the day following application (Majewski, et al. 1995). Applications using a “very high barrier” tarpaulin may be an exception. Air concentrations during removal of a “very high barrier” tarpaulin were comparable to the peak 24-hour period. However, as discussed below other data for “very high barrier” tarpaulins may contradict this finding.

Field fumigations using three different types of tarpaulins have been monitored. Permeability for the standard “high barrier” tarpaulin is 5 to 8 milliliters of methyl bromide per hour per square meter per 1000 ppm at 30 degrees Celsius; “very high barrier” is 4; “virtually impermeable film” is 0.1. Studies conducted under controlled conditions show that flux rates correlate with tarpaulin permeability (Wang, et al. 1997a; 1997b). The lower the permeability, the lower the flux rates. However, studies of commercial field applications do not correlate with permeability. Five applications using very high barrier tarpaulins have been monitored (Table 1, applications 25 to 29). The average proportion of methyl bromide emitted in 24 hours was twice as much as

applications that used a high barrier tarpaulin (Table 2). In addition, a series of field tests with a virtually impermeable film showed no difference in air concentrations between the virtually impermeable film and a standard high barrier tarpaulin (Table 1, study 164-10, applications 16 to 19, 30 to 34). This study also compared plots that included an extra tarpaulin panel (11 ft width) around the perimeter of the treated area, to plots with no extra tarpaulin panel. While the plots with extra tarpaulin panels has slightly lower flux rates (Table 1, applications 17, 19, 31, 33), they were not statistically significantly different from those without the extra tarpaulin (Table 1, applications 16, 18, 32, 34).

Within any one type, most application methods are very similar with a few commercial applicators conducting most of the fumigations. Applications using tarpaulin bed methods are an exception since individual growers conduct the majority of these applications. Many different types of fumigation rigs are used for this application method. There is insufficient data to show clear differences between the various tarpaulin bed methods (Table 1, applications 35 to 43). However, most tarpaulin bed methods have higher flux rates than the tarpaulin broadcast methods. Two common bed tarpaulin methods were compared side-by-side with a common tarpaulin broadcast method. Tarpaulin bed flux rates during the peak 24-hour period were several times higher than the tarpaulin broadcast flux rates (Table 1, applications 23 to 24, 38 to 41). Although not evaluated side-by-side, the data also indicate that tarpaulin bed fumigations have a higher flux rate than non-tarpaulin fumigations. The eight non-tarpaulin fumigations monitored had 24-hour emission rates ranging from 4.2 to 33 percent of the methyl bromide applied (unadjusted for recovery). The eight tarpaulin-covered bed fumigations that used a tractor with a bed shaper had 24-hour emission rates ranging from 34 to 58 percent of the methyl bromide applied (unadjusted for recovery). The three tarpaulin-covered bed fumigations that used the hot-gas application method had 24-hour emission rates ranging from 32 to 90 percent of the methyl bromide applied (unadjusted for recovery). A single tarpaulin-covered bed study that did not use a bed shaper or hot-gas method had a low 24-hour emission rate, 3.1 percent. However, we cannot estimate the variability of this method with a single study.

There may be several reasons that tarpaulin-covered bed fumigations have higher emission rates than non-tarpaulin fumigations. The depth of injection for tarpaulin-bed fumigations ranges from one to ten inches below the top of the bed. The depth of injection for non-tarpaulin fumigations ranges from 10 to 24 inches below the surface. The greater injection depth for non-tarpaulin fumigations probably decreases the emission rate. The tarpaulin-covered bed fumigations have a higher surface area in comparison to broadcast fumigations, for the same size field. The greater surface area probably increases the emission rate for tarpaulin-covered bed fumigations. There may be other reasons for the difference in emission rates that cannot be determined from the available information.

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Peak concentrations and flux rates generally occurred during the first 36-hour period from start of application. As a time-saving measure, only the peak flux rate was determined from the available data. Flux rates over time were estimated by fitting a lognormal function to the air concentration data for selected applications and constrained by the average emission ratios of the application categories (Johnson 1999b). Table 3 shows the estimated emission ratios over time.

Attachment



## References

Biermann, Heinz W. and Terrell Barry. 1999. Evaluation of charcoal tube and SUMMA canister recoveries for methyl bromide air sampling. June 1999 State of California, Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring and Pest Management Branch, Environmental Hazards Assessment Program 830 K St, Sacramento, CA 95814-3510 EH99-02.

Gan, J., S.R. Yates, D. Wang, and W.F. Spencer. 1996. Effect of Soil Factors on Methyl Bromide Volatilization After Soil Application. *Environmental Science and Technology*. Vol 30, No. 5, p. 1629 – 1636.

Johnson, Bruce, Terrell Barry and Pamela Wofford. 1999a. Workbook for gaussian modeling analysis of air concentration measurements. EH99-03. State of California, Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring and Pest Management Branch, Environmental Hazards Assessment Program Sacramento, California 95814-3510

Johnson, B. 1999b. Buffer Zone Duration. Memorandum to Randy Segawa, dated November 29, 1999. California Environmental Protection Agency, Department of Pesticide Regulation.

Kolbezen, M.J. and F.J. Abu-El-Haj. 1977. Permeability of Plastic Films to Fumigants. p 476 – 481 in *Proceedings of the 7th International Agricultural Plastics Congress in San Diego, California, April 11 – 16, 1977*. Sponsored by National Agricultural Plastics Association in cooperation with the University of California Cooperative Extension Service and the U.S. Department of Agriculture.

Lim, L. 1999. Draft Methyl Bromide Risk Characterization Document for Inhalation Exposure. California Environmental Protection Agency, Department of Pesticide Regulation.

Majewski, M.S., M.M. McChesney, J.E. Woodrow, J.H. Preuger, and J.N. Seiber. 1995. Aerodynamic Measurements of Methyl Bromide Volatilization from Tarped and Nontarped Fields. *Journal of Environmental Quality*. Vol. 24, p. 742 – 752.

Nelson, L. 1992. Methyl Bromide Preliminary Risk Characterization. Memorandum to Jim Wells, dated February 11, 1992. California Environmental Protection Agency, Department of Pesticide Regulation.

Rice, P.J., T.A Anderson, J.H. Cink, and J.R. Coats. 1996. The Influence of Soil Environmental Variables on the Degradation and Volatility of Methyl Bromide in Soil. *Environmental Toxicology and Chemistry*. Vol 15, No. 10, p. 1723 – 1729.

Ross, L.J., B. Johnson, K.D. Kim, and J. Hsu. 1996. Prediction of methyl bromide flux from area sources using the ISC model. *Journal of Environmental Quality* 25(4):885-891.

USEPA. 1995. User's Guide for the Industrial Source complex (ISC3) Dispersion Models. Volume 1. User Instructions. USEPA Office of Air Quality Planning and Standards; Emissions, Monitoring and Analysis Division, Research Triangle Park, North Carolina.

Wang, D., S.R. Yates, E.F. Ernst, J. Gan, F. Gao, J.A. Jury. 1997a. Reducing Methyl Bromide Emission Reduction with a High Barrier Plastic Film and Reduced Dosage. *Environmental Science and Technology*. Vol 31, No. 12, p. 3686 – 3691.

Wang, D., S.R. Yates, E.F. Ernst, J. Gan, F. Gao, J.O. Becker. 1997b. Methyl Bromide Emission Reduction with Field Management Practices. *Environmental Science and Technology*. Vol 31, No. 10, p. 3017 – 3022.

Table 1. Summary of methyl bromide air monitoring data

Application Monitored and Study ID <sup>a</sup>	Bed/Broadcast	Tarpaulin <sup>b</sup>	Chisel Type <sup>c</sup>	Injection Depth	Tractor Implements <sup>d</sup>	Date Applied	County	Applic Rate (lb/ac)	Acres	Measured Max Conc @ 30 ft (ppm) <sup>e</sup>	Proportion Volatilized in 24 hrs (unadjusted) <sup>e</sup>	Proportion Volatilized (recovery adjusted) <sup>f</sup>
1: SE1.1	Bed	None	Rearward	12	Shoes, Shaper	8/19/92	Monterey	186	19	0.21@0ft	0.17	0.34
2: SE1.2	Bed	None	Rearward	12	Shoes, Shaper	9/24/92	Monterey	180	15	0.31@0ft	0.28	0.56
3: SE1.3/EH127-2	Bed	None	Rearward	12	Shoes, Shaper	10/27/92	Monterey	180	15	0.55@50ft	0.20	0.40
4: EH164-8	Broadcast	None	Winged	16	Press Wheel	3/12/98	Merced	150	7.5	0.37	unable to model	
5: SE2.1	Broadcast	None	Forward	20	None	7/28/92	Kern	350	17	1.1@30ft	unable to model	
6: SE2.2	Broadcast	None	Forward	20	None	10/21/92	Kern	396	15	0.97@0ft	0.31	0.62
7: EH164-7	Broadcast	None	Forward	20	None	1/22/98	Madera	348	33	0.31	0.16	0.32
8: S104.2-1	Broadcast	None	Forward	24	Shoes, Roller	3/8/93	Fresno	396	40	0.36@100ft	0.22	0.44
9: S100B1.1	Broadcast	None	Forward	24	Shoes, Roller	3/13/93	Madera	400	20	0.30@50ft	0.11	0.22
10: S110.1	Broadcast	None	Forward	24	Shoes, Roller	10/31/95	San Joaquin	450	7	0.20	0.042	0.084
11: TC199	Broadcast	HB	Nobel Plow	12	None	6/30/92	Kern	396	20	0.25@0ft	0.13	0.26
12: EH127-1	Broadcast	HB	Nobel Plow	12	None	10/26/92	Monterey	235	10	0.15	0.079	0.16
13: EH150-6	Broadcast	HB	Nobel Plow	12	None	2/13/97	SLO	200	10	0.082	0.049	0.098
14: EH163-2	Broadcast	HB	Nobel Plow	12	None	8/21/97	Ventura	180	9	0.069	0.20	0.40
15: EH164-5	Broadcast	HB	Nobel Plow	12	None	11/1/97	Monterey	205	12	0.12	0.18	0.36
16: EH164-10A	Broadcast	HB	Nobel Plow	12	None	6/5/98	Orange	231	1	0.069	0.18	0.36
17: EH164-10C	Broadcast	HB	Nobel Plow	12	None	6/5/98	Orange	234	1	0.060	0.15	0.30
18: EH164-10E	Broadcast	HB	Nobel Plow	12	None	6/7/98	Orange	231	1	0.053	0.087	0.17
19: EH164-10G	Broadcast	HB	Nobel Plow	12	None	6/7/98	Orange	226	1	0.046	0.085	0.17

Application Monitored and Study ID <sup>a</sup>	Bed/ Broadcast	Tarpaulin <sup>b</sup>	Chisel Type <sup>c</sup>	Injection Depth	Tractor Implements <sup>d</sup>	Date Applied	County	Applic Rate (lb/ac)	Acres	Measured Max Conc @ 30 ft (ppm) <sup>e</sup>	Proportion Volatilized in 24 hrs (unadjusted) <sup>e</sup>	Proportion Volatilized (recovery adjusted) <sup>f</sup>
20: TC324.1	Broadcast	HB	Nobel Plow	12	None	7/25/98	Monterey	216	5	0.052@60ft	0.034	0.068
21: TC324.2	Broadcast	HB	Nobel Plow	12	None	8/7/98	Ventura	206	4		unable to model	
22: EH163-4	Broadcast	HB	Nobel Plow	12	None	9/2/98	SLO	214	2	0.10	0.13	0.26
23: BR787.1A	Broadcast	HB	Nobel Plow	12	None	6/24/99	Orange	186	1	0.049	0.098	0.20
24: BR787.2A	Broadcast	HB	Nobel Plow	12	None	6/30/99	Santa Barb	178	1	0.19	0.24	0.48
25: TC233.2	Broadcast	VHB	Nobel Plow	12	None	10/19/93	Monterey	392	7	0.090	0.047	0.094
26: EH150-5	Broadcast	VHB	Nobel Plow	12	None	2/6/97	Madera	350	19	0.99	0.33	0.66
27: EH163-1A	Broadcast	VHB	Nobel Plow	12	None	7/28/97	Monterey	240	12	0.23	0.21	0.42
28: EH163-1B	Broadcast	VHB	Nobel Plow	12	None	8/1/97	Monterey	240	10	0.44@60ft	0.40	0.80
29: EH163-3A	Broadcast	VHB	Nobel Plow	12	None	9/25/97	Santa Cruz	210	10	0.054@60ft	unable to model	
30: EH164-9	Broadcast	VIF	Nobel Plow	12	None	5/2/98	Orange	235	11	0.16	0.16	0.32
31: EH164-10B	Broadcast	VIF	Nobel Plow	12	None	6/5/98	Orange	234	1	0.066	0.19	0.38
32: EH164-10D	Broadcast	VIF	Nobel Plow	12	None	6/5/98	Orange	233	1	0.072	0.22	0.44
33: EH164-10F	Broadcast	VIF	Nobel Plow	12	None	6/7/98	Orange	220	1	0.065	0.11	0.22
34: EH164-10H	Broadcast	VIF	Nobel Plow	12	None	6/7/98	Orange	238	1	0.042	0.081	0.16
35: S110F1	Bed	HB	Rearward	6	Shoes, Roller	7/13/93	SLO	256	9	0.092	0.031	0.062
36: EH164-2	Bed	HB	Rearward	6	Colby Shaper	9/8/97	Orange	160	4	0.17@20ft	0.34	0.68
37: EH 164-11	Bed	HB	Rearward	6	Colby Shaper	10/6/98	SLO	206	9	0.45	-0.56	1.00
38: BR787.1B	Bed	HB	In	6	Shaper	6/24/99	Orange	177	1	0.19	0.53	1.00

Application Monitored and Study ID <sup>a</sup>	Bed/Broadcast	Tarpaulin <sup>b</sup>	Chisel Type <sup>c</sup>	Injection Depth	Tractor Implements <sup>d</sup>	Date Applied	County	Applic Rate (lb/ac)	Acres	Measured Max Conc @ 30 ft (ppm) <sup>e</sup>	Proportion Volatilized in 24 hrs (unadjusted) <sup>f</sup>	Proportion Volatilized (recovery adjusted) <sup>g</sup>
39: BR787.1C	Bed	HB	Ahead	6	Shaper	6/24/99	Orange	176	1	0.17	0.58	1.00
40: BR787.2B	Bed	HB	Ahead	6	Shaper	6/30/99	Santa Barb	245	1	0.26	0.38	0.76
41: BR787.2C	Bed	HB	In	6	Shaper	6/30/99	Santa Barb	174	1	0.26	0.38	0.76
42: EH150-2	Bed	HB	Rearward	6	Kenco Shaper	12/12/96	Riverside	200	20	0.82@5ft	0.55	1.00
43: EH164-6	Bed	HB	Rearward	6	Kenco Shaper	12/17/97	Riverside	196	16	0.64@200ft	0.53	1.00
44: TC203	Broadcast	HB	Forward	20	None	11/9/92	Merced	405	7	0.06@300ft	0.028	0.056
45: EH150-1	Bed	HB	Drip Tubing	1	None	12/11/96	Riverside	200	25	1.7@330ft	0.6-0.9	1.00
46: EH150-3	Bed	HB	Drip Tubing	1	None	1/20/97	Kern	200	14	0.38	0.32	0.64
47: EH150-4	Bed	HB	Drip Tubing	1	None	1/27/97	Imperial	200	14	0.74	0.50	1.00

a Studies are grouped by application method and numbered sequentially. Study identifications beginning with S were conducted by Siemer and Associates under contract to methyl bromide registrants. Studies beginning with EH were conducted by the Environmental Hazards Assessment Program of the Department of Pesticide Regulation. Studies beginning with TC were conducted by TRICAL, Inc. Studies beginning with BR were conducted by Bolsa Research.

b Applications using three different types of tarpaulins were monitored, plus untarped. HB is a "high barrier" tarpaulin with permeability between 5 and 8 ml/hr/m<sup>2</sup>/1000 ppm at 30° C. VHB is a "very high barrier" tarpaulin with a permeability of 4. VIF is a "virtually impermeable film" with a permeability of 0.1.

c Several types of chisels were monitored. Most common chisels are either curved away from the direction of travel (rearward) or toward the direction of travel (forward). Applications 11 – 34 employed a Nobel plow which consists of a horizontal v-shaped blade mounted by a vertical arm to the tractor tool bar. Applications 38 – 41 compared rearward chisels placed inside a bed shaper to rearward chisels placed ahead of a bed shaper. Applications 45 – 47 employed a drip irrigation system to introduce methyl bromide into the soil.

d Implements were used to close the channel created by the chisels such as angled plates (shoes), rollers to compress the soil, and shapers to form the beds.

e Highest 24-hour concentration detected 30 ft from the edge of the field, or the distance indicated. Concentrations are not adjusted for recovery.

f The estimated emissions over 24 hours expressed as the proportion of the amount of methyl bromide applied. For example, a proportion of 0.17 means that 17% of the applied methyl bromide volatilized from the field during the peak 24 hour period. The proportions shown are not adjusted for recovery.

g The estimated emissions over 24 hours expressed as the proportion of the amount of methyl bromide applied, adjusted for the estimated recovery of the sampling and analytical method. In most cases the proportion volatilized is adjusted for 50% recovery. In cases where this results in the proportion exceeding one, the proportion volatilized is set to one.

Table 2. Summary of Proportion Volatilized in 24 Hours

Application Method <sup>a</sup>	Number of Studies	Range of Proportion Volatilized <sup>b</sup>	Average Proportion Volatilized (unadjusted)	Average Proportion Volatilized (recovery adjusted) <sup>c</sup>
Nontarp Shallow Bed	3	0.17 - 0.28	0.22	0.43
Nontarp Deep Broadcast	5	0.042 - 0.31	0.17	0.34
Tarp Shallow Broadcast	13	0.034 - 0.33	0.13	0.25
Tarp Shallow Broadcast (VHB)	4	0.047 - 0.40	0.25	0.49
Tarp Shallow Broadcast (VIF)	5	0.10 - 0.28	0.15	0.30
Tarp Shallow Bed	9	0.031 - 0.58	0.43	0.81
Tarp Deep Broadcast	1	0.028	0.028	0.056
Drip Tubing-Hot Gas	3	0.32 - 0.90	0.60	0.88

<sup>a</sup> Application methods are classified by type of tarpaulin, injection depth, and if applied to preformed beds or a flat field (broadcast). VHB is a "very high barrier" tarpaulin with a permeability of 5 ml/hr/m<sup>2</sup>/1000 ppm at 30° C. VIF is a "virtually impermeable film" with a permeability of 0.1 ml/hr/m<sup>2</sup>/1000 ppm at 30° C.

<sup>b</sup> Range of estimated emissions over 24 hours expressed as the proportion of the amount of methyl bromide applied. For example, a proportion of 0.17 means that 17% of the applied methyl bromide volatilized from the field during the peak 24 hour period. The proportions shown are not adjusted for recovery.

<sup>c</sup> Estimated emissions over 24 hours expressed as the proportion of the amount of methyl bromide applied, adjusted for the estimated recovery of the sampling and analytical method. In most cases the proportion volatilized is adjusted for 50% recovery. In cases where this results in the proportion exceeding one, the proportion volatilized is set to one.

Table 4. Emission Ratios Over Time.

Hours After Start of Fumigation	Emission Ratio		
	No Tarpaulin	Broadcast Tarpaulin	Bed Tarpaulin
0 - 24	0.369	0.240	0.803
24 - 48	0.316	0.205	0.099
48 - 72	0.146	0.095	0.037
72 - 96	0.071	0.047	0.018
96 - 120	0.038	0.025	0.011
120 - 144	0.021	0.014	0.007
144 - 168	0.013	0.008	0.005