



Department of Pesticide Regulation



Brian R. Leahy
Director

MEMORANDUM

Edmund G. Brown Jr.
Governor

TO: Saturnino Yanga
Acting Environmental Program Manager I
Worker Health and Safety Branch

HSM-13002

FROM: Harvard R. Fong, CIH
Senior Industrial Hygienist
916-445-4211

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SUBJECT: SURVEY OF METHYL BROMIDE AND CHLOROPICRIN AIR
CONCENTRATIONS DURING SHANKED FIELD APPLICATIONS

During the fall of 2012, an air monitoring survey of methyl bromide field applications was conducted in several California counties: Ventura, San Luis Obispo, Siskiyou, Santa Cruz and Monterey. These counties were selected for the amount of field application methyl bromide reported in the Department of Pesticide Regulation's 2010 Pesticide Use Report Summary. The reported totals ranged from a low of 12 thousand pounds applied (Siskiyou) to the highest reported use of 1.16 million pounds applied (Monterey). The purpose of this monitoring was to verify that the application method restrictions found in Title 3 California Code of Regulations (CCR) Section 6447.3 were effective in not only reducing environmental/off-site effects, but also decreasing potential exposures for application crews. Applicator exposure was supposed to be reduced, not only by reduction in field emissions but also by regulatory work-hour reductions (Title 3 CCR Section 6784(b)(3)) and the use of "blow down" cab-ventilation systems. Additionally, Title 3 CCR Section 6784(b)(2)(C) potentially requires handlers applying methyl bromide per Section 6447.3 to wear respiratory protection specifically recommended for use in methyl bromide concentrations of 5 ppm or less. Depending on the concentrations found during this survey, this requirement may be excessively restrictive if potential worker exposure were low, or alternatively it may be inadequate if the survey indicates average air concentrations exceeded 5 ppm.

Monitoring was conducted using a Sensidyne AP-20S Aspirating Pump equipped with either a Sensidyne/Kitagawa methyl bromide detection tube (Tube # 157SB) or a Sensidyne/Kitagawa chloropicrin detection tube (Tube #172S). The methyl bromide tube has a measuring range of 0.4 ppm to 80 ppm, depending on the number of strokes of the pump; likewise the chloropicrin tube's range is 0.05 ppm to 16 ppm. Field environmental conditions were within operational parameters of both tubes (temperature range 0° to 40° C; unaffected by humidity, negligible atmospheric pressure effect).

The majority of soil applications in the selected coastal counties were for pre-plant strawberries and raspberries. Additionally, Siskiyou County had some pre-plant strawberry use, as it was a major propagation area for strawberry plantings done on the coast. These counties were selected as potential monitoring sites. The local County Agricultural Commissioner's (CAC) office of



each county was contacted to provide information as to upcoming methyl bromide applications. This information was obtained from Notice of Intents (NOIs) that must be filed by the applicator/grower before an application is scheduled to be performed. CAC personnel also informed potential cooperators of intended monitoring activities. In all cases, permission to conduct air sampling was secured from cooperator representatives. A data collection sheet (Survey Form: Attachment One) was used to record site/application data.

Thirty-six sampling events were performed from early August to early October. During this time, the soil application crews for methyl bromide tend to migrate up the coast, starting in Ventura and moving north. Additionally, soil pre-plant treatment for strawberry nursery stock in Siskiyou County was underway at this time.

On arrival to an application site, the monitoring equipment would be deployed. Before entering a field under application, an "Edge of Field" (EOF) methyl bromide sample would be taken to establish that entry into the field under application was likely of low potential exposure hazard to the field scientists (FS). A sample would be drawn at the field edge as close to the active application as possible. In all cases, a methyl bromide sample was taken before further entry into the field. Chloropicrin sampling was optional unless the investigator experienced sensory irritation. In such case, a chloropicrin sample would also be taken and recorded. All results were recorded on the Survey Form. If the methyl bromide concentration was below 10 ppm, entry was allowed. Values above 10 ppm would be immediately retested; if the second result was consistent with the first, no field entry would be made and the results would be recorded on the Survey Form, noting that the EOF sampling detected concentrations of methyl bromide above 10 ppm.

After establishing if the field could be entered, the FS would approach the application rig, taking care not to interfere with the operation and not placing themselves into a dangerous location. An air sample would be drawn as close to the application rig as practical and safe, on the trailing end of the operation. In most cases, the rig would be actively injecting fumigant and moving at a rate of speed higher than the FS could maintain pace, so the FS would trail the rig within the field. Multiple strokes of the aspiration pump were usually required, performed as the FS continued walking in the direction of the receding rig. Once the rigs turned around at the field end and returned, the FS would continue to pace the rig as it approached and passed. The majority of the time the FS would be traveling in a "back and forth" circuit within the field, sampling air, following the application rigs as they passed by, avoiding the tarped section of the field. A minimum of one methyl bromide sample was drawn. If the result was greater than 2 ppm, a second, confirmatory sample was required. If the initial sample detects between 5 ppm and 20 ppm, multiple subsequent samples were to be drawn. If the initial sample were greater than 20 ppm, the FS was to exit the field and record the result off-site. In most cases, one chloropicrin sample was also taken.

As the study progressed, a potential exposure condition outside the initial parameters of the protocol was noted. During the application rig's turn at the end of the row, the injection shanks

are raised clear of the soil. Label requirements (exemplar label Tri-Con 50/50: Section “Mandatory Good Agricultural Practices”; subsection “Prevention of End Row Spillage”; EPA Registration Number 11220-10) mandate:

“Do not lift injection shanks from the soil until the shut-off valve has been closed and the fumigant has been depressurized (passively drained) or purged (actively forced out via air compressor) from the system.”

However, minor drippage was noted a few times from the shanks, though the identity of the drippage material was not established. It was decided that not only would in-field methyl bromide and chloropicrin concentrations be measured, but that fumigant emission possibly released during the raising and lowering of the shanks (shanks up/shanks down: “SUSD”) would also be measured. Such emissions could result in exposures to end-of-row handlers (shovelers and other crewmembers not actively in-field).

Thirty-six separate field locations were sampled: Eight each in the counties of Ventura, Monterey and Santa Cruz; ten in Siskiyou; and two in San Luis Obispo. Application rates varied from 275 pounds per acre to 400 pounds per acre, though the majority was in the 300 to 350 pound per acre range. Since the applied material was a 50/50 mix of methyl bromide and chloropicrin, actual respective active ingredient rates were half of the reported application rates.

Thirty-four EOF samples were taken for methyl bromide and 11 EOF samples were taken for chloropicrin. All EOF samples for chloropicrin were either at (1 sample) or below (10 samples) the limit of detection of 0.05 ppm. For methyl bromide, only one EOF sample exceeded 1 ppm (4 ppm), four samples were recorded as 1 ppm and the remainder were below 1 ppm (29 samples). Two sites in Siskiyou did not have EOF samples taken.

Seventy-seven in-field samples were taken for methyl bromide. Fifty-four samples were below the limit of detection (<0.4 ppm); twelve samples were above 0.4 ppm but below 1 ppm; ten samples were above 1 ppm but below 5 ppm; one sample was at 5 ppm. Three of these in-field samples that were above 1 ppm had a subsequent sample also above 1 ppm (1.4 to 2 ppm; 2.5 to 2 ppm; 2.5 to 5 ppm). Four other samples that were above 1 ppm showed a drop below 1 ppm on subsequent sampling. Subsequent sampling of the 5 ppm sample yielded <0.4 ppm.

In-field sampling for chloropicrin were uniformly either at (4 samples) or below (32 samples) the level of detection (0.05 ppm).

Twenty SUSD samples were collected. Thirteen samples were below the limit of detection (<0.4 ppm); five samples were above 0.4 ppm but below 1 ppm; one sample was above 1 ppm but below 5 ppm; and one sample was 20 ppm. An immediate resampling was done after the extreme outlier of 20 ppm and the result was 0.8 ppm. According to the FS notes on the Survey Form:

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“One rig up-down sample was collected when the tractor was approaching the end but the rig blade broke the tarp. One stroke reached 20 ppm. Another up-down sample was collected and the conc. was at 0.8 ppm”

This was the only high concentration detected under the survey conditions and appears to have been related to an accidental integrity breach of the plastic film. This exposure concentration appears to have been a transient emission and dissipated rapidly, as the subsequent resampling indicates.

The data table generated from the Survey Form information is in Attachment Two.

Label requirements for methyl bromide air concentrations reference 5 ppm (previously cited exemplar label Tri-Con 50/50: Section “Protection for Handlers”; subsection “Respiratory Protection and Stop Work Triggers”) as the upper limit concentration, beyond which handlers must exit the work environment and cease operations until detected concentrations drop to 1 ppm or below. The Department of Industrial Relations’ Permissible Exposure Limit (PEL), found in Title 8 CCR Section 5155, is a time-weighted average (TWA) of 1 ppm, with a Ceiling (a level not to be exceeded at any time) of 20 ppm. The Federal Department of Labor does not have a TWA for methyl bromide and only references a Ceiling of 20 ppm.

Though the air monitoring was of a point-in-time nature and not an integrated 8-hour sampling, it would appear that worker exposure may be within recognized exposure limits, either time-weighted PEL/Ceilings or label-specified limits. Colorimetric tube sampling of active methyl bromide field applications suggests that handler exposure reduction via method restriction may be a viable engineering control of worker exposure. This also suggests that use of respiratory protection may be less indicated than previously believed. Further investigation of full-shift airborne methyl bromide levels associated with field application of the fumigant may be warranted to ascertain if the regulatory requirement for respiratory protection (Section 6784(b)(2)(C)) is redundant.

Attachment 1

Methyl Bromide Field Fumigation Air Survey

Investigator _____

Date ____/____/____ **TIME:** _____ **Entry Denied** _____

Location _____ **County** _____ **Site Number**

Application Method **Rate:** [_____]

- | | |
|-----------------------------|--------------------------|
| Nontarpaulin/Shallow/Bed | Tarpaulin/Shallow/Bed |
| Nontarpaulin/Deep/Broadcast | Tarpaulin/Deep/Broadcast |
| Tarpaulin/Shallow/Broadcast | |

Edge of Field Sample Results:

MBr result: _____ppm Chloropicrin result: _____ppm

In- Field Sample Results:

MBr result: _____ppm Chloropicrin result: _____ppm

MBr result: _____ppm Chloropicrin result: _____ppm

MBr result: _____ppm Chloropicrin result: _____ppm

Odor/Irritation Detected:

By Industrial Hygienist Y/N By Workers Y/N

Temperature _____ **Wind speed** _____ **RH%** _____

Notes (include fumigator information if available):

Attachment 2

Methyl Bromide Applicator Air Survey 2012 (ppm)

County	Date	EOF ¹ MBR	EOF ¹ PIC	MBR 1	MBR 2	MBR 3	MBR 4	PIC 1	PIC 2	PIC 3	SUSD ² 1	SUSD ² 2	Appl. Rate (Pounds/Acre)
Ventura	16-Aug	1	ND	<0.4	0.4			ND					275
Ventura	16-Aug	<0.4	<0.05	<1.0	0.4								275
Ventura	15-Aug	<0.4	<0.05	<0.4	<0.4	<0.4	<0.4	<0.05	<0.05				275
Ventura	14-Aug	0.4		0.4	1								275
Monterey	23-Aug	<0.4									<0.4		350
Monterey	23-Aug	<1.0	<0.05	<0.4	<0.4								350
Monterey	12-Aug	<1.0		<0.4	0.5	<0.4		<0.05			1.5		350
Monterey	22-Aug	<0.4		<0.4	<0.4	<0.4		<0.05					400
Siskiyou	22-Aug	0.4		<0.4	<0.4			<0.05					360
Siskiyou	21-Aug			1.4	2			<0.05					350
Siskiyou	22-Aug	0.4		<0.4	<0.4			<0.05					351
Siskiyou	22-Aug	1		1	<0.4			0.05					351
Siskiyou	21-Aug			0.4	0.4								360
Siskiyou	21-Aug	<1.0		1	<0.4			<0.05					360
Siskiyou	23-Aug	<0.4		0.4				0.05					350
Siskiyou	23-Aug	<0.4		<0.4	<0.4	1		0.05					351
Siskiyou	23-Aug	<0.4		0.4	2.5	2		0.05					360
Siskiyou	22-Aug	0.4		0.5	2.5	<0.4		0.05					350
Ventura	30-Aug	0.4	<0.05	<0.4	<0.4	<0.4		<0.05	<0.05		<0.4	<0.4	275
Ventura	29-Aug	<0.4	<0.05	<0.4	<0.4	<0.4		<0.05			<0.4	<0.4	275
Ventura	28-Aug	0.4	<0.05	1.4	1	0.4		<0.05	<0.05	<0.05	<0.4	<0.4	275
Ventura	31-Aug	<0.4	<0.05	0.4	0.4	0.4		<0.05	<0.05		0.6	<0.4	275
Santa Cruz	20-Sep	4	0.05	<0.4	2.5	5	0.4	<0.05	<0.05				300
Santa Cruz	20-Sep	<0.4		<0.4	0.5			<0.05					300
Santa Cruz	19-Sep	1.0	<0.05	2.5	<0.4	1		<0.05					300

County	Date	EOF ¹ MBR	EOF ¹ PIC	MBR 1	MBR 2	MBR 3	MBR 4	PIC 1	PIC 2	PIC 3	SUSD ² 1	SUSD ² 2	Appl. Rate (Pounds/Acre)
SLO	26-Sep	<0.4	<0.05	<1.0	0.4	<0.4							275
SLO	28-Sep	<1.0		<0.4	<0.4	<0.4		<0.05					275
Monterey	3-Oct	<0.4		<0.4				<0.05			<0.4		
Monterey	4-Oct	<0.4		<0.4				<0.05			<0.4		350
Santa Cruz	3-Oct	<0.4		0.8				<0.05			20	0.8	300
Santa Cruz	4-Oct	<0.4		<0.4				<0.05			<0.4		320
Monterey	3-Oct	<0.4		<0.4				<0.05			<0.4		350
Monterey	3-Oct	<0.4		0.8				<0.05			1		350
Santa Cruz	2-Oct	<0.4		<0.4				<0.05			1		350
Santa Cruz	2-Oct	<0.4		<0.4				<0.05			<0.4		350
Santa Cruz	2-Oct	1		2	<0.4			<0.05			1		350

¹ – End of Field (EOF)

² – Shanks Up/Shanks Down (SUSD)