A STUDY OF THE INHALATION EXPOSURE OF WORKERS TO METHYL BROMIDE DURING PREPLANT SOIL FUMIGATIONS (SHALLOW INJECTION) IN 1980 and 1981

by

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Summary

Potential inhalation exposure of workers involved with preplant soil fumigations using methyl bromide in Monterey and Santa Cruz Counties, California was measured during 1980 and 1981. This study was limited to fumigations involving shank-injecting methyl bromide into the soil to a depth of eight inches. A tarp was immediately laid behind the shanks to prevent volatilization of methyl bromide from the soil. Samples were collected from the breathing zones of the workers involved.

The data suggests there is no significant safety hazard due to inhalation exposure to the workers during this type of application. There were no levels of methyl bromide found in the air above the Cal/OSHA PEL (Permissable Exposure Limit) of 15 ppm. Three of the 40 measurements of worker exposure to methyl bromide vapors were in excess of 5 ppm, the recommended Threshold Limit Value of the American Conference of Governmental Industrial Hygienists (ACGIH).

Introduction

Methyl bromide is a colorless, tasteless, nonflammable gas which is odorless at low concentrations (20 ppm and below). It is known to cause damage to the lungs, nervous system, kidneys, and skin. The onset of symptoms can be delayed for up to several hours.

Methyl bromide is a toxicity Category I pesticide, registered for numerous uses in California including application as a preplant soil fumigant to control weed and grass seeds, nematodes, and other soil-borne pests.

Seven preplant soil applications were monitored, with air samples being collected from the breathing zones of various workers during the application.

Application

The major use period of methyl bromide in fallow fields is from early July to October. Methyl bromide is shank-injected into the soil approximately eight inches deep using a positive pressure closed system (with nitrogen gas). A one mil polyethylene tarp is automatically laid down over the soil behind the shanks to slow down the dissipation of the gas into the atmosphere. The actual application rate of methyl bromide ranged from approximately 214-235 lbs/acre for preplant use in strawberry fields and 375 lbs/acre for preplant use in a turf field. The application rates for the seven studies may be found in Table 1.

Three employees normally perform a field fumigation: The "driver," who operates the tractor; the "co-pilot," an individual seated at the rear of the tractor rig who takes care of routine problems with the application equipment; and a "shoveler," who shovels soil on the perimeter of the tarp, sealing the methyl bromide under the tarp.

Sampling Methods

Air samples were collected from the breathing zones of the tractor driver, the co-pilot, and one shoveler. The sampling period lasted approximately 30 minutes. Methyl bromide was trapped on charcoal sorbent tubes (SKC #226-09, Lot 120) drawn with either the MSA Model S pump or the DuPont Constant Flow (Model P-4000) pump. Pumps were calibrated to draw 250 ml. of air/minute by a Kurz Portable Mass Flow Calibrator (Model 540S). The pumps were calibrated before and after each sampling period. The flow rate and duration of the sampling period were limited to 250 ml. of air/minute for 30 minutes to minimize breakthrough of methyl bromide into the back section of the charcoal tube.

All sample tubes were capped and placed on dry ice and were shipped to CDFA's Chemistry Laboratory Services for analysis by gas chromatography (see Appendix 1).

Results

Results showed that methyl bromide exposures to the workers during the application were well below the Cal/OSHA PEL of 15 ppm. Exposure to the tractor driver ranged from 0.29 to 5.26 ppm and averaged 2.17. Exposure to the co-pilot ranged from nondetected (ND) to 7.42 ppm and averaged 2.97 ppm. Exposure to the worker at the edge of the field ranged from ND to 2.25 ppm and averaged 0.67 ppm. See Table 1 for the accumulated data.

Discussions

The objective of this study was to determine the inhalation exposure of workers to methyl bromide at the application site. All the measurements were far below the Cal/OSHA eight-hour PEL of 15 ppm methyl bromide. Only one of the 15 measurements of the tractor driver and two of the 14 measurements on the co-pilot were above 5 ppm, the ACGIH's recommended eight-hour TWA. These measurements were 5.26 ppm, 7.42 ppm, and 6.89 ppm. The highest measurement was drawn during the single preplant turf application, where the actual application rate of methyl bromide was considerably higher compared to the other six applications. The other two measurements in excess of 5 ppm were during sampling periods where small leaks occurred in the closed delivery system which were promptly repaired. None of the 11 measurements made on the shoveler, at the edge of the tarp, were in excess of 5 ppm.

Several application crews were monitored, i.e. worker exposure to methyl bromide was not monitored during an entire workday. Eight hour TWA values were not calculated because it could not be assumed that exposure is zero during the time where monitoring does not occur. The occurrence of preplant soil fumigation is somewhat intermittent and seasonal. However, it has been estimated that during an average workday, a crew may spend about four hours fumigating, with the balance of the day devoted to driving to and from jobs (2). Wind is the most important factor that determines the length of workdays.

Assuming that a worker is exposed to methyl bromide four hours a day, it can be calculated that exposures would not exceed an eight-hour TWA of 5 ppm until levels of 10 ppm were found under study conditions (30 minute air samples). Levels of this magnitude were not detected in this study.

The results were obtained where the soil temperature ranged from 66°F to 72°F in predominately sandy loam to loam soil types. Soil moisture contents were not measured. These variables will affect the rate of volatilization of methyl bromide from the soil, hence affecting the magnitude of worker exposure.

Abdalla, et al., (1) and Kolbezen, et al., (4) found that increasing the application rate of methyl bromide increases mobility through the soil. This could account for the higher worker exposure levels found from the application in which methyl bromide was applied at a considerably higher rate (application #4 in Table 1) than the other applications. The available pore space in the soil has the greatest affect on mobility. Soil mobility of methyl bromide is directly related to the availability of pore space. The amount of available pore space is dependent upon variables such as soil type and soil moisture. Kolbezen, et al., (4) and McKenry (5) both state there is an inverse relationship between pore space and clay content. Increasing soil moisture will reduce available pore space (1,3,5).

Methyl bromide is appreciably soluble in water (1.6%) (5) and diffuses more slowly through water than air (2). Diffusion through water laden soil will be reduced by the physical presence of water in the pore spaces.

Soil temperature influences the volatility of methyl bromide. As soil temperature increases a corresponding increase occurs in the amount of methyl bromide in the vapor phase (5). Therefore, high soil temperatures potentially increase worker inhalation exposure. Potential inhalation exposure will be greatest under conditions of high application rate, low clay content in soil, low soil moisture and high soil temperatures. Sufficient sampling was not conducted to properly evaluate the influence of environmental conditions on potential inhalation exposure. Under study conditions, potential inhalation exposure during typical methyl bromide applications in the strawberry growing region in Monterey and Santa Cruz counties appear to pose no significant hazard to the workers. Further work in the Orange County strawberry fields and the Kern County rose fields would be needed to determine inhalation exposure to methyl bromide under different environmental conditions.

Conclusions

Potential worker inhalation exposures to methyl bromide during preplant soil fumigations (in Monterey and Santa Cruz Counties) generally do not exceed 5 ppm. A variety of environmental conditions, including clay content, pore size, moisture content and soil temperatures can influence the volatilization of methyl bromide from the soil, therefore influencing worker exposure.

References

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DETERMINATION OF METHYL BROMIDE ON CHARCOAL TUBES

Scope

This method is for the desorption and analysis of methyl bromide from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle

Methyl bromide (MeBr) that has been absorbed from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using flame ionization or electron capture detection.

Reagents and Equipment

1. Ethyl acetate, nanograde.
2. Analytical grade methyl bromide.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes--SKC #226-09.
5. Developing vials with teflon liners--SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.
10. Gas sampling bulb--Supelco 500 ml. with spetum (#2-2148).

Analysis

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.
3. Transfer the charcoal in the upstream section to a labeled desorption vial which contains a known amount of nanograde ethyl acetate. 2-4 ml. is suggested. Adding solvent to the charcoal may cause loss of MeBr.

4. Remove and discard the foam partition from the tube.

5. Transfer the second section of charcoal to a second labeled desorption vial which contains a known amount of nanograde ethyl acetate.

6. Allow the samples to desorb for one hour while rotating @30 rpm.

7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.

8. Determine by GLC.

Determination of Desorption Efficiency

1. Inject a known amount of MeBr (1 microgram to several milligrams) into the charcoal with a syringe and cap the tube with the supplied caps. The tube should be from the same lot that was used for the samples.

2. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete adsorption. A blank tube should be treated the same way except that no sample is added.

3. Analyze the tubes by the analytical procedure.

4. Desorption efficiency = $\frac{\text{Response sample-response blank}}{\text{Response standard}}$

   The standard(s) should be the same amount as injected into the charcoal tubes. This eliminates standard variation errors.

Calculations:

1. Determine weight of MeBr present on charcoal tube sections by GLC analysis.

2. Correct this total weight of MeBr by subtracting any blank value present on the blank tube.

3. The corrected weight is divided by the desorption efficiency to obtain the final weight of MeBr present.

4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = \frac{V \times P \times 298}{760 \times (T+273)}$$

Where

VS = Volume of air at standard conditions.
V = Volume of air as measured.
P = Barometric pressure in mm Hg.
T = Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{\text{ng} \times 24.45}{\text{VS} \times 94.9} = \frac{\text{ng}}{\text{VS}} \times 0.2576$$

24.45 is the mole volume of MeBr at 25° and 760 mm.
94.9 is the molecular weight of MeBr.

Gas Chromatographic Conditions:

Gas chromatograph with Ni^{63}, H^3, or flame ionization detector.

Temperatures - Injector: 125°C
Detector: Follow manufacturer's suggestions

Column: 20' x 1/8" O.D. nickel tubing
10% SP-2100 on 100/120 Chromosorb W-HP
70°C, 10 ml/min N_2 carrier gas
MeBr retention time approximately 1.9 minutes

Column: 6' x 2 mm I.D. glass
80/100 Poropak Q
130°C, 30 ml/min N_2 carrier gas
MeBr retention time approximately 1.4 minutes

Column: 20' x 1/8" O.D. nickel tubing
10% FFAP on 100/120 Chromosorb W-HP
70°C, 25 ml/min N_2 carrier gas
MeBr retention time approximately 1.9 minutes

References

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TABLE 1

POTENTIAL INHALATION OF METHYL BROMIDE BY WORKERS DURING PREPLANT SOIL FUMIGATION

Study Site	County	Product Used	Application Rate: Product	Application Rate: Actual Methyl Bromide	Driver's Breathing Zone (ppm)	Co-Pilot's Breathing Zone (ppm)	Shoveler's Breathing Zone (ppm)	Air Temperature °F
1	Monterey	Terr-O-gas 67 5785-24-AA	350 lbs/A	234.5 lbs/A	3.23 (a)	----------	--------	79
					3.19 (a)			79
2	Monterey	Tri-Con 57/43 11220-50005-AA	375 lbs/A	213.75 lbs/A	1.38	4.44	--------	59
					4.46	2.12		61
3	Monterey	Tri-Con 67/33 11220-50006-AA	350 lbs/A	234.5 lbs/A	5.26 (b)	2.58 (b)	ND	82
					0.35	ND	1.31	64
					1.34	1.94	0.25	74
4	Santa Cruz	Tri-brom 11220-50018-AA	375 lbs/A	375 lbs/A	4.18	7.42	--------	56
5	Monterey	Tri-Con 67/33 11220-50006-AA	325 lbs/A	217.75 lbs/A	2.68	2.88	0.89	63
					2.53 (b)	6.89 (b)	0.21	63
					0.31	3.03	2.25	70
6	Monterey	Tri-Con 67/33 11220-50006-AA	350 lbs/A	234.5 lbs/A	2.12	4.26	ND	60
					1.08	3.20	ND	64
7	Monterey	Terr-O-gas 67 5785-24-AA	350 lbs/A	234.5 lbs/A	0.29	ND	0.83	59
					0.94	1.93	0.92	58.5
					2.45	0.83	0.73	61

(a) The samples were taken side by side at the same time from one driver.
(b) A small leak developed in the closed system, which was promptly repaired during the sampling period.
(c) Not available.