ADDITIONAL MONITORING OF THE INHALATION EXPOSURE OF WORKERS TO METHYL BROMIDE AND CHLOROPICRIN DURING PREPLANT SOIL FUMIGATIONS (SHALLOW INJECTION) IN 1983

By

Keith T. Maddy, Staff Toxicologist
Dennis Gibbons, Environmental Hazards Specialist III
Donald M. Richmond, Environmental Hazards Specialist
A. Scott Fredrickson, Agricultural Chemist

HS-1175 June 11, 1984

Department of Food and Agriculture
Division of Pest Management, Environmental Protection and Worker Safety
Worker Health and Safety Unit
1220 N Street, Sacramento, California 95814

SUMMARY

The concentrations of methyl bromide and chloropicrin in the breathing zone of preplant soil fumigation workers were monitored in Orange County in August and September 1983. Monitoring was conducted during three fumigations. The monitoring results for the first two fumigations showed methyl bromide concentrations below the Cal/OSHA Permissible Exposure Limit (PEL) of 15 ppm. The highest concentration found was 8.3 ppm. The monitoring results showed chloropicrin concentrations ranging up to almost twice (190 ppb) the established PEL for chloropicrin of 0.1 ppm. The calculated 8-hour Time-Weighted Averages (TWA) for both pesticides were below the established PELs, but the possibility exists that the PEL for chloropicrin would have been exceeded if monitoring was conducted over the course of the entire fumigation. The results for the third fumigation show that careful work practices are necessary on the part of the workers to prevent gross overexposure. Concentrations as high as 47.4 ppm of methyl bromide and 1,544 ppb of chloropicrin were found during 2-hour sampling periods.

INTRODUCTION

Methyl bromide and chloropicrin are Toxicity Category I pesticides. Mixtures of the two chemicals are registered for use in California as a preplant soil fumigant. The mixture is used to kill weed and grass seeds, nematodes, and other soil-borne organisms.

Methyl bromide is a colorless gas at atmospheric pressure and is odorless except at extremely high concentrations (2). It is known to cause damage to the lungs, nervous system, heart, kidneys and skin with sufficient dosage. The onset of symptoms from overexposure can be delayed for up to several hours. The Cal/OSHA Permissible Exposure Limit (PEL) for methyl bromide is 15 ppm for an 8-hour TWA in the workplace environment. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) of 5 ppm (2). The Cal/OSHA ceiling (level not to be exceeded) for methyl bromide is 50 ppm.

Chloropicrin is a colorless, oily liquid. The odor threshold is reported from 0.78 ppm to 1.1 ppm (3, 6). Concentrations of 0.3 ppm result in painful irritation to the eyes in approximately three to 30 seconds (1). No threshold level for eye irritation was found in the literature. The 8-hour PEL for chloropicrin is 0.1 ppm in the workplace environment. No Cal/OSHA exposure ceiling has been set for chloropicrin, but using the guidelines in Title 8, Section 5155 of the California Administrative Code, 0.3 ppm would be the recommended maximum exposure concentration. The ACGIH has recommended a TLV of 0.1 ppm and a Short-Term Exposure Limit (STEL) of 0.3 ppm (1). These recommendations were made to provide freedom from eye irritation and prevent potential pulmonary changes.

The major use period of the methyl bromide/chloropicrin mixture as a soil fumigant to fallow fields is from early July to early October. The methyl bromide and chloropicrin are premixed in compressed gas cylinders by the registrant. The mixture is shank-injected into the soil approximately eight inches deep using a positive pressure closed system (pressurized with nitrogen gas). A one mil polyethylene tarp is automatically laid down over the soil behind the shanks. The tarp reduces the dissipation rate of the gases into the air which lessens the hazards to the workers and increases the overall efficacy of the gases. Current pesticide regulations and the product labels do not require the workers to wear any type of respiratory protection.

MATERIALS AND METHODS

Monitoring was conducted on workers performing two types of activities. They were the "driver," who operates the tractor, and the "copilot," an individual seated at the rear of the tractor rig who takes care of routine problems with the fumigation and/or equipment. The samples were collected in the breathing zone of each worker.

The sampling period for both methyl bromide and chloropicrin was for either one hour or two hours. Methyl bromide was trapped on charcoal sorbent tubes (SKC# 226-09, Lot 120), while the chloropicrin was trapped on two XAD-4 resin tubes (SKC# 226-30-11-04, Lot 146) connected in series. Separate MSA model C-210 portable pumps were used with each type of tube. The pumps were

calibrated to draw 10 liters of air or less per sampling period. The pumps were calibrated at 150 ml of air/minute for 1-hour sampling periods and at 75 ml of air/minute for 2-hour sampling periods. The counters on the C-210 portable pumps were calibrated to determine the ml/count ratio. The counters were read before and after each sample period. The net count was multiplied by the ml/count ratio to determine the volume of air (in mls) per sample.

All samples were capped and placed on dry ice and shipped to the Department's laboratory for analysis. In the laboratory, the sampling tubes were divided into sections to determine if breakthrough occurred, indicating nonquantitative trapping of methyl bromide or chloropicrin. The charcoal tubes were separated into front and back sections with each section analyzed separately. See Appendix 1 for the analytical method for methyl bromide. The chloropicrin sample was analyzed in two sections to detect the amount of breakthrough. The first section was the first tube and the second was the second tube. See Appendix 2 for the analytical method for chloropicrin.

RESULTS AND DISCUSSION

The results of the first two fumigations will be discussed separately from the results of the third fumigation because of the large difference in the results. The methyl bromide results from the first two fumigations were well below the 8-hour PEL of 15 ppm (see Table 1). They ranged from 3.1 ppm up to 8.3 ppm. These results were compared to the previous studies on soil fumigation workers done by the Worker Health and Safety Unit (4, 5). Although no statistical analysis was done, the 1983 data appeared to show higher levels of methyl bromide in the worker's breathing zone. Three of the six samples from the two fumigations contained at least 5.0 ppm of methyl bromide, while only four of the 45 samples in the previous studies (4, 5) were found to have at least this amount of methyl bromide.

The chloropicrin results from the first two fumigations ranged from 86 ppb up to 190 ppb (see Table 1). Four of the six samples contained chloropicrin concentrations above the established PEL of 0.1 ppm. These results support the previous work of the Worker Health and Safety Unit (4) when three of the nine samples contained concentrations of chloropicrin above 100 ppb. The results indicate a real possibility of the workers being exposed to chloropicrin concentrations which exceeds the PEL for an average 8-hour workday.

The concentrations of methyl bromide found in the samples drawn during the third application ranged from 4.8 ppm up to 47.4 ppm with four of the six samples having concentrations above the established PEL for methyl bromide. The results for all six samples must be considered invalid, though, because severe breakthrough was found upon sample analysis. Although the samples are invalid, the amount of methyl bromide which was trapped on charcoal shows that the workers were overexposed during the five-hour fumigation. The breakthrough problem which occurred appears to be an isolated occurrence since the monitoring of all other fumigations from 1980 to 1983 showed no breakthrough problem.

The results of the chloropicrin sampling for the third application showed all six samples being over the established PEL for chloropicrin of 0.1 ppm. The concentrations of chloropicrin ranged from 116 ppb up to 1,544 ppb.

Four of the samples were above 300 ppb which is the recommended maximum exposure concentration. These samples show that the workers were over-exposed to chloropicrin during the five-hour fumigation. Unlike the methyl bromide samples for the third application, there was no breakthrough with the chloropicrin samples.

Eight-hour TWAs for methyl bromide and chloropicrin were calculated for workers whose exposure was monitored two or more times per fumigation. See Table 2 for these values.

The TWAs show the worker exposure for application two to be below the established standards while the worker exposure for application three to be above the established standards.

Downwind concentrations of methyl bromide and chloropicrin were monitored during the first and third fumigations. This data is discussed in a separate report (HS-1183).

CONCLUSIONS

The concentration of methyl bromide measured in the breathing zone of workers during the first two soil fumigations are well within the acceptable exposure limits and do not pose a known health hazard to the workers. These values are similar to the results from prior methyl bromide studies of soil fumigations conducted by the Worker Health and Safety Unit (4, 5). On the other hand, the margin of safety is probably very small, if any, for chloropicrin. The concentrations from the first two soil fumigations showed exposure near or above the established PEL of 0.1 ppm. The calculated 8-hour TWAs were below this level, but exposure monitoring was for 2.25 hours or less for each worker. However, due to severe irritation of the eyes and mucous membranes at low concentrations, the National Institute of Occupational Safety and Health considers chloropicrin to be a material with good warning properties for the workplace environment. The concentrations of methyl bromide and chloropicrin found in the third application show that workers need to be cautious, use good work practices and be alert to prevent unnecessary exposure to themselves and their co-workers at all times. More soil fumigation monitoring is needed to further characterize worker exposure and determine compliance with exposure standards for this type of work activity. Furthermore, monitoring should be conducted continually throughout the entire fumigation for a given day.

TABLE 1

Potential Inhalation of Methyl Bromide and Chloropicrin by Workers During Preplant Soil Fumigation in Orange County

Study Site No.	Sampling Time (minutes)	Driver's Breathing Zone		Copilot's Breathing Zone		Air Temp. (°F)
		Methyl Bromide (ppm)	Chloropicrin (ppb)	Methyl Bromide (ppm)	Chloropicrin (ppb)	
1[a]	60	3.1	90	3.8	86	66
2[a]	67	3.5	101	8.3	190	68
	64	5.0	154	5.9	178	72
3[b]	127	34.0[c]	1,186	47.4[c]	608	75
	120	38.1[c]	1,544	12.0[c]	474	76
	60	4.8[c]	244	15.7[c]	116	75

[a] Tri-Con 75/25 (EPA #11220-50007-AA) was applied at a rate 275 lbs/A. This product contains a mixture of 75% methyl bromide and 25% chloropicrin.

[b] Terr-o-gas 75 (EPA #5785-40-AA) was applied at a rate of 275 lbs/A. This product contains a mixture of 75% methyl bromide and 25% chloropicrin.

[c] Severe breakthrough of methyl bromide occurred on the sampling medium.

TABLE 2

Calculated Eight-Hour Time-Weighted Averages for Methyl Bromide and Chloropicrin for Workers Whose Exposure was Monitored During at Least Two Time Periods per Fumigation

Application Number	Driver/Copilot	Methyl Bromide (ppm)	Chloropicrin (ppb)
2	Driver	1.2	35
	Copilot	1.9	50
3	Driver	19.1	730
	Copilot	17.5	294

REFERENCES

1. American Conference of Governmental Industrial Hygienists. 1980. Chloropicrin. Documentation of the Threshold Limit Values, 4th Edition. Cincinnati.

2. American Conference of Governmental Industrial Hygienists. 1980. Methyl Bromide. Documentation of the Threshold Limit Values, 4th Edition. Cincinnati.

3. Amoore, J. E. and E. Hautala. Odor as an Aid to Chemical Safety. Odor Thresholds Compared with Threshold Limit Values and Volatilities for Industrial Chemicals (In Press).

4. Maddy, K. T., D. Gibbons, D. M. Richmond, and A. S. Fredrickson. 1983. A Study of the Inhalation Exposure of Workers to Methyl Bromide and Chloropicrin During Preplant Soil Fumigations (Shallow Injection) in 1982--A Preliminary Report. California Department of Food and Agriculture Report HS-1076.

5. Maddy, K. T., D. Richmond, J. Lowe and A. S. Fredrickson. 1982. A Study of the Inhalation Exposure of Workers to Methyl Bromide During Preplant Soil Fumigations (Shallow Injection) in 1980 and 1981. California Department of Food and Agriculture Report HS-900.

6. National Institute for Occupational Safety and Health/Occupational Safety and Health Administration. 1981. Occupational Health Guidelines for Chloropicrin. Occupational Health Guidelines for Chemical Hazards. Washington, D.C.

APPENDIX 1

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 adsorbed 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 septum (#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 at 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 (one 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°C 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 suggetions

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 is 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 is approximately 1.4 minutes

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

REFERENCES:

1. NIOSH Manual of Analytical Methods, Second Edition. Method S372. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

2. Determination of EDB on Charcoal Tubes, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 95832.

3. Malone, B., Analysis of Grains for Multiple Residues of Organic Fumigants. AOAC, 52, p. 800, 1969.

4. Clower, M., Modification of the AOAC Method for Fumigants in Wheat. FDA Laboratory Information Bulletin #2169, August 1978.

5. Mr. Mario Fraccia, Air Industrial Hygiene Lab, Berkeley, California. Personal Communication.

APPENDIX 2

THE ANALYSIS OF AIR SAMPLES FOR CHLOROPICRIN

SCOPE:

This analysis is for the determination of chloropicrin on XAD-4 resin air sample tubes.

PRINCIPLE:

Chloropicrin is trapped on XAD-4 resin tubes at the sampling site, frozen during transport to the lab, desorbed with ethyl acetate, and analyzed on a capillary GLC using electron capture detection.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate--pesticide grade, checked for interferences

2. Appropriate glassware

3. Gas Chromatograph

Instrument: Hewlett Packard 5880 with ECD detector at 300°C

Column: 30 M x .25 mm J&W 1701 at 40°C. Operated in split mode--approx. 100:1 split
Column pressure: 20 psi
Split flow: 40 ml/min

Injector: Split injector liner at 220°C

Under these conditions chloropicrin elutes in 6.5 minutes.

Column: 12 ft x 2 mm 10% SP 2100 at 70°C and 35 ml/min Ar/Me

Under these conditions chloropicrin elutes in about 4 minutes.

ANALYSIS:

Break the XAD-4 tubes and place the resin in five ml vials containing four ml ethyl acetate. Desorb tubes for an hour on a rotator. Proceed to the GLC with no further preparation.

DESORPTION COEFFICIENT:

The desorption coefficient is 94% at the two microgram/spl level.

CALCULATIONS:

Results should be reported in ppb and mg/cu meter using the appropriate air sample calculations. The molecular weight of chloropicrin is 164.4. The concentration of analyte in the air sampled can be expressed in mg/m^3, which is numerically equivalent to micrograms per liter of air.

$$mg/m^3 = \frac{\text{mg analyte/sample x 1000}}{\text{liters of air sampled}}$$

The concentration in ppb can be expressed as follows:

$$ppb = mg/m^3 \times \frac{24.45 \times 760 \times (T + 273)}{MW \times P \times 298}$$

Where:

P = air pressure in mm Hg
T = air temperature in degrees C
24.45 = molar volume (L/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = NIOSH standard pressure in mm Hg
298 = NIOSH standard temperature--degrees Kelvin

DISCUSSION:

At the present time, a single sample consists of two tubes in series. The entire first tube is treated as the 'front' section, and the second tube is treated as two additional sections. This system was used to check out breakthrough. If the sample size is kept to 10 L or less, and the sample flow rate is about 200 ml/min, the breakthrough will be 10% or less.

Recoveries are 94% for levels of about 30 ppb, or two ug/spl.

REFERENCES:

1. Guide to Chemicals Used in Crop Production, Information Canada, p. 118, 1973. NIOSH Manual of Analytical Methods, Method S212, S104, 260.