STUDIES OF METHYL BROMIDE AND CHLOROPICRIN USED AS STRUCTURAL FUMIGANTS IN CALIFORNIA, 1984
I. EVALUATION OF CHLOROPICRIN AS A WARNING AGENT
II. EMPLOYEE EXPOSURE TO METHYL BROMIDE AND CHLOROPICRIN
III. PENETRATION OF METHYL BROMIDE INTO PLASTIC FOOD STORAGE BAGS

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by

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Summary

From 1977 to 1984, 16 persons have died in California from unauthorized entry into structures undergoing fumigation with methyl bromide. Chloropicrin currently used as a warning agent does not seem to always deter persons from entering an atmosphere containing a lethal concentration of methyl bromide. In 1984, seven residential structures undergoing tarpaulin fumigation with methyl bromide were monitored in an air sampling study. Chloropicrin and methyl bromide concentrations inside these structures were measured during fumigation and following removal of the tarpaulins, using infrared gas analyzers and portable gas chromatographs. Chloropicrin concentrations were generally above an odor threshold (1 ppm). Uncertainties in recommending an adequate warning agent concentration include a limited toxicological data base on sensory irritation produced by chloropicrin. The warning agent concentration should be sufficient to deter entry or deter anyone from staying inside a structure for more than a few seconds. Exposure to methyl bromide in the fumigation environment can be fatal within a few minutes. Employee exposure to methyl bromide and

chloropicrin were measured during tarpaulin removal and house clearance operations with personal air sampling. Employee exposures to methyl bromide during tarpaulin removal ranged from 1.2 to 57 ppm. Exposures to chloropicrin ranged from less than 0.01 to 0.04 ppm. Potential exposures (measured outside of respiratory protection devices) during initial reentry into houses for aeration procedures ranged from 77 to 982 ppm for methyl bromide and from 0.01 to 1 ppm for chloropicrin. Respiratory protection devices should always be worn when entering recently fumigated structures. However, work practices coupled with high velocity fans could be employed to reduce exposures to employees removing tarpaulins where use of respiratory protection devices may increase the hazards of falling from roofs or ladders. Plastic bags used to store food left inside fumigated structures may not prevent contamination of that food. High concentrations of methyl bromide left inside the bags may pose an exposure hazard to the homeowner. Food or other items should not be stored in bags, inside the structure, but should instead be removed prior to fumigation.

Introduction

Wood-destroying insects account for damage to wood structures in the United States amounting to millions of dollars annually. In 1981, it was estimated that termites alone accounted for over $500 million in property damage each year. Classes of wood-destroying insects include termites and wood-boring beetles. Fumigation may be employed to control wood-destroying insects. The advantages of fumigation are: it is often the quickest method for controlling pests; fumigants can kill insects in places insecticidal sprays cannot reach (i.e., behind baseboards, wall spaces and inside building timbers); and, in certain instances, fumigation may be less expensive than repeated treatments with sprays. Drawbacks to fumigant use include substantial labor requirements to prepare the structure, a high degree of technical skill necessary to apply fumigants, the use of specialized equipment to protect employees from exposure, and the high toxicities of chemicals used as fumigants (Mallis, 1982).

Methyl bromide is commonly used as a structural fumigant. In 1984, over one million pounds were used to fumigate thousands of structures in California.

Work Practices. Structural fumigations generally are performed with gas proof sheets or tarpaulins, which are not impermeable, but hold the desired fumigant concentration inside the structure for a required time period. Prior to tarping a structure, the fumigators determine the structure volume and calculate the required fumigant dose; inspect the structure and roof for possible leak points (attached buildings, tunnels, vents or drains connecting to the outside or other buildings, roof vents and television antennas); shut off gas valves; remove necessary furnishings, foods and personal items; clear shrubbery from the walls; pad sharp edges, corners and projections and wet the soil around the perimeter of the structure. Tarpaulins are carried up to the roof and draped over the structure. The tarpaulin edges are rolled and clamped together at regular intervals with steel clothespins. During tarping, the fumigant delivery hose and several fans are placed inside the structure. The tarpaulin edges are then sealed at the bottom with sandsnakes (long canvas tubes filled with sand). Secondary locks, designed to enclose a doorknob and prevent it from being operated, are placed on all doors.

After inspecting the integrity of the tarpaulin and checking the location of all the workers, the fumigant and warning agent are introduced into the structure. Methyl bromide is introduced into the structure from a compressed gas cylinder. The fumigant is heated in a gas-fired manifold, or a truck-mounted manifold heated by the engine, before introduction into the structure. The fumigant dose, in total pounds, is measured by the loss in weight in the cylinder. The application rate commonly ranges from 1.5 to 3.0 pounds of methyl bromide per 1000 cubic feet of structure volume. This should result in a methyl bromide concentration of approximately 6,000 to 12,000 ppm inside the structure. There are two methods of introducing the warning agent into the structure: pouring liquid chloropicrin by hand or using fumigant formulations containing chloropicrin. Hand pouring is performed by a single individual a few minutes prior to introducing the fumigant. Chloropicrin is volatilized in an open pan (sometimes with cotton wicking added for increased surface area) which is set in front of a fan. Chloropicrin doses are 1 ounce per 10,000 or 15,000 cubic feet of structure volume. This application rate should result in a concentration of chloropicrin of from 16 to 26 ppm. Following fumigant introduction, warning signs are posted and fumigation proceeds for 24 to 48 hours, after which, tarpaulins are removed. After tarpaulin removal, a fumigator equipped with respiratory protection (commonly self-contained-breathing-apparatus) enters the structure, opening doors and windows to aid ventilation, and monitors fumigant dissipation with direct-reading instruments (NPCA, 1982, 1983).

Methyl Bromide

Toxicity. Methyl bromide is a colorless gas at room temperature (the boiling point is 3.6 degrees C at atmospheric pressure) with a vapor pressure of 1,390 mm Hg measured at 20 degrees C. Methyl bromide has practically no odor, and causes no immediate irritation of the nose or respiratory tract, even at severely poisonous concentrations (NIOSH, 1978).

Three reviews of methyl bromide toxicity have been published recently (Alexeeff and Kilgore, 1982, Torkleson and Rowe, 1981, and NIOSH, 1984). Much of the information in this section is condensed from these reviews. The reader is encouraged to consult them for more complete discussions of the toxicity of methyl bromide.

Acute exposure to IDLH (immediately dangerous to life and health) concentrations of methyl bromide produces rapid narcosis and death from respiratory failure. If death does not result, the most consistent response is lung irritation with congestion and edema. The effects have been observed in both animals and man (Torkleson and Rowe, 1981). Neurotoxicity is the primary effect from exposure to methyl bromide. Early symptoms of exposure include headache, nausea and vomiting, following by neurological effects including tremors, twitching and seizures. The onset of neurological effects from acute exposure may be delayed from one to 36 hours, complicating the diagnosis of methyl bromide toxicity. The onset of neurological effects shorten when acute exposure episodes are superimposed on chronic exposure. Signs and symptoms reported from chronic exposure include those from acute exposure, plus visual and hearing disorders, numbness or tingling in the extremities, incoordination, ataxia and loss of consciousness. Psychological symptoms have been associated with chronic exposure, including loss of initiative, depressed libido, personality changes, hallucinations and an intolerence to alcohol (Alexeeff and Kilgore, 1982).

Inhalation exposure studies performed with animals confirm the neurotoxicity observed in humans. Rats and rabbits were exposed to 65 ppm methyl bromide for 7.5 hours/day, 4 days/week for 4 weeks. In rabbits, this exposure produced changes in locomotion (hindlimb paralysis and cessation of grooming), decreased nerve conduction velocity and decreased magnitude of the eyeblink response. Neuropathic effects were not demonstrated in rats (Anger, et al, 1981). These results confirm earlier studies demonstrating neurotoxicity in rabbits but not in rats (Irish, et al, 1940). Neurotoxic effects were investigated in rabbits exposed to lower concentrations for a longer period of time. An exposure concentration of 27 ppm for 7.5 hours/day, 4 days/week for 8 months produced no neurological impairments (Russo, et al, 1984).

The mutagenicity of methyl bromide has been tested in bacterial assays. Methyl bromide is mutagenic in two strains of <u>Salmonella typhimurium</u> used in the Ames assay (NIOSH, 1984). In a study conducted by the Netherlands National Institute of Public Health, methyl bromide was considered carcinogenic in rats exposed by gavage (orally). Tumors were found in the forestomachs of rats exposed to the highest dose, 50 mg/kg/day for 90 days. At all doses, except the lowest (0.4 mg/kg/day for 90 days), the animals exhibited inflammation and hyperplasia (increased numbers of cells in a tissue or organ, not considered tumor formation) of the stomach epithelium (Danse, et al, 1984). A panel of pathologists from the National Toxicology Program (NTP) reviewed the data from the Netherlands study and concluded that the effects did not represent carcinogenicity (Anon., 1984). Currently, the Netherlands National Institute of Public Health is conducting lifetime inhalation exposure studies in rats, using 3, 30 and 90 ppm concentrations. The NTP planned to initiate lifetime inhalation exposure studies with methyl bromide late in 1984 (NIOSH, 1984).

Inhalation is the primary route of exposure, but liquid methyl bromide can produce systemic effects from absorption through the skin. Serious skin burns can occur from contact with methyl bromide, particularly when underneath clothing, or inside shoes or gloves. Exposure can produce dermatitis, itching, swelling and blistering of the skin. Methyl bromide has practically no odor nor irritating effects, therefore provides no warning of exposure, even at acutely hazardous concentrations (Torkelson and Rowe, 1981).

<u>Standards</u>. Worker exposure to methyl bromide is regulated with a Permissible Exposure Limit (PEL) enforced in California by the California Department of Industrial Relations, Division of Occupational Safety and Health (Cal/OSHA). The Cal/OSHA PEL is 15 ppm, allowed as an 8-hour time-weighted-average (TWA) period. The Excursion Limit is 25 ppm, measured over a five-minute period. The Ceiling Limit is 50 ppm, not to be exceeded at any time (Title 8, California Administrative Code, Section 5155). The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value (TLV[R]) of 5 ppm, based on an 8-hour TWA. In 1984, the ACGIH proposed to delete the Short-Term-Exposure-Limit (STEL, 15 ppm, measured over a 15 minute period) for methyl bromide. In the absence

of a STEL value, the ACGIH recommends that occupational exposure not exceed three times the TLV for more than 30 minutes a work day, and under no circumstances, should exceed five times the TLV. Skin exposure may potentially contribute to the overall exposure, and may invalidate the TLV or PEL if there is skin contact, especially with liquid methyl bromide. Methyl bromide is a restricted use pesticide, requiring the fumigator to obtain a permit from the County Agricultural Commissioner's (CAC) office.

Chloropicrin

Toxicity. Chloropicrin is an oily liquid substance with a sharp, penetrating odor. It has a boiling point of 112 degrees C at atmospheric pressure and a vapor pressure of 20 mm Hg measured at 20 degrees C (NIOSH, 1978).

Much of the data on the toxicity of chloropicrin to man and animals was obtained during World War I. Chloropicrin is a lung irritant (at concentrations far above the TLV or PEL), lacrimator and potent skin irritant. In humans, an exposure of 15 ppm for one minute was considered intolerable; exposure to 7.5 ppm for 10 minutes was also considered intolerable. A 4 ppm exposure for a few seconds reportedly "rendered a man unfit for combat." The lowest concentration producing irritation (type unspecified) was 1.3 ppm. An odor threshold of 1.1 ppm was reported. A concentration range from 0.3 to 3.7 ppm produced, "closing of the eyelids according to individual sensitivity," (Stokinger, 1981; ACGIH, 1980). Chloropicrin has been tested for carcinogenicity in National Cancer Institute (NCI) animal bioassays using rats and mice. Doses were administered by gavage and ranged from 20 to 66 mg/kg/day for 78 weeks. Exposure to chloropicrin produced high mortality in the test animals, but did not provide conclusive, statistical evidence for the carcinogenicity of chloropicrin (NCI, 1980).

Standards. The PEL and TLV for chloropicrin both are 0.1 ppm, and are designed to prevent irritating effects and possible adverse pulmonary system changes. The ACGIH STEL is 0.3 ppm.

Fatalities associated with structural use fumigants. Under a program mandated by state law, pesticide exposure incidents in California are reported by attending physicians, investigated by the County Agricultural Commissioners (CAC) offices and tabulated by the Worker Health and Safety Branch of the California Department of Food and Agriculture (CDFA). Deaths reported from pesticide exposure are flagged for priority investigation, under a cooperative program between CDFA, the CACs and the EPA. Between 1977 and 1984, 16 fatalities have been associated with the use of methyl bromide and chloropicrin in structural fumigation in California. In 5 cases, victims reportedly were burglarizing residences. In 2 cases, the victims apparently entered a structure for shelter. In 2 cases, the victims reportedly were under the influence of drugs or alcohol. In 2 cases, residents had forced entry into a structure and in one case, a resident had apparently fallen asleep inside the structure to be fumigated (individual narratives are in Appendix One).

Study Purpose

Methyl bromide presents a hazard to fumigators, particularly during untarping a structure. Hazardous levels of methyl bromide may remain inside a structure while the tarpaulin is being removed, presenting excessive, though transient exposure concentrations to nearby workers. Regardless of the manner of introduction, the proper application of chloropicrin is intended to produce concentrations sufficient to prevent unauthorized entry into structures undergoing fumigation; however the reporting of fatalities seems to indicate that chloropicrin is not always present in concentrations high enough to be an effective warning agent. In the summer and fall of 1984, an air sampling study was conducted to measure short-term inhalation exposure of structural fumigators and study the inside-structure dissipation of methyl bromide and chloropicrin during residential structure tarpaulin fumigations. Additionally, a study was designed to evaluate the practice, often specified on fumigant labels, of storing food inside plastic bags left inside the structure undergoing fumigation.

Materials and Methods

Inside-structure monitoring. Pest control operators willing to cooperate in the study were located with the assistance of the CAC's office. Prior to tarping a structure, a 1/2 in. (o.d.) polypropylene hose was positioned at the height of 6 feet in the center of a single room. The hose was connected with Swagelok fittings to a pair of gas analyzers and a sampling pump installed in a mini-motorhome van. Air from inside the structure undergoing fumigation was drawn through the sampling train system at a rate of about 25 liters per minute. All measuring instruments were located upstream of the pump, for safety considerations, so that any leak that might develop would be in a system at a pressure of less than atmospheric and not leak out. The exhaust hose was run back into the structure. Both hoses were equipped with one-way Swagelok ball valves, permitting the disconnection of the monitoring train from the structure when necessary. The inlet line was equipped with a Swagelok two-way valve to periodically admit clean air to rezero the analyzers. See figure 1.

Methyl bromide and chloropicrin concentrations were determined individually with MIRAN 1A infrared gas analyzers (Foxboro, Inc.). Gas samples were flushed continuously through the analyzers with a Gast carbon vane vacuum pump. Methyl bromide was quantitated at a wavelength of 7.6 um in a 4 meter path length gas cell. Chloropicrin was quantitated at 11.5 um in a 21 meter path length gas cell. Real-time IR absorbance measurements were recorded on strip chart recorders (Linear Instruments Co.) operating at an input of 1 volt equalling full scale deflection and a chart-speed of 10 cm/hr. Absorbance measurements were not corrected for humidity. The methyl bromide analyzer was calibrated with undiluted methyl bromide gas supplied from a lecture cylinder (Matheson Gas Products) over a range from 20 to 12,500 ppm. The chloropicrin analyzer was calibrated with 99 percent chloropicrin (see the Acknowledgements), diluted to one percent by volume in air, over a range from one to 30 ppm. Methyl bromide interferences in the chloropicrin determination were quantitated from 1,500 to 13,000 ppm. Use of the above arrangement allowed simultaneous continuous real time measurement of the concentrations of both gases.

Absorbance measurements were collected beginning 15-30 minutes before the start of fumigant introduction. Fumigant dissipation was monitored continuously, constrained only by the limited availability of field staff and considerations of personal safety during late evening and early morning hours. Except for study site #1 (see Table 1), monitoring was not performed overnight; sampling hoses were disconnected and locked in the van holding the monitoring train.

Fumigant concentrations at specified times were obtained by comparing measured absorbances with absorbances on a calibration curve. Measured absorbance values were obtained from interpolating percent deflection on the strip chart. Above 1,500 ppm, absorption of methyl bromide at the chloropicrin wavelength became substantial and was subtracted from the measured chloropicrin absorbance. Concentrations were plotted against time in hours on normal-coordinate graph paper. The exhaust (ventilation) phase was defined as beginning the moment the crew began opening gaps in the tarpaulin. Concentrations fluctuated rapidly in this phase and were plotted against time in minutes on log-normal graph paper.

During the latter portion of this study, a portable gas chromatograph (AID model 511) was obtained from the Plant Industry Division of CDFA. This instrument was equipped with a thermal conductivity detector and was purchased initially to measure methyl bromide concentrations inside commodity fumigation chambers. After calibration, this instrument was used to obtain a second, independent measurement of the methyl bromide concentrations being followed on a real-time continuous basis by the Miran instrument. By periodically withdrawing a syringe air sample from the sampling lines and injecting directly into the GC, the second, independent measurement was obtained. This instrument was also utilized to analyze the methyl bromide concentrations inside the plastic bagged boxes for the portion of the study that examined the issue of potential food contamination (see below). An additional AID portable gas chromatograph was obtained from the Cal/OSHA Consultation Services. This instrument was equipped with an electron capture detector and was used to obtain the corresponding second, independent measurement of the chloropicrin concentrations during the latter portion of the study.

In two structures studied, methyl bromide concentrations fluctuated beyond the calibrated range of the analyzer. In one case (Site 5), the calibration was assumed to be linear past the highest concentration measured. In the second case (Site 7), the concentration was confirmed by thermal conductivity gas chromatography (see below).

Employee exposure monitoring. Methyl bromide and chloropicrin were measured with personal air samples, collected from the employees' breathing zones, during tarpaulin removal and house clearance operations. Methyl bromide was trapped on 600 mg charcoal sampling tubes (SKC, Inc. Catalog No. 226-09). Chloropicrin was trapped on 150 mg XAD-4 porous polymer resin tubes (SKC, Inc. Catalog No. 226-30-11-04). Air was drawn through both types of tubes at 0.1 L/min with MSA model C-210 battery-powered personal sampling pumps. The pump flow rates were periodically calibrated with a bubble tube. For routine use, the factory calibrations for the pump-stroke counters were used for measuring sample volumes. Following sampling, all tubes were stored on ice during transportation, then held in freezer storage in the laboratory. Analyses were completed within one week after sampling. Front and back sorbent sections of the sampling tubes were analyzed separately. Both sorbents were desorbed for one hour in 2 mL of nanograde ethyl acetate with occasional agitation. Analyses were performed by electron-capture gas chromatography (EC-GC). The instrument was a Hewlett-Packard 5880 chromatograph equipped with a Ni^{63} EC detector. The column was 20 ft. x 1/8 in. o.d. nickel tubing, packed with 10 percent SP2100 on 100/120 Chromosorb WHP and eluted with argon/5%methane carrier gas at 10 mL/min. Column temperatures were 70°C for methyl bromide and 90°C for chloropicrin. Under these conditions, methyl bromide eluted in approximately 2 minutes and chloropicrin in approximately 6 minutes. Minimum detectable quantities for each compound was 0.02 ug per sample. The analytical methods used were adopted from NIOSH method S-372 for methyl bromide (NIOSH, 1977) and a method developed by the California Department of Food and Agriculture for chloropicrin (Maddy, et al, 1983).

Potential food contamination during fumigation. Some fumigant labels recommend that any food that is to remain within a structure undergoing fumigation be bagged in plastic bags. To simulate the requirements on these product labels, identical cardboard boxes, 12 x 12 x 12 inches were wrapped with varying thicknesses of household plastic bags. The thicknesses used were 1.4 mil, 4 mil (2 x 2 mil) or 6 mil (3 x 2 mil) polyethylene bags. The boxes were then placed inside a structure (site 7, Sacramento County 10/22/84) prior to fumigation. Following aeration, the boxes were removed to outside air. Air samples were withdrawn with a syringe and methyl bromide concentrations were determined directly by GC. The instrument used was an AID model 511 chromatograph (Analytical Instruments Development) equipped with a thermal conductivity detector. The column was a 6 ft. x 1/8 in. glass column packed with 10 percent SP2100 on 80/100 mesh Chromosorb WHP and eluted with helium carrier gas flowing at 25 mL/min. Column temperature was 40°C. Samples were introduced through an unheated 1 mL gas sampling loop. Under these conditions, methyl bromide eluted in 36 seconds (chart speed was 2 cm/min). Methyl bromide concentrations were quantitated with gas standards prepared in 3 liter Tedlar gas sampling bags (SKC, Inc., catalog no. 231-03). To prepare this on-site standard, clean outside air was pumped into the bags with a personal sampling pump. Next, this air was tested by GC for methyl bromide contamination at a minimum detection limit of 50 ppm. Finally, a calculated amount of undiluted methyl bromide was introduced into the bag with a syringe to make the desired standard. Concentrations inside the boxes were monitored at 2 hours, 24 hours and 5 days after fumigation was completed.

Results

Workplace observations. Site data for each structure monitored are tabulated in Table 1. Generally, one hour was required to prepare and tarpaulin a structure for fumigation and 5 to 10 minutes required to introduce the fumigant. Time required to prepare and tarpaulin a structure depend on size, pitch of the roof and presence of obstructions, such as antennas or vegetation. For example, at site 1, 7 hours were required to complete tarping, due to the structure size and pitch of the roof. Similarly, untarping a structure required from 10 minutes to 1 hour. Work rates varied between fumigation companies working in Los Angeles and Sacramento Counties. In the Los Angeles area, fumigators generally tarped in the morning and untarped structures fumigated the previous day in the afternoon. Crews in the Los Angeles area generally spent the entire day on fumigation activities. In Sacramento County, fumigations occurred more sporadically, at a rate of 1 or 2 per week. The size of the crews were between 3 and 7 persons, including supervisors. Employees working outside the structure, removing or folding tarpaulins wore no respiratory protection, while workers entering structures (the supervisors) generally wore respiratory protection. In four cases, workers entering structures wore self-contained-breathing-apparatus (SCBA), in one case a charcoal-canister respirator, in two cases (with the same company), no protection was used. Generally, the workers spent from 30 seconds to 5 minutes inside the structure.

Inside structure monitoring. Results from this activity are summarized in Figures 1 and 2. Concentration profiles in Figure 1 cover changes in fumigant and warning agent concentrations during the fumigation period, while profiles in Figure 2 cover changes following removal of the tarpaulin. Methyl bromide and chloropicrin concentration profiles appeared to parallel each other during fumigation. Fumigant concentrations declined quite rapidly at sites 3 through 6, and less rapidly at sites 1, 2 and 7. The company which fumigated sites 3 and 4 was observed using tarpaulins in poor repair (numerous pinholes and heavily patched; one large hole, approximately 6 inches in length was seen). The companies which fumigated sites 1, 2 and 7 used tarpaulins in better condition. Site 6 had numerous trees and shrubs growing close to the structure, which could have reduced the effectiveness of the tarpaulin seal. At site 4, after the structure was untarped, methyl bromide and chloropicrin concentrations fell to non-detectable levels within 2 minutes; a concentration profile for fumigant dissipation after untarping was not drawn for this site. At site 3, a chloropicrin concentrations profile after untarping was not plotted for similar reasons.

Worker Monitoring. Methyl bromide and chloropicrin concentrations measured in employee breathing zones are tabulated in Table 2. Generally, employee exposures were higher at the sites where inside-structure fumigant concentrations exhibited the slowest decline (see sites 1 and 2).

Food contamination study. Instead of preventing methyl bromide from penetrating into the test boxes, it appears that all boxes (various thickness of plastic) reached the same concentration as in the structure. The declines of methyl bromide concentrations inside the boxes after fumigation are displayed in Figure 3. Generally, the boxes with thicker layers of polyethylene exhibited slower losses of methyl bromide.

Discussion

Some problems are present in establishing what constitutes an effective warning concentration. The original toxicology data on chloropicrin is old, and has not been replicated recently. This old data is still being cited in the 1980's. It is also not known if the test concentrations used in the original studies were verified analytically, or if the methods of chemical analysis of the day possessed enough sensitivity to detect part-per-million concentrations. Unauthorized entry into fumigated structures containing warning agent may have several causes. A small number of persons may be unusually tolerant of sensory irritation produced by chloropicrin. Low concentrations of chloropicrin, which are detectable by the presence of odor or mild irritation, may simply be ignored by some individuals. Some of the victims were reportedly under the influence of narcotics or alcohol, raising the speculation that these substances may alter an individual's response to chloropicrin-induced irritation. Finally, the concentrations of methyl bromide may be sufficiently large to rapidly incapacitate a person entering a fumigation atmosphere.

Considering the nature of the methyl bromide exposure hazard, a sufficient warning agent concentration should prevent entrance into the fumigation atmosphere. Based on the limited information available on the irritant effects of chloropicrin exposure, a minimum warning agent concentration should probably be between 7.5 and 15 ppm, throughout the duration of fumigation.

The goal would be to maintain a relatively consistent concentration during fumigation, which could be accomplished by good work practices, including the use of only new or well maintained tarpaulins, tightly rolled seams, having soil well moistened on the structure perimeter, and liberally using clamps and sandsnakes. The simplest expedient of introducing a larger dose of chloropicrin may not be suitable to maintain a warning agent concentration. The excess chloropicrin may diffuse too rapidly, if the structure is not tarpaulined properly. A large dose of chloropicrin may render a structure uninhabitable for substantial length of time following fumigation by causing objectionable odors or irritation to the occupants. Since chloropicrin is much less volatile than methyl bromide, it can more readily adsorb to wood, carpeting and furnishings, to later slowly desorb into the structure atmosphere once fumigation and aeration are completed.

Concentration profiles for methyl bromide and chloropicrin inside a structure will vary based on the arrangement of the rooms, placement of fans and application hose, age and condition of the tarpaulins, the manner in which the structure is tarped and the location of the sampling hose. At site 2 the fumigant was introduced into the subfloor plenum, so many hours elapsed before concentrations peaked inside the living area, where the sampling hose was located. Concentrations peaked very rapidly in structure 3 because the fumigant delivery hose was in the same room as the sampling hose, with a circulating fan close by. Use of a worn tarpaulin at sites 3 and 4 probably allowed faster dissipation of fumigant.

High concentrations of methyl bromide in employees' breathing zones at site 2 were probably related to the high concentrations left inside the structure. Most methyl bromide exposures were between the Cal/OSHA excursion and ceiling limits, for short durations. Compliance with exposure limits is not known because of the non-uniform sampling method; an air sample of 5 minutes duration is necessary to properly make a determination of compliance with Cal/OSHA excursion standards. Two samples were at or slightly above the Cal/OSHA Ceiling standard. None of the exposures were above the 8-hour TWA of 15 ppm. Further studies should use a uniform sampling period to facilitate an evaluation of employee exposure when performing the untarping job functions. The variation in air sampling data suggests that tarpaulin removal represents an operation not under good ventilation control, providing unpredictable fluctuations in exposure. Data from the personnel air samples also suggests that chloropicrin is not a reliable warning agent for employee exposure to methyl bromide during untarping.

At site 6, the crew used a high-velocity fan, commonly used by fire departments for smoke clearance, to ventilate the structure. The concentration profiles for this site, following untarping, show a rapid decline in inside-structure concentrations for both compounds. Further studies of structural fumigations could focus on combining modified work practices with the use of high-velocity fans, instead of personal respiratory protection to control workplace exposure to methyl bromide. A suggested work practice during tarpaulin removal is to "crack" the tarpaulin initially (one or two employees wearing SCBA would remove a few clamps), providing air inlets and an exhaust outlet, and ventilate the structure while the crew waits at a safe distance. This operation might be done prior to the arrival of the untarping crew. After a designated period of time, the tarpaulin can be removed while maintaining an allowable workplace exposure.

The food contamination study showed that methyl bromide penetrates polyethylene storage bags. All boxes had several thousand ppm inside, at the end of the fumigation. It appears that methyl bromide diffuses through the plastic. The thickness only appears to slow the rate of penetration into the bag or the dissipation out. These results suggest that any food stored in polyethylene plastic bags in a fumigated structure (except for canned goods) may become contaminated with methyl bromide. Also, opening a bag after fumigation may provide a homeowner with a very brief, though potentially large inhalation exposure to methyl bromide.

Conclusions

Fatalities from unauthorized entry into fumigated structures occur, despite the apparent presence of odorous and irritating concentrations (in excess of 1 ppm) of chloropicrin. Some individuals may possess a greater tolerance to the effects of exposure, and intoxication with alcohol or drugs may blunt an individual's response to chloropicrin exposure. A minimum warning agent concentration to help prevent fatal exposure to methyl bromide from unauthorized entry cannot be recommended with any certainty at this time. Insufficient data exists on the sensory effects of chloropicrin in humans to determine the concentration which will deter unauthorized entry or prevent residence by any person before they are incapacitated by methyl bromide exposure. A warning agent concentration should be large enough to prevent anyone from staying in the fumigation atmosphere for more than a few seconds, and should persist throughout the duration of fumigation. Worker inhalation exposures to methyl bromide, during tarpaulin removal ranged from 1.5 to 57 ppm, for periods of time from 10 to 53 minutes. These exposures occasionally exceeded currently regulated exposure standards. Employee exposure to chloropicrin during tarpaulin removal did not exceed current exposure standards. Respiratory protection (self-contained-breathing-apparatus) should always be worn by employees entering structures following tarpaulin removal, however SCBA is not feasible for employees removing the tarpaulin. Encumbering employees with SCBA may increase the hazard of falling from roofs and ladders. Further research should focus on work practices and fan selection to effectively ventilate structures prior to tarpaulin removal. The use of plastic bags to protect food left in a fumigated structure may not prevent contamination with methyl bromide and may provide an exposure to homeowners. Food, or other items, should not be stored in a fumigated structure. Fumigant labels should no longer recommend this practice.

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Table 1

Acknowledgements

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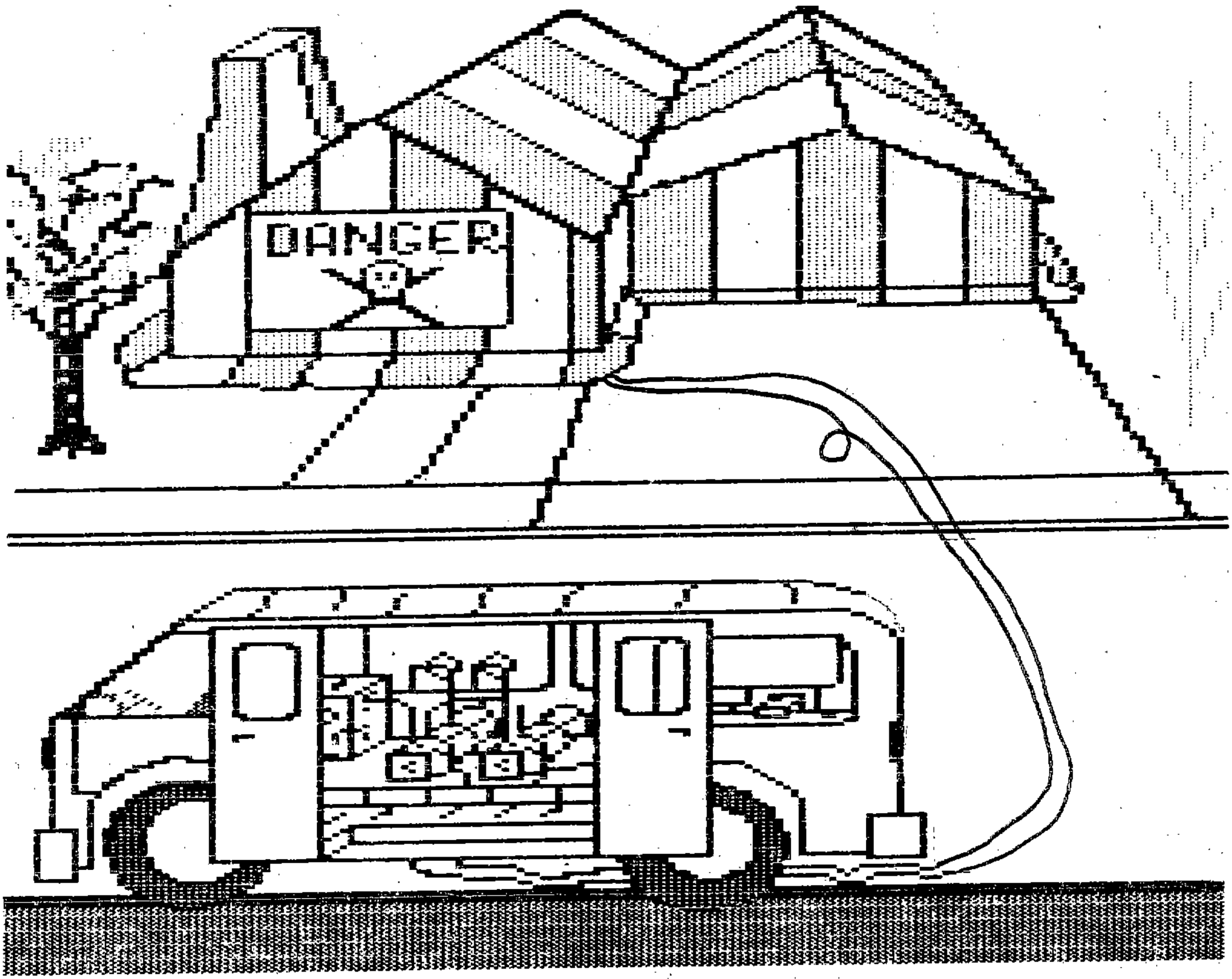


Figure 1

Monitoring equipment and physical layout of typical fumigation in this study.

APPENDIX I

Priority Investigations Conducted by Counties Pursuant to EPA/State/County Cooperative Agreement

In October 1975, the Department of Food and Agriculture, County Agricultural Commissioners, and the Environmental Protection Agency entered into a cooperative agreement relative to pesticide enforcement. A provision of the agreement provides for the priority investigation of certain suspected pesticide-related incidents. Incidents are given investigation priority based upon triggers contained in the agreement. The triggers are:

1. Human Effects.

    a. Death.

    b. Serious illness - hospitalization of over 24-hours.

    c. Group illness - five or more persons exhibiting symptoms and observed by a physician.

2. Environmental Effects.

    a. Contamination of drinking water affecting 10 or more households.

    b. Contamination of air requiring evacuation of 25 or more persons.

    c. Land clean-up or decontamination costs exceeding $50,000.

    d. Loss of nontarget wildlife - 50 or more game or migratory birds; 500 or more other birds; 500 or more game fish; 5,000 or more other fish; five or more of any game animals or fur-bearers; or one or more of any endangered vertebrate species.

3. Property Effects.

    a. Loss or damage to crops, livestock, or other property exceeding $50,000.

Fatalities in California associated with the structural use of methyl bromide, listed by CDFA priority number:

12-LA-77 April 4, 1977
Death
Methyl Bromide
A 34 year-old Torrance man died from methyl bromide poisoning during the residential fumigation of his uncle's home. This victim apparently fell asleep in the residence that was to be fumigated. A complaint of negligent homicide was filed against the structural pest control business owners, but was dismissed by the Superior Court judge hearing the case.

22-LA-77 June 24, 1977
Death
Methyl Bromide
A Long Beach man was found in a fumigated house when the tarpaulins were removed. The victim died in the hospital a couple of hours later. The District Attorney determined that there was not sufficient evidence to sustain criminal charges in this case. A Notice of Violation was issued to the pest control operator for minor violations unrelated to the victim's death.

31-LA-80 July 12, 1980
Human Effects (Death)
Methyl Bromide
A 29-year old man died from exposure to methyl bromide and chloropicrin when he broke into his home being tarpaulin fumigated. Apparently all locks had been secured by the Structural Pest Control operator as required. The deceased was a known drug user.

51-LA-80 August 23, 1980
Human Effects (Death)
Methyl Bromide and Chloropicrin
An alledgedly intoxicated man died after being exposed to methyl bromide and chloropicrin. The chemical was applied to his apartment building in the morning, and that afternoon the victim was found comatose between the tarpaulin and the garage by the apartment building manager. He was taken to a hospital where he later died.

57-ALA-80 September 10, 1980
Human Effects (Death)
Methyl Bromide
A 23-year old retarded man died after he entered his home while it was being fumigated with methyl bromide. He had been cautioned numerous times about the dangers and possible fatal effects the pesticide would have on him if he was exposed, but he disregarded the warnings. There is a question as to whether or not the warning agent, chloropicrin, was used because the victim was apparently able to stay in the house long enough to be overcome by the methyl bromide, as were others who came in contact with the fumigated structure and reportedly suffered no eye irritation or tearing usually

caused by the material.

84-LA-80 November 22, 1980
Human Effects (Suicide)
Methyl Bromide
A 33-year old woman died after exposure to methyl bromide. During the fumigation for termites, she forced entry into her home through the posted tarpaulin and sliding door. Police investigators found a note on the kitchen table that led them to determine this episode was a suicide.

61-LA-81 August 26, 1981
Human Effects (Death)
Methyl Bromide
A 21-year old man died after entering a home being fumigated with a methyl bromide product. Apparently the man climbed through a window and was attempting to burglarize the house when he became ill. He tried to escape but was overcome. His body was found between the house and the tarpaulin the following morning. It was determined that the house was properly posted and locked prior to fumigation.

81-LA-82 November 23, 1981
Human Effects (Death)
Methyl Bromide
A would be burglar died as a result of entering a properly tarpaulined and posted home under fumigation with methyl bromide. He apparently broke a window to gain access to the house.

14-LA-83 March 25, 1983
Human Effects (Death)
Methyl Bromide/Chloropicrin
A male resident of an apartment complex that had been fumigated with methyl bromide and chloropicrin was found dead by a fumigation crew while removing tarpaulins. The apartment complex was fumigated on the previous day. Investigation revealed that all the residents had been notified, secondary locks were in place, and the victim had attempted to break down the door. No violations were uncovered.

32-LA-83 June 4, 1983
Human Effects (Death)
Methyl Bromide and Chloropicrin
A man described by police as a transient was found dead on a porch area by a fumigation crew removing tarpaulins a day after a home was fumigated with methyl bromide and chloropicrin. The fumigation crew found that the transient had removed clips and opened a seam to gain entry. No violations were found.

90-LA-83 October 7, 1983
Human Effects (Death)
Methyl Bromide
This episode involves the death of a 31-year old man who returned to his apartment during a fumigation to look for money. The victim was found by his wife when she returned after the fumigation period. Although necessary precautions were taken to prevent entry, the fumigation company was issued a Notice of Violation for not properly clearing and testing all rooms.

101-LA-83 November 7, 1983
Human Effects (Death)
Methyl Bromide
A 22-year old man burglarized an apartment building that was being fumigated. The victim forced entry and made repeated trips inside. He later developed severe symptoms, was taken to a hospital, and died. No use violations of the structural pest control or Food and Agricultural Code were found.

1-LA-84 January 6, 1984
Human Effects (Death)
Methyl Bromide
A man and a woman were found dead by workers of a fumigation company when they returned to remove the tarpaulins. The victims had apparently cut the tarpaulin to find shelter. No violations of the Structural Pest Control or Food and Agricultural Code were found.

29-LA-84 July 17, 1984
Human Effects (Death)
Methyl Bromide
A 56-year old man died after he was found under a tarpaulin at a motel being fumigated when the crew came to remove the tarpaulins. He reported looking for a place to sleep. He was hospitalized and died the next day. No violations were found.

56-LA-84 December 6, 1984
Human Effects (Death)
Methyl Bromide
A 55-year old man was found dead inside a house being fumigated when the crew arrived to remove the tarpaulins. The victim was a neighborhood handyman hired to protect the house and reportedly became cold and went under the tarpaulin for protection. No violations were found.

Appendix II

PROTOCOL FOR THE DETERMINATION OF ENVIRONMENTAL AND OCCUPATIONAL EXPOSURE CONCENTRATIONS OF STRUCTURAL FUMIGATION

I. Introduction

The human health hazards from exposure to methyl bromide as a fumigant are well recognized, however, the exposures of workers handling fumigants are poorly characterized. This lack of data hinders consideration of the human toxicology and epidemiology of these chemicals, as well as development of methods for mitigating exposure hazards. Methyl bromide used for structural fumigation is mixed with a small amount of chloropicrin as a warning and clearing agent. Since these two compounds have different physical properties thus different degrees of mobility in air, the concern is that chloropicrin may not adequately mix in an atmosphere containing methyl bromide and not provide adequate warning properties. A number of deaths have occurred from unauthorized entry into structures fumigated with methyl bromide, which indicates that chloropicrin may not always deter entry.

II. Scope

This outlines procedures for quantitatively determining workplace and environmental fumigant concentrations and performing field investigations of fumigant exposure hazards. With modifications, these procedures can be applied to numerous types of fumigant uses. The user is encouraged to refer to studies by the Worker Health and Safety Unit for further details on fumigant monitoring methods.

III. Purpose

These studies ar designed to: 1) measure peak and time-weighted-averaged inhalation exposures of structural fumigation workers. 2) Measure the persistance of methyl bromide and chloropicrin in tarpaulin fumigations. 3) Measure the decay of methyl bromide and chloropicrin while tarpaulins are being removed.

IV. Methods

Site Selection. Cooperators and study sites will be located with the assistance of the County Agricultural Commissioner's office. Arrangements will be made to: 1) set up monitoring equipment prior to tarping structures, 2) collect employee breathing zone samples, and 3) obtain information on fumigation techniques.

Sampling and Analysis Methods. Methyl bromide and chloropicrin air will be sampled and analyzed by three different methods:

1) Charcoal tube sampling and electron capture gas chromatography,
2) Infrared gas analyzers, and
3) Thermal conductivity gas chromatography.

Charcoal Tube Sampling Method

Scope.

This method is for the collection of methyl bromide from air onto charcoal sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Worker Health and Safety Branch.

Equipment.

Required equipment for charcoal tube sampling:

1. Calibrated MSA C-210 personal sampling pumps, with appropriate flow rates (normally 0.1 L/min).
2. Large Charcoal sorbent sampling tubes and sealing caps (SKC, Inc #226-09) for sampling methyl bromide. XAD-4 resin (SKC 224-30-11-04) for sampling chloropicrin.
3. Tape labeler.
4. Tygon tubing, assorted diameters. Sufficient length to position sampling tube in the worker's breathing zone.
5. Binder clips or safety pins (to affix sampling tube to shirt lapel.
6. Glass bottles, ice chest and ice for sample storage.
7. Bubble tube.
8. Duct tape.
9. Sample data sheets

Sampling procedures (worker exposure). 1) Calibration of sampling pumps. Each pump must be calibrated with a representative sample tube in line. Use the bubble tube, rotometer or electronic flow indicator to determine pump flow rate. 2) Immediately before sampling, score and break tips of each tube to be used to provide openings of at least 2 mm diameter. 3) Attach tube to a pump with the back-up section nearest to the pump by means of a piece of Tygon tubing of desired length. 4) Set air flow based on the minimum detectable quantity required for chemical analysis and limitations on sample volume. See the references for data on particular compounds. 5) Record stroke count (if using a pump with a stroke counter), time, temperature, relative humidity and barometric prossure when air sampling is started. 6) At the end of the sample time, stop pump, seal ends of sample tube, record stroke count (if using a pump with a counter), time, temperature, relative humidity and barometric pressure. Attach an identifying label and return tube to the laboratory for analysis.
Note: Limit sampled volumes for both compounds to a total of 10L.

Sampling procedures(real-time continuous monitoring.)

This method is for the real-time measurement of methyl bromide and chloropicrin vapors using MIRAN gas analyzers. It is used to monitor the dissipation of fumigants introduced underneath tarpaulins. Chloropicrin vapors can be measured over a range from 0.9 to 30 ppm; methyl bromide can be measured from 18 to 12,500 ppm. This method is intended solely for the use of the California Department of Food and Agriculture, Worker Health and Safety Branch.

Principle

Atmospheric sampling is performed by pumping air into the analyzer through a sampling hose and particulate filter. Detection of the particular contaminant gas involves measuring the absorption of infrared radiation at a characteristic wavelength. Absorbance measurements are converted to ppm concentrations when the analyzer is calibrated with standard gas mixtures.

Equipment

1. 2 Foxboro MIRAN-1A infrared gas analyzers
2. 2 Linear strip chart recorders, chart paper and pens
3. Recorder leads and power cords (for MIRANs and recorders)
4. Assorted lengths of polypropylene tubing, 1/2" o.d.
5. Assorted Swagelok fittings, 1/2" i.d.
6. Teflon tape
7. Duct tape
8. Gast air pump, operating at approximately 25 L/min.
9. Electrical junction box
10. 110 volt electrical hook-up (provided by the homeowner)
11. Tedlar air sampling bags, 3 L, SKC, Inc. #231-03.
12. Swagelok "T" fitting with 1/4" reduction and septum fitting
13. Assorted gas-tight syringes
14. Extension cord, 200' and 3 to 2 adaptor plug
15. 2 one-way ball-valves with Swagelok fittings
16. Two-way valve with Swagelok fittings
17. Foxboro closed loop calibrator
18. Lecture bottle of methyl bromide and regulator (Matheson Gas Products)
19. Chloropicrin liquid analytical standard, 99%
20. MSA model C-210 sampling pumps
21. "Mini-Motorhome" as a traveling laboratory (instruments will be installed in this vehicle)

Equipment Set-up

BE SURE TO READ THE OPERATOR'S MANUAL PROVIDED BY FOXBORO PRIOR TO USING THE ANALYZERS!

1. String a length of polypropylene hose from the van to one room of the structure. Tape the air inlet to the ceiling, to hang midway between the ceiling and the floor.

2. Connect the MIRANs and the sampling pump to this line. The MIRANs should be located between the air inlet and the pump (pulling air through the MIRANs). Run an exhaust line back into the structure.

3. Connect a one-way valve on each line, and a two-way valve on the exhaust line. The one-way valves allow for disconnecting the van and instruments from the structure. The two-way valve is used to introduce clean air to zero the analyzers.

4. Connect recorders to the MIRANs and allow both to warm up a few minutes.

5. Check MIRAN and recorder operating conditions (see the attached calibration sheets); zero the MIRANs and recorders.

Data Collection

1. Record the date, address of structure and instrument conditions on the strip chart.

2. Obtain the following information from the fumigators: volume of the structure, dosages of methyl bromide and chloropicrin to be used, duration of the fumigation, method of introducing chloropicrin into the structure and a product label or product registration number.

3. Record the times that chloropicrin and methyl bromide are introduced into the structure.

4. Periodically (every 2 to 4 hours) record the absorbance on the IR meter and the time this reading is made on the strip chart.

5. Record any changes of instrument conditions on the strip charts including changes in measurement ranges or chart speeds.

6. Re-zero the analyzers and recorders by introducing clean air into the analyzers, using the two-way valve.

Calibration Principles

The analyzers must be calibrated to quantitatively measure gas concentrations. Standard gas mixtures (of known concentrations) are injected into the analyzer, and the change in absorbance (registered as a needle deflection on the meter) is recorded along with the ppm concentration calculated to be in the gas cell. The values are graphed to prepare the standard curve.

Instrument Conditions

See the attached calibration charts for instrument conditions.

Procedures for Methyl Bromide

1. Fill a Tedlar bag with methyl bromide from the lecture bottle. This should be done in a laboratory hood, or outdoors. CAUTION! EYE PROTECTION SHOULD BE WORN DURING THIS STEP.

2. Connect the closed loop calibrator to the analyzer.

3. Inject aliquots of methyl bromide into the calibrator using a gas-tight syringe. Record the absorbance, percent strip chart deflection, total milliliters injected into the system and ppm concentration, following each injection.

4. Calculate ppm using 5.64 L as the volume of the MIRAN gas cell and calibrator:

$$ppm = \frac{uL\ MeBr\ injected}{5.64\ L}$$

Procedures for Chloropicrin

1. Fill a Tedlar bag with 1 L of clean air.

2. Calculate the volume of liquid chloropicrin needed to prepare a 1% vapor standard gas mixture (see the attached calculations in Appendix III). Inject this volume into the bag. Disassemble the syringe following use and allow to air out; chloropicrin is corrosive.

3. Inject aliquots into the analyzer as with methyl bromide. Calculate ppm:

$$ppm = \frac{(uL\ standard\ injected)(0.01)}{5.64\ L}$$

For both compounds, record data on the attached calibration charts (see Appendix I). Test at least three concentrations at each range. Allow overlap from one range to another (switch the range selector to the next higher range then record the new absorbance and recorder deflection before injecting the next aliquot). Prepare standard curves for each range setting by graphing absorbances against concentrations. Draw lines of best fit through each set of points.

Correcting for Methyl Bromide Interferences

There is no IR absorption peak for methyl bromide at the wavelength used to quantitate chloropicrin, however methyl bromide can interfere with the chloropicrin determination at concentrations of 1,500 ppm or greater.

1. Calibrate the analyzer with methyl bromide using instrumental conditions for chloropicrin.

2. Following the injection of each aliquot, determine absorbances at each range selection.

3. Prepare standard curves for each range setting and draw lines of best fit. The lines at the 1.0 and 0.25 range settings may be bi-phasic. The lines for all three ranges can be plotted on the same graph.

Data Analysis

1. Tabulate clock times, elapsed time (hours or minutes), percent deflection and absorbance range from the strip chart.

2. Interpolate absorbance from percent deflection, using the calibration chart information (be sure to use the correct range). If the absorbance data are already available (see step 4 from Data Collection), tabulate these values.

3. Read ppm from a standard curve of ppm versus absorbance (be sure to use the correct range).

4. Range corrections.

   a. Relative to the 1.0 scale, 0.25 is 4x more sensitive and 0.1 is 10x more sensitive.

   b. Range corrections are sometimes necessary to obtain an absorbance reading on an accurate part of a standard curve; e.g. linearity is poor in both cases with methyl bromide below 0.09 absorbance units at the 1.0 range or chloropicrin below 0.04 absorbance units at the 1.0 range; another purpose is to obtain an absorbance value "on scale" after subtracting the absorbance due to methyl bromide interference.

   c. To convert absorbance readings to the proper range, multiply the absorbance by the appropriate factor:

		Convert From		
		0.1	0.25	1.0
Convert To	0.1	-	2.5	10
	0.25	1/2.5	-	4
	1.0	1/10	1/4	-

5. Perform steps 1-4 for methyl bromide. Plot concentration versus elapsed time and connect the points.

6. Correct for methyl bromide interferences in chloropicrin determination.

   a. Perform steps 1-2 for chloropicrin. Find the methyl bromide concentrations from the plotted or tabulated data for the elapsed times that chloropicrin absorbances are determined.

   b. Determine the absorbances at those methyl bromide concentrations from the corrections standard curve (be sure to use the proper range).

   c. Subtract the methyl bromide absorbances from the range-corrected absorbances. Use these absorbances to determine ppm from the standard curves in step 3.

7. Plot chloropicrin data as in step 5.

8. Examples of calibration data tables are attached.

The Determination of Methyl Bromide in Air with Gas Chromatography

Scope

This method is used for the direct determination of methyl bromide vapor in air. It is intended solely for the use of the California Department of Food and Agriculture, Worker Health and Safety Branch.

Principle

Methyl bromide is sampled from air using gas tight syringes or gas sampling bags. It is quantitated by introducing gas aliquots into a gas chromatograph equipped with a thermal conductivity detector.

Equipment

1. Tedlar gas sampling bags, 3 liter, SKC, Inc. #231-03
2. Lecture bottle of methyl bromide (Matheson Gas Products) and regulator
3. Gas-tight syringes, assorted volumes
4. MSA model C-210 personal sampling pump
5. Thermometer
6. Barometer

Preparation of Gas Standards

1. Introduce methyl bromide from the lecture bottle into a labelled Tedlar bag ("100% methyl bromide" is a suitable legend).

   CAUTION! THIS STEP SHOULD BE DONE OUTDOORS OR IN A LABORATORY HOOD. EYE PROTECTION SHOULD BE WORN.

2. Pump a known volume of clean air into a second, labelled Tedlar bag. In field situations, withdraw an aliquot and determine the presence of interferences with gas chromatography prior to preparing the standard.

3. Inject an aliquot of methyl bromide into the bag to obtain the desired concentration. Knead the bag to mix the standard. Calculate ppm according to the following formula:

$$ppm = \frac{uL\ methyl\ bromide}{L\ of\ air}$$

   The volume of air pumped into the bag should be corrected to standard conditions of 25 degrees C and 760 mm Hg according to the following formula:

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

Where: VS = Volume at standard conditions

V = Volume introduced into the bag

P = Barometric pressure in mm Hg

T = Air temperature in degrees C

Chromatographic Conditions

BE SURE TO READ THE OPERATOR'S MANUAL PROVIDED BY THE MANUFACTURER PRIOR TO USING THIS INSTRUMENT.

Instrument: AID model 511 gas chromatograph equipped with thermal conductivity detector and 1 mL gas sampling loop.

Temperatures: Injector and detector are slaved to column temperature.

Column: 6 ft. x 1/8 in. O.D. glass tubing, 10 % SP2100 on 80/100 Chromosorb WHP. Column temperature: 40 degrees C. Carrier gas: He, 25 mL/min.

Recorder: Linear strip chart recorder; full scale response = 1 mv, chart speed = 2 cm/min.

Quantitation

1. A standard should be injected following each sample.

2. Quantitation is performed by comparision of sample and standard peak heights. Calculate ppm in the sample with the following formula:

$$\text{ppm} = \frac{\text{mm sample peak height} \times \text{ppm in standard}}{\text{mm standard peak height}}$$

Minimum detectable level with this method is approximately 50 ppm.

DATA COLLECTION FORMS

Structural Fumigation Log Sheet

Fumigator:
Address:
Phone:
Contact:
Structure Address:
Data Fumigated/Vented:
EPA Product No.:
Application Rate:
Structure Volume:
Method for Adding Chloropicrin:
Comments:

MIRAN Calibration Chart

Date: Compound:

Instrument Conditions

Wavelength:
Pathlength:
Slit:

Response Time:
Gain Switch:
Recorder Speed:
Recorder Span:

Volume Injected	Total Volume	ppm	Absorbance	Range	Recorder Deflection

TABLES FOR CALCULATING CONCENTRATIONS
FROM IR SPECTROPHOTOMETRIC DATA

METHYL BROMIDE

Location	Date	Time	Elapsed Time (min/hr)	Percent Deflection	Observed A	Range	ppm MeBr

CHLOROPICRIN

Location	Date	Time	Elapsed Time (min/hr)	Percent Deflect	Observed A	Range	Range Corrected A	Range	ppm MeBr	A	MeBr Corrected Cpic

Sample Calibration Charts

MIRAN Calibration Chart

Date: 8/23/84 Compound: Methyl Bromide, 100% gas

Instrument Conditions

Wavelength: 7.6 um
Pathlength: 4 m (1.3 on meter)
Slit: 2 mm

Response Time: 1 second
Gain Switch: 10x
Recorder Speed: 10 cm/hour
Recorder Span: 1 volt = full scale

Volume Injected (mL)	Total Volume (mL)	ppm	Absorbance	Range	Recorder Deflection(%)
0.1	0.1	17.7	0.006	0.1	2
0.4	0.5	88.7	0.024		11
1.5	2.0	335	0.106		42
		335	0.043	0.25	17
4.0	6.0	1,064	0.109		43
6.0	10.0	1,773	0.170		68
		1,773	0.043	1.0	17
10	20	3,546	0.090		36
10	30	5,319	0.130		52
10	40	7,092	0.170		66
10	50	8,870	0.196		78
10	60	10,638	0.224		89
10	70	12,411	0.250		99

MIRAN Calibration Chart

Date: 8/23/84 Compound: Chloropicrin 1% vapor in air

Instrument Conditions

Wavelength: 11.5 um
Pathlength: 21 m (14.0 on meter)
Slit: 1 mm

Response Time: 1 second
Gain Switch: 10x
Recorder Speed: 10 cm/hour
Recorder Span: 1 volt = full scale

Volume Injected (ml)	Total Volume (ml)	ppm	Absorbance	Range	Recorder Deflection(%)
0.5	0.5	0.9	0.030	0.1	13
1.5	2.	3.5	0.114		45
2.5	4.0	7.1	0.230		91
		7.1	0.091	0.25	36
4	8	14.2	0.167		65
		14.2	0.042	1.0	16
4	12	21.3	0.232		88
		21.3	0.055		22
4	16	28.4	0.070		28

APPENDIX III

CALCULATIONS FOR PREPARING A 1% CHLOROPICRIN VAPOR STANDARD

1% = 10,000 ppm

Chloropicrin data:
MW = 164.5
Density = 1.64 mg/uL

$$\text{ppm} = \frac{\text{mg/m}^3 \times \text{molar volume of vapor at } 25^{\circ}\text{C}}{\text{molecular weight}}$$

$$10{,}000 \text{ ppm} = \frac{\text{mg/m}^3 \times 24.45}{164.5}$$

or, $10{,}000 \text{ ppm} = 67{,}280 \text{ mg/m}^3$

then,

$$67{,}280 \text{ mg/m}^3 \times \underset{\text{(bag volume)}}{0.001 \text{ m}^3} = 67.28 \text{ mg}$$

67.28 mg of Chloropicrin required to prepare st'd.

$$67.28 \text{ mg} \times \frac{\text{uL}}{1.64 \text{ mg}} = 41.02 \text{ uL}$$

inject 41 ul of Chloropicrin liquid
into 1 L to prepare 1% vapor standard

Table 1

Structural Fumigation Site Data

Site Number	Company Number	Location	Date	EPA Product No.	Methyl Bromide Application Rate	Method of Introducing Chloropicrin	Amount of Chloropicrin Introduced	Volume of Structure (ft^3)
1	1	Sacramento	6/27-29/84	8536-15-AA	3 lbs/1,000 ft^3	Hand Poured	1 oz/1,000 ft^3	40,000
2	2	Long Beach	7/9-10/84	550-131-AA	3 lbs/1,000 ft^3	Pre-mixed	0.25 %	14,000
3	3	Long Beach	7/11-12/84	8536-12-AA	1.5 lbs/1,000 ft^3	Pre-mixed	0.50 %	19,000
4	3	Long Beach	7/12-13/84	8536-12-AA	1.5 lbs/1,000 ft^3	Pre-mixed	0.50 %	18,000
5	4	Long Beach	7/16-17/84	8536-50003	2 lbs/1,000 ft^3	Hand Poured	1 oz/1,000 ft^3	14,000
6	5	Hermosa Beach	7/18-19/84	8536-12-AA	2 lbs/1,000 ft^3	Pre-mixed	0.50 %	16,000
7	1	Sacramento	10/22-24/84	8536-15-AA	3 lbs/1,000 ft^3	Hand Poured	1 oz/1,000 ft^3	14,000

Table 2

Employee Inhalation Exposures to Methyl Bromide and Chloropicrin During Structural Fumigation Tarpaulin Removal Operations

Site Number	Company Number	Date	Sampling Duration (min.)	Exposure Concentrations	
				Methyl Bromide (ppm)	Chloropicrin (ppm)
1	1	6/29/84	53	27.2	0.037
			53	23.6	0.034
			53	10.5	0.015
2	2	7/10/84	30	57.4	0.013
			30	50.8	0.012
3	3	7/12/84	10	29.1	0.019
5	4	7/17/84	10	17.2	<0.01[a]
			6[b]	12.3	<0.01
6	5	7/19/84	6[b]	26	<0.01
7	1	10/24/84	40	2.3	<0.01
			40	6.6	<0.01
			40	1.2	NA[c]

Table 2 (continued)

House Clearance Operations

Site Number	Company Number	Date	Sampling Duration (min.)	Employee Potential Exposure		Respiratory Protection Used
				Methyl Bromide (ppm)	Chloropicrin (ppm)	
2	2	7/10/84	5	982[d]	0.21	SCBA
3	3	7/12/84	10	211.7	1.0	Respirator (gas mask type)
5	4	7/17/84	3[b]	77.4	0.012	SCBA
6	5	7/19/84	6[b]	155.8	0.55	SCBA

a/ None detected, minimum detection limit is 0.01 ppm.

b/ Same employee monitored with separate samples.

c/ Not available, sample lost during collection.

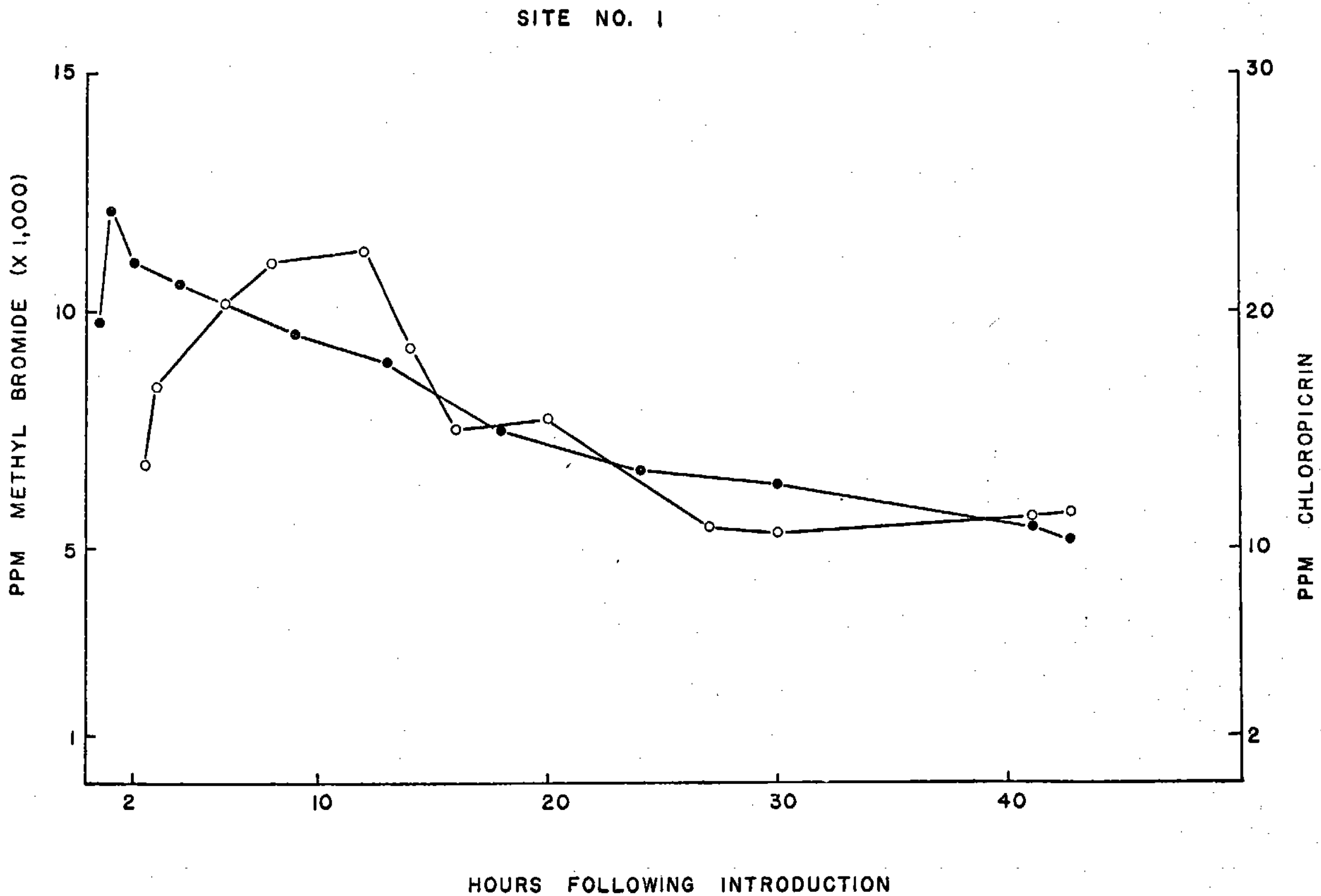
d/ Sampling tube overloaded, minimum quantity present is reported.

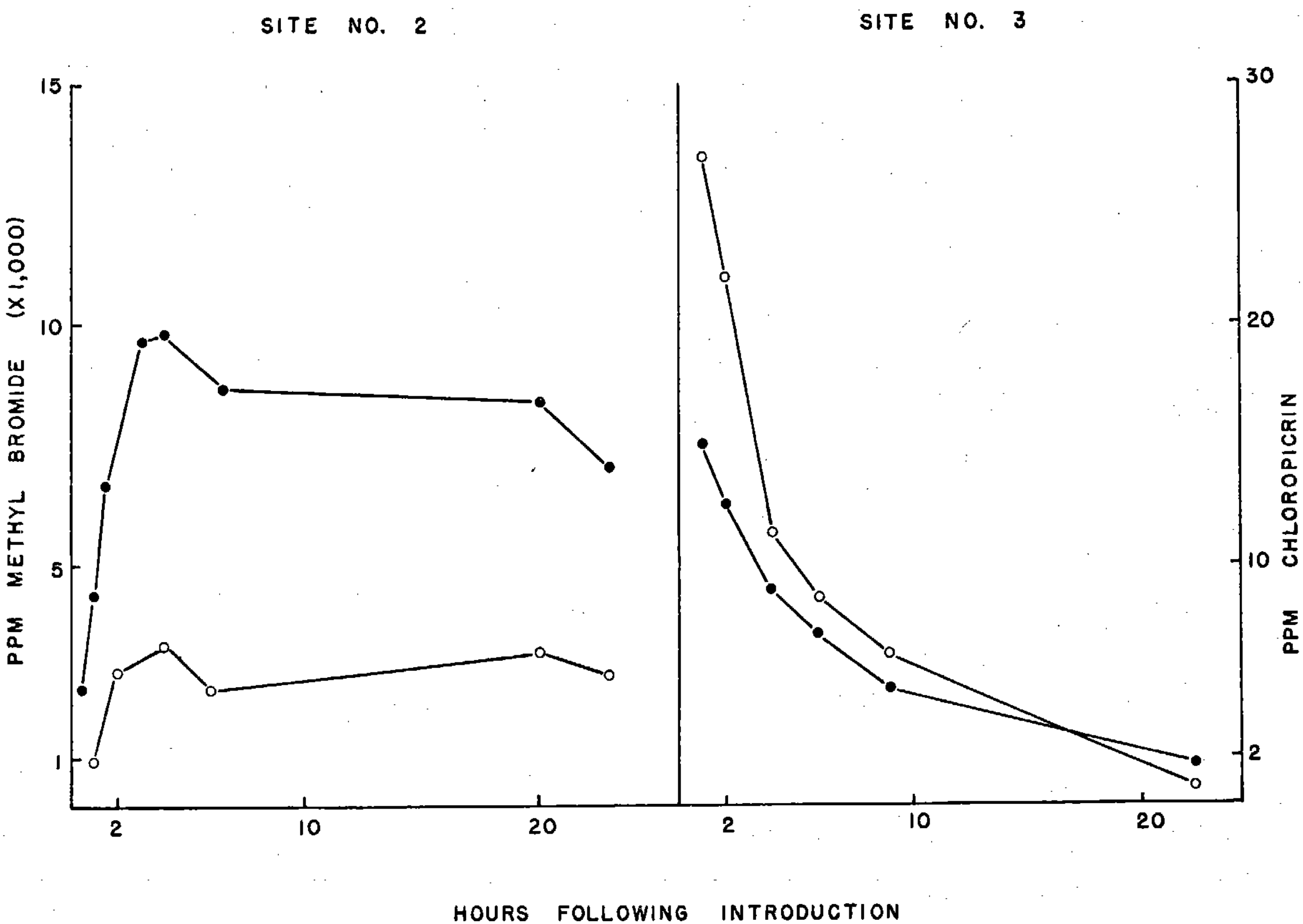
Figure Set 1.

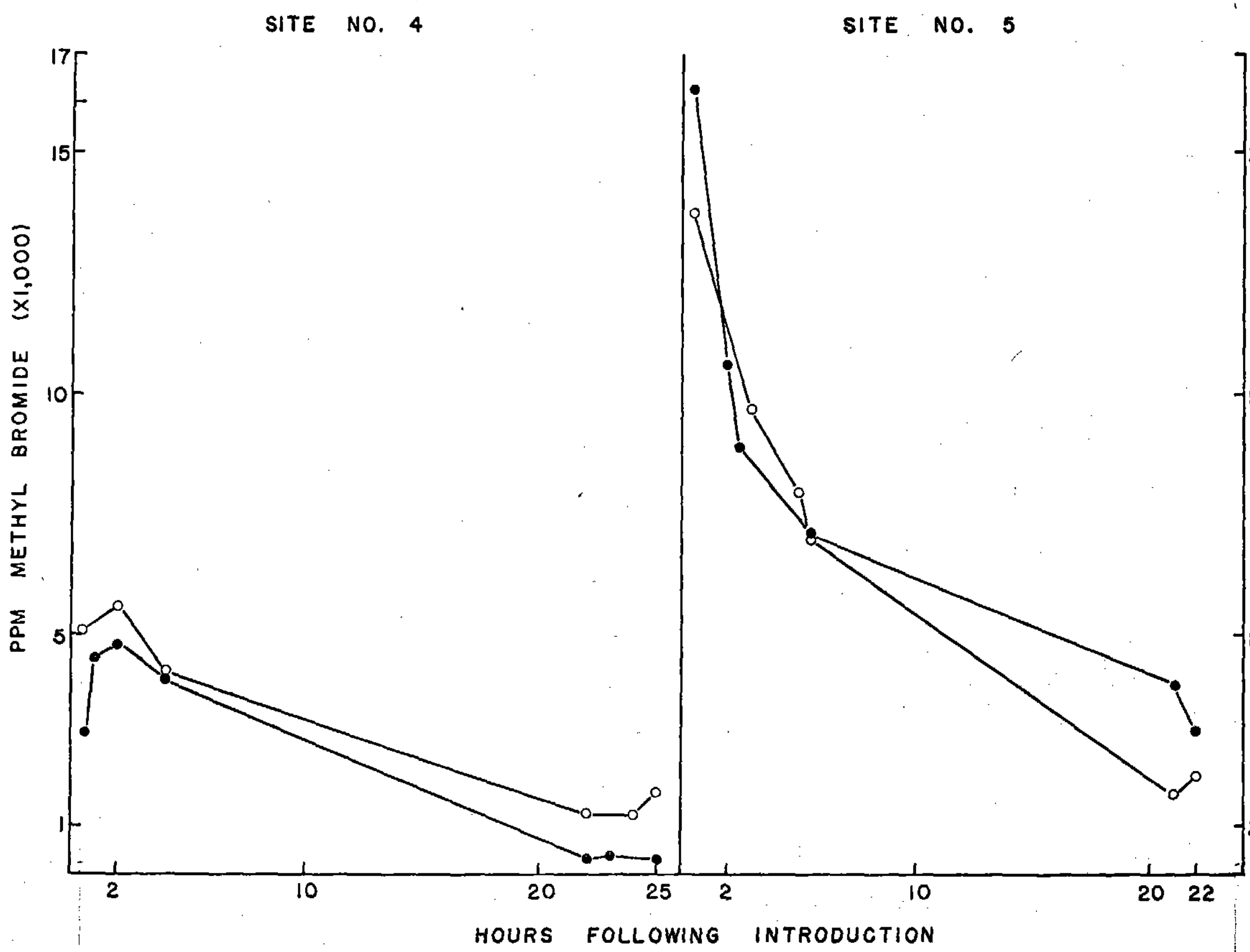
Dissipation of Methyl Bromide and Chloropicrin in Structures After Fumigant Introduction

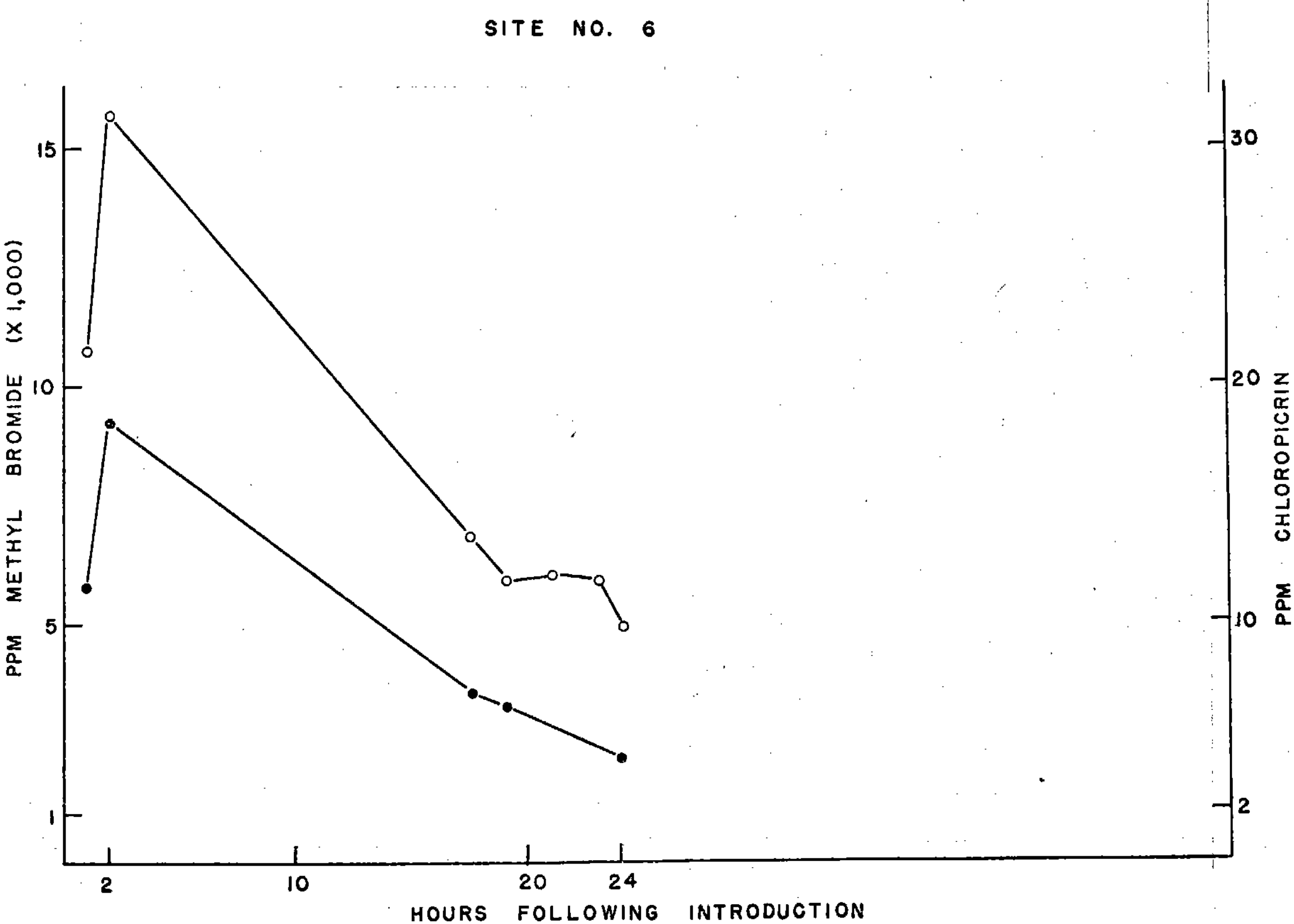
Methyl Bromide - Blackened Points

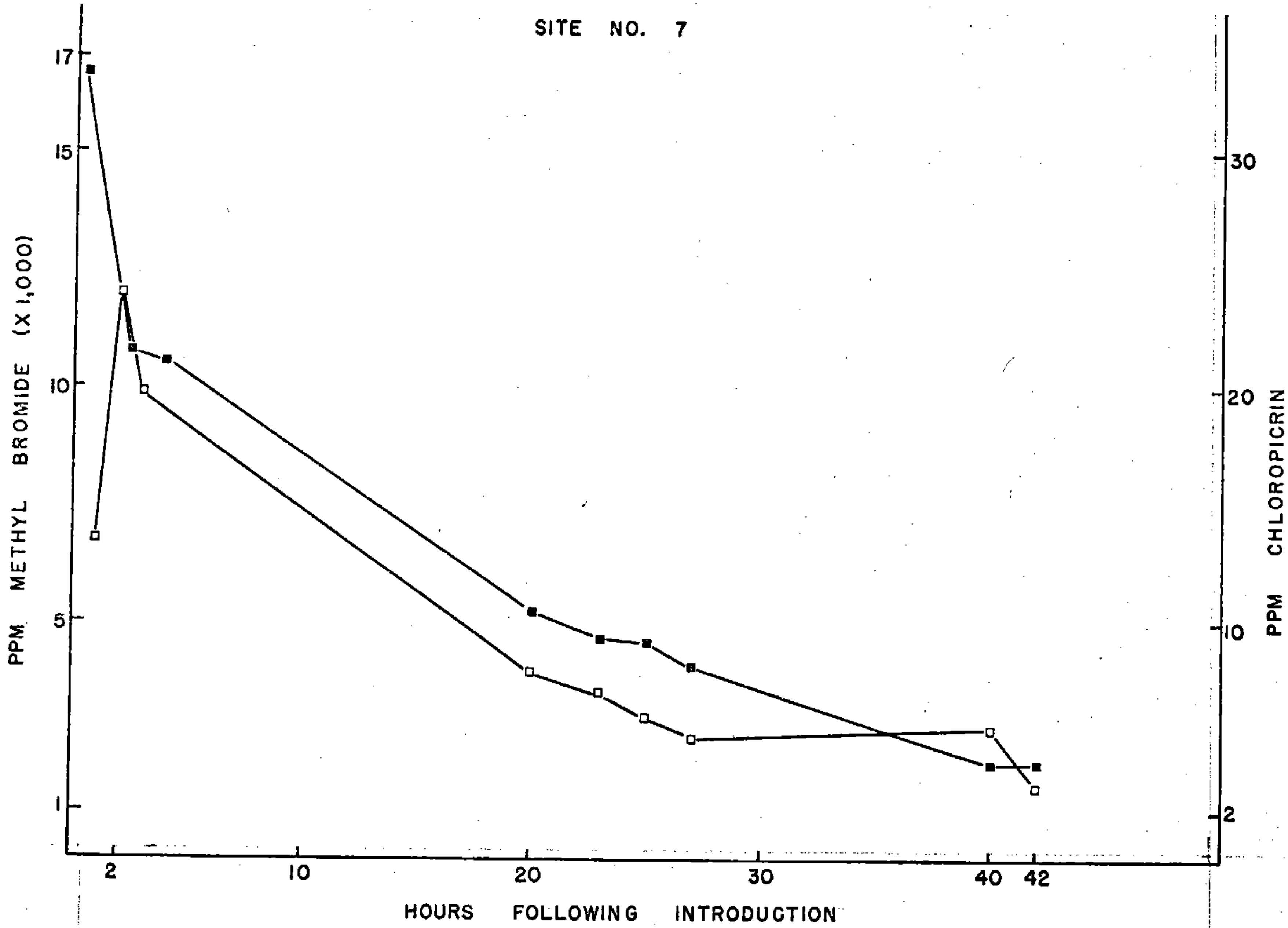
Chloropicrin - Open Circles


SITE NO. 1
15
10
5
1
PPM METHYL BROMIDE (X 1,000)
30
20
10
2
PPM CHLOROPICRIN
2
10
20
30
40
HOURS FOLLOWING INTRODUCTION


SITE NO. 2
SITE NO. 3
PPM METHYL BROMIDE (X1,000)
PPM CHLOROPICRIN
15
10
5
1
30
20
10
2
2
10
20
2
10
20
HOURS FOLLOWING INTRODUCTION


SITE NO. 4
SITE NO. 5
PPM METHYL BROMIDE (X1,000)
PPM CHLOROPICRIN
HOURS FOLLOWING INTRODUCTION
17
15
10
5
1
30
20
10
2
2
10
20
25
2
10
20
22

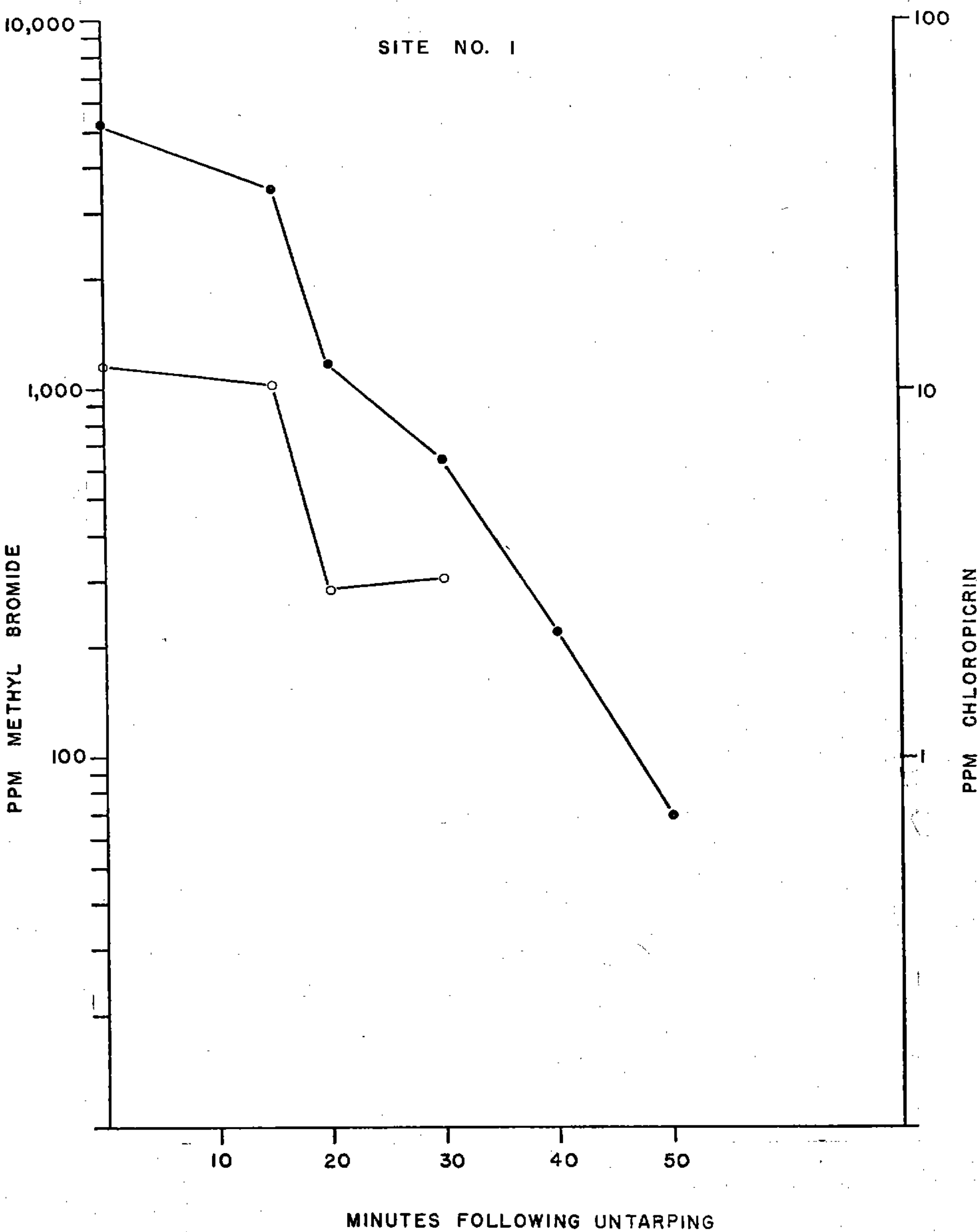

SITE NO. 6
PPM METHYL BROMIDE (X 1,000)
15
10
5
1
PPM CHLOROPICRIN
30
20
10
2
2
10
20
24
HOURS FOLLOWING INTRODUCTION



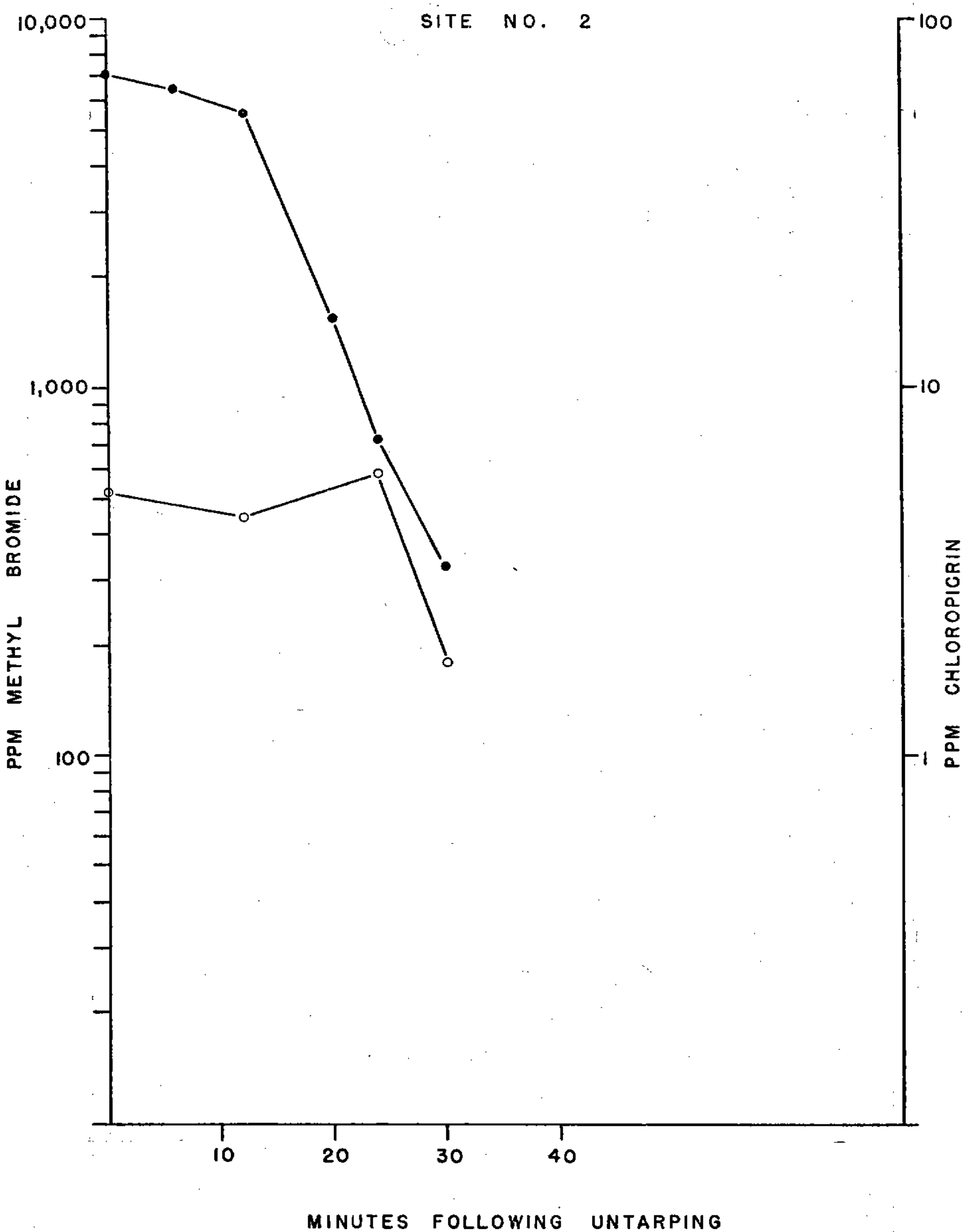
SITE NO. 7
PPM METHYL BROMIDE (X 1,000)
17
15
10
5
1
PPM CHLOROPICRIN
30
20
10
2
2
10
20
30
40
42
HOURS FOLLOWING INTRODUCTION

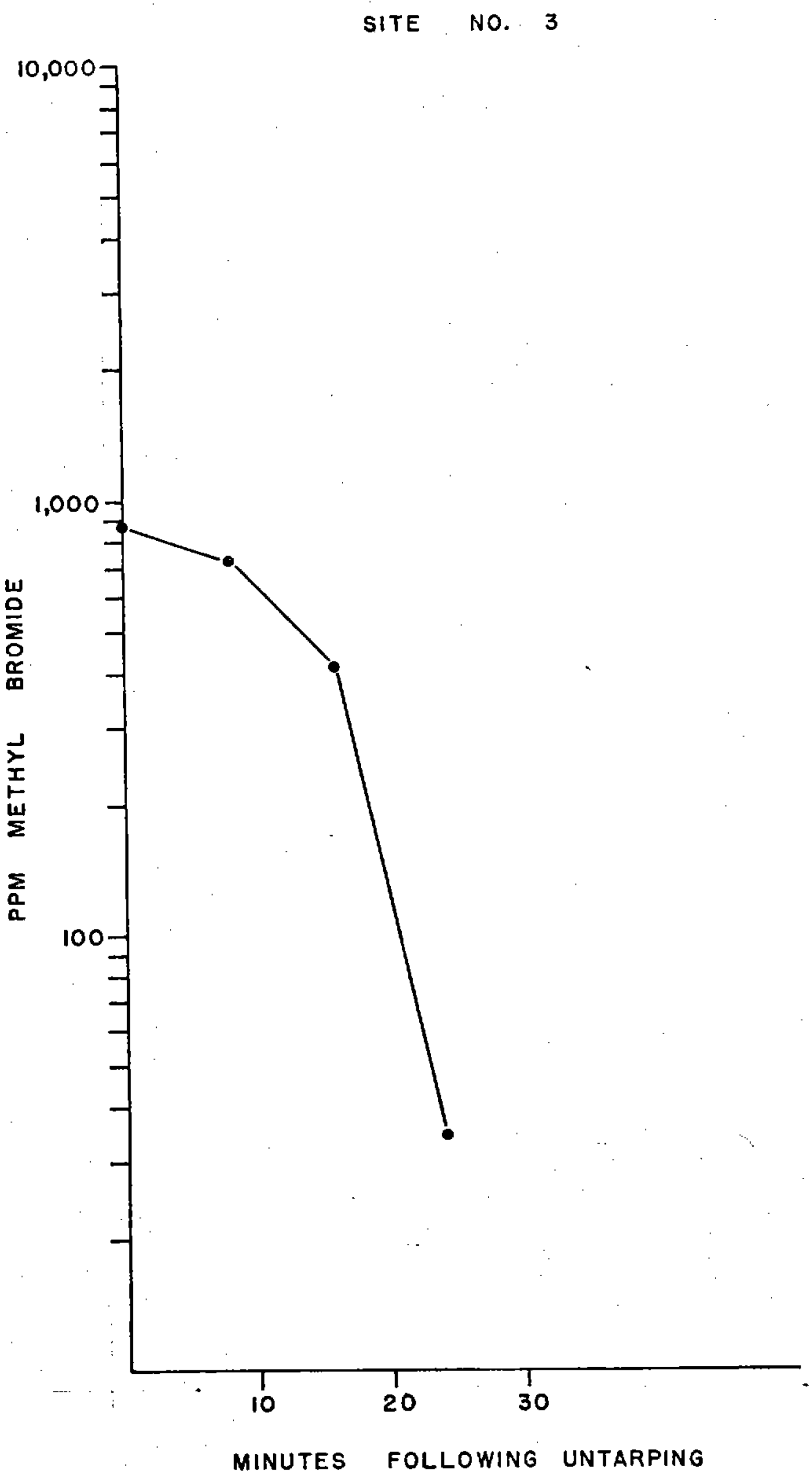
Figure Set 2.

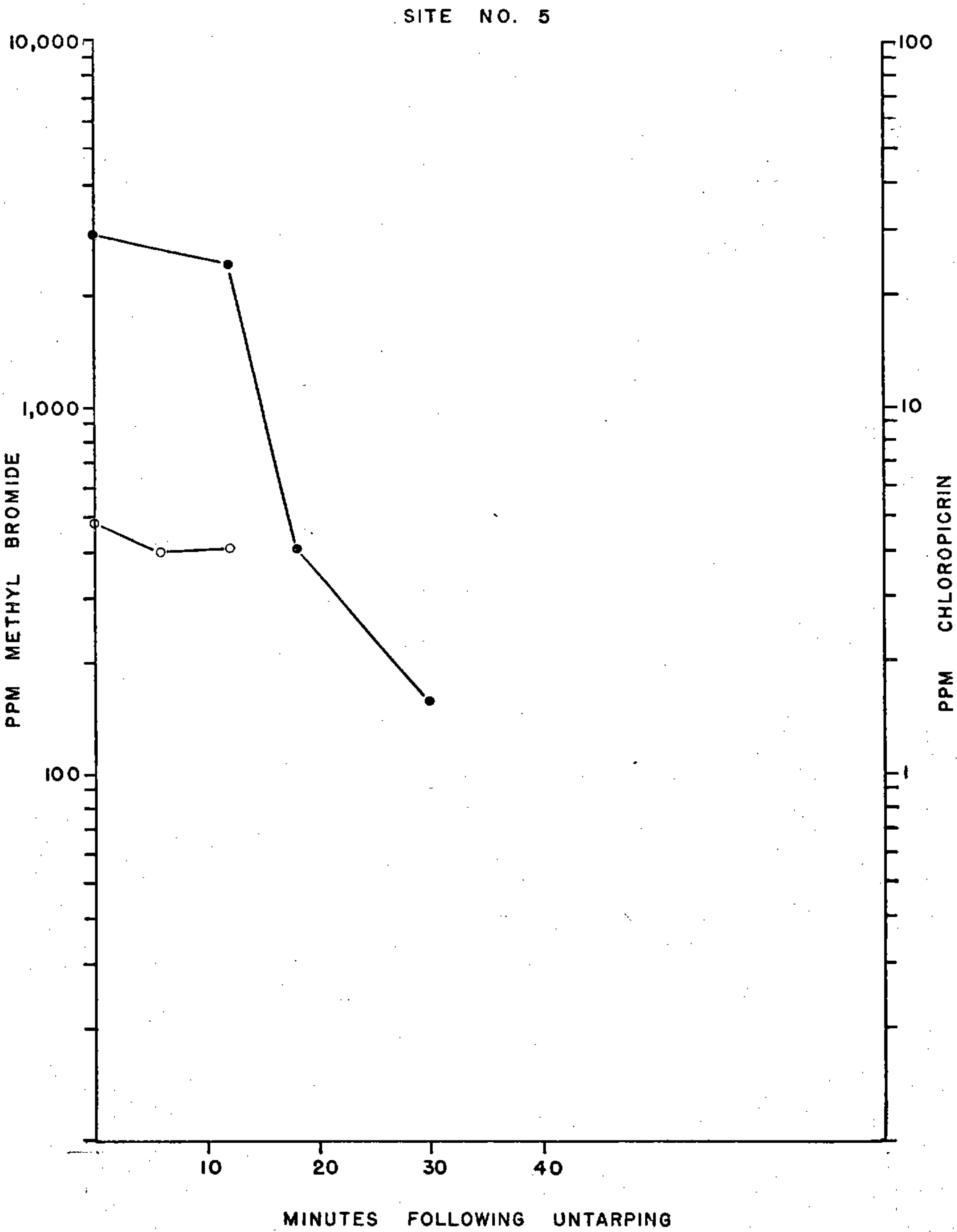
Dissipation of Methyl Bromide and Chloropicrin from Structures After Tarpaulin Removal



10,000
1,000
100
100
10
1
SITE NO. 1
PPM METHYL BROMIDE
PPM CHLOROPICRIN
10
20
30
40
50
MINUTES FOLLOWING UNTARPING


SITE NO. 2
10,000
1,000
100
100
10
1
PPM METHYL BROMIDE
PPM CHLOROPICRIN
10
20
30
40
MINUTES FOLLOWING UNTARPING


SITE NO. 3
10,000
1,000
100
PPM METHYL BROMIDE
10
20
30
MINUTES FOLLOWING UNTARPING


SITE NO. 5
10,000
1,000
100
PPM METHYL BROMIDE
100
10
1
PPM CHLOROPICRIN
10
20
30
40
MINUTES FOLLOWING UNTARPING

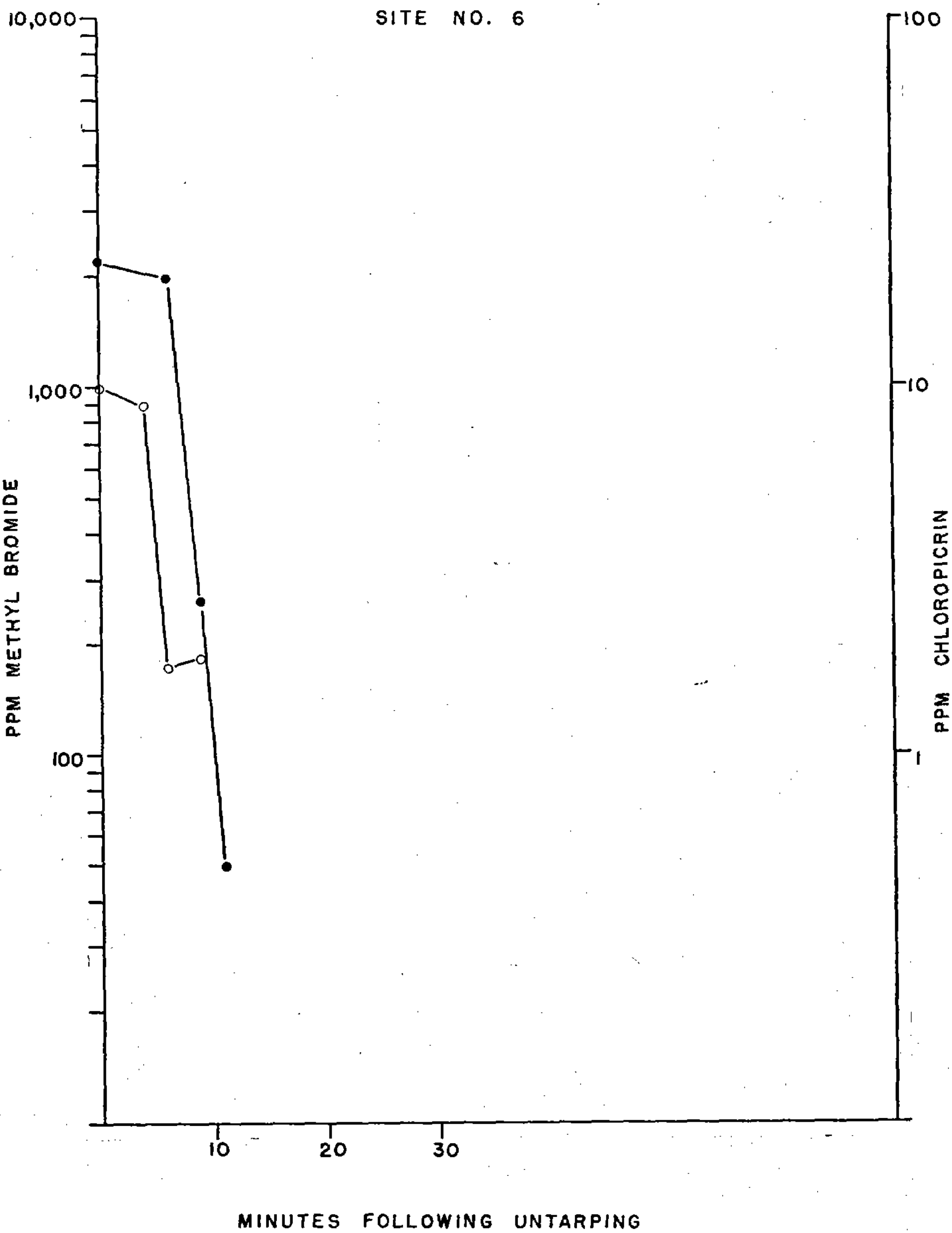

SITE NO. 6
10,000
1,000
100
100
10
1
PPM METHYL BROMIDE
PPM CHLOROPICRIN
10
20
30
MINUTES FOLLOWING UNTARPING

FIGURE 3.

DISSIPATION OF METHYL BROMIDE FROM UNOPENED PLASTIC-BAGGED BOXES