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Raleigh, North Carolina

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PREFACE

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Steven W. Lenhart, CIH of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies and Yvonne T. Gagnon of the Analytical Research and Development Branch, Division of Physical Sciences and Engineering. Desktop publishing was done by Juanita Nelson and Ellen E. Blythe. Review and preparation for printing was done by Penny Arthur.

Copies of this report were sent to the Safety, Health, and Environmental Staff of USDA's Animal and Plant Health Inspection Service (APHIS) in Riverdale, Maryland; the APHIS State Operations Support Officer in Raleigh, North Carolina; OSHA Regional Office IV in Atlanta, Georgia; and the Environmental Protection Agency's Methyl Bromide Program in Washington, D.C. This report is not copyrighted and may be freely reproduced. Single copies will be available for three years from the date of this report. To expedite your request, please include a self-addressed mailing label along with your written request to:

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SUMMARY

Officers of the U.S. Department of Agriculture's witchweed eradication program spot-fumigate small areas of land to kill witchweed seeds. A spot fumigation involves puncturing a pressurized 1.5-pound can of 98% methyl bromide and 2% chloropicrin under a plastic tarp covering an area of 10 feet by 15 feet. (Chloropicrin is added as a warning agent because methyl bromide has poor warning properties.) After waiting at least 48 hours, an officer removes the tarp. Because of a concern that methyl bromide exposures may still occur after the waiting period, the director of the witchweed eradication program requested a National Institute for Occupational Safety and Health (NIOSH) health hazard evaluation of the spot-fumigation process.

During a pilot study, methyl bromide was measured under tarps at 27 hours and 47 hours after two spot fumigations were started on packed soil. Methyl bromide and chloropicrin measurements were later taken under six spot-fumigation tarps covering tilled soil. After five days, one tarp was removed, and two others were cut for aeration. Methyl bromide and chloropicrin measurements were taken under three remaining intact tarps at two weeks after starting. Air sampling for methyl bromide was done according to NIOSH Method 2520 and using short-term detector tubes. Air sampling for chloropicrin was done using an Occupational Safety and Health Administration (OSHA) stopgap method. NIOSH considers methyl bromide a potential occupational carcinogen. OSHA's permissible exposure limit is a ceiling value of 20 parts per million (ppm). The Environmental Protection Agency (EPA) requires that workers wear respiratory protection any time methyl bromide exposures exceed 5 ppm. The American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Value® is a time-weighted average (TWA) of 1 ppm. For chloropicrin, NIOSH, OSHA, and ACGIH® exposure limits are a TWA of 0.1 ppm, and EPA requires respirator use any time this concentration is exceeded.

Methyl bromide air concentrations during the pilot study were approximately 23,000 ppm and 26,000 ppm after 27 hours and 16,000 ppm and 18,000 ppm after 47 hours. Methyl bromide air concentrations under six tarps declined from greater than 15,000 ppm to 50 ppm after 5 days. Chloropicrin air concentrations declined from 340 ppm to 0.7 ppm. The day after a tarp was removed, methyl bromide and chloropicrin were not detected directly above the soil. Methyl bromide was measured under two tarps at 24 hours after they were cut for aeration. Residual chloropicrin also remained, but at levels below those expected to warn that methyl bromide was present. Methyl bromide air concentrations under three intact tarps were less than 5 ppm two weeks after the fumigations started; chloropicrin was not detected.

High air concentrations of methyl bromide and chloropicrin were measured under plastic tarps 48 hours after spot fumigations started. After two weeks, methyl bromide air concentrations were less than 5 ppm. Besides extending the waiting period, detector tubes should be used to ensure that methyl bromide air concentrations under a tarp are less than 5 ppm before tarp removal.

Keywords: SIC 9199 (general government), agriculture, chloropicrin, pesticide, methyl bromide, witchweed.

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INTRODUCTION

Witchweed (*Striga asiateca*) is a parasitic annual that attacks and severely damages corn, sorghum, sugarcane, dryland rice, and more than 60 other grass species.[1,2] After its seeds germinate, witchweed penetrates the roots of host plants, robbing them of water and nutrients.[2] Witchweed stunts plant growth, and severe infestations can kill an entire crop. Witchweed and related *Striga* species are among the most serious crop pests hindering cereal-crop production in Africa, the Middle East, and Far East countries. Parts of eastern North Carolina and South Carolina are the only places in the western hemisphere where witchweed occurs.[1]

The U.S. Department of Agriculture's (USDA) witchweed eradication program started in 1957, with a goal of eradicating witchweed from affected areas of North and South Carolina. To eradicate witchweed, Plant Protection and Quarantine (PPQ) officers of the USDA's Animal and Plant Health Inspection Service used a variety of methods to apply soil fumigants and postemergence herbicides. One eradication method involved spraying herbicides (e.g., paraquat, 2,4–D, or glyphosate) on witchweed-infested fields, gardens, idle parcels of land, and areas where grass and weeds were present in non-host crops such as cotton, peanuts, and soybeans. Work crews of PPQ officers also did chisel fumigations using tractor-mounted injection equipment to apply methyl bromide to witchweed-infested fields. Both eradication methods were the subjects of previous NIOSH health hazard evaluations.[3,4]

Another PPQ eradication method involved using methyl bromide to spot fumigate small, isolated witchweed infestations. Spot-fumigated areas included plowed land, corn stubble, knocked down corn stalks, and heavy grass cover. A PPQ spot fumigation involved puncturing a pressurized 1.5-pound can of 98% methyl bromide and 2% chloropicrin (by weight) under a raised plastic tarp covering an area of 10 feet by 15 feet. After starting a fumigation, PPQ officers followed the agricultural-use requirements for this product, which required that they wait a minimum of 48 hours before removing a tarp.

Because of the health risks associated with overexposure to methyl bromide, the director of the witchweed eradication program requested a National Institute for Occupational Safety and Health (NIOSH) health hazard evaluation of the PPQ spot-fumigation process. The purpose was to evaluate the adequacy of the 48-hour waiting period by estimating the time needed for methyl bromide and chloropicrin to decay to safe levels. Air sampling methods, findings, and recommended improvements to the tarp-removal process are described in this report.

BACKGROUND

The first steps of a PPQ spot fumigation were clearing away all debris and, if possible, tilling the soil. Tilling increases the likelihood that methyl bromide will penetrate the soil. A narrow trench was dug around the perimeter of an area to be fumigated, and a 4-foot section of 4-inch polyvinyl chloride pipe, with three sections cut from it, was placed near the center.

A 1.5-pound can of BROM-O-GAS® (Great Lakes Chemical Corporation, West Lafayette, Indiana) was placed in the first pipe section on top of a block of wood with a nail through it. A sheet of clear 6-mil plastic having a thickness of 0.15 millimeters was then laid over the area, and its edges were covered with dirt to make a secure enclosure. The can punctured when pressed against the nail, and the pipe acted like a trough, holding the released methyl bromide and chloropicrin until the liquid evaporated completely. PPQ officers left the site immediately after puncturing the can.

Though done on a much smaller scale, PPQ spot-fumigations are similar to the fumigation methods used to apply methyl bromide to soil before planting crops (e.g., tomatoes, strawberries, tobacco, and peppers).[5-7] Releasing a 1.5-pound can of BROM-O-GAS® under a tarp covering an area of

150 square feet equals an application rate of 436 pounds per acre (490 kilograms/hectare), which is similar to the rates recommended for the larger tarp applications.[7,8]

METHODS

A pilot study was conducted involving two spot fumigations. The pilot study's purposes were to gain insight to the air concentrations of methyl bromide that might occur initially under spot-fumigation tarps and to estimate a sampling duration that would not result in overloading of the sampling media. Methyl bromide and chloropicrin measurements were later taken under six tarps over a two-week period to estimate when safe levels existed.

Just before the field work started on this health hazard evaluation, problems were reported with NIOSH Method 2520 for methyl bromide. Because it had not been fully evaluated, problems with the first version of Method 2520 included reduced adsorption capacity at high humidity, difficult-to-prepare standard solutions, sample instability, decreasing recovery as loading decreased, and an insufficiently low quantitation limit.[9] Method 2520 was revised to include the addition of a drying tube to the sampling train, and changes were made to the analytical technique, the desorption solvent, and the time limit between sample collection and analysis.[9,10]

Methyl bromide air samples were collected and analyzed according to the revised version of NIOSH Method 2520.[10] Each sampling train consisted of three tubes in series, a drying tube holding 9 grams of sodium sulfate, a 400-milligram charcoal tube, and a 200-milligram charcoal tube. Sampling trains were connected by tubing to low-flow sampling pumps. Direct-reading detector tubes were also used. Dräger tube 3/a for methyl bromide (part number 6728211) measures methyl bromide concentrations from 3 to 100 ppm.[11]

Because of concerns about methyl bromide recovery and storage stability, steps were taken to keep samples cold before analysis and reduce the time between sample collection and analysis. Immediately after a sampling period, all sampling tubes were capped and placed in an insulated 1-quart cooler containing cold packs. Samples were then taken to the NIOSH researcher's motel room, removed from the cooler, and put in a refrigerator's freezer compartment. Later that evening, methyl bromide samples were put back in a cooler and mailed overnight to the NIOSH laboratory for analysis.

Air samples for chloropicrin were collected only during the six-tarp study and were analyzed using a 1991 Occupational Safety and Health Administration (OSHA) stopgap method for which recovery and storage stability studies were completed. Each sampling train consisted of two XAD–4 tubes connected by tubing to a low-flow sampling pump. Samples were analyzed using a gas chromatograph having an electron capture detector.

To sample under a tarp, slits slightly smaller than the diameter of a drying tube and an XAD–4 tube were made in the plastic. The tips of the tubes were then carefully inserted through the holes so that the plastic sealed around them. The tips of each tube were positioned midway between the tarp and the soil. After each sampling period, both sampling holes were covered with tape.

During the pilot study, methyl bromide measurements were taken after a 1.5-pound can of BROM-O-GAS® was punctured under each of two 10-feet by 15-feet plastic tarps. Low-flow sampling pumps ran at 0.02 liters per minute (L/min) for one hour. Air samples were collected at 27 hours and 47 hours after spot fumigations were started simultaneously on packed soil.

Methyl bromide and chloropicrin measurements were taken above and below six tarps covering freshly-tilled, sandy soil at 15 minutes after the start of the six-tarp study. Collecting an air sample directly above each tarp was done to learn if 6-mil plastic prevented methyl bromide and chloropicrin from leaking through. To measure methyl bromide, sampling pumps ran at 0.02 L/min for durations ranging from 5 minutes, soon after the start, to 60 minutes on the last day of sampling. To measure chloropicrin, sampling pumps ran at 0.1 L/min for durations ranging from 12 to 60 minutes. Also, methyl bromide and chloropicrin measurements were taken under all six tarps after six hours and daily for five days after the start, and under three tarps at two weeks after the start.

Five days after the start, one tarp was removed completely, and two others were cut for aeration. One tarp was cut once in the center along its entire length and perpendicular to the wind's direction. The other trap was cut at three equidistant locations along its width and in the same direction as the wind. Twenty-four hours later, methyl bromide and chloropicrin measurements were taken directly above the soil where the first tarp had been and under the two tarps that were cut.

EVALUATION CRITERIA

General Guidelines

To assess the health hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria suggest exposure levels to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However, because of wide variation in individual susceptibility, some workers may experience health effects even if exposures are maintained below these limits. The evaluation criteria do not take into account individual hypersensitivity, pre-existing medical conditions, or possible interactions with other workplace agents, medications being taken by the worker, or environmental conditions. Evaluation criteria may change when new information on the toxic effects of an agent become available.

The primary sources of evaluation criteria for the workplace are NIOSH criteria documents and recommended exposure limits (RELs),[12,13] the American Conference of Governmental Industrial Hygienists (ACGIH®) threshold limit values (TLV®),[14] and OSHA permissible exposure limits (PELs).[15] These values are usually based on a time-weighted average (TWA) exposure, which refers to the average airborne concentration of a substance over an entire 8- to 10-hour workday. Concentrations are usually expressed in parts per million (ppm), milligrams per cubic meter (mg/m^3), or micrograms per cubic meter ($\mu g/m^3$). In addition, some substances have only a ceiling limit, a concentration that should not be exceeded during any part of a workday.

Other substances have a short-term exposure limit (STEL) to supplement a TWA limit where there are recognized toxic effects from short-term exposures. A STEL is a 15-minute TWA concentration that should not be exceeded anytime during a workday even if the 8-hour TWA is within the TLV-TWA. The ACGIH® recommendation for a substance without a STEL is that "excursions in worker exposure levels may exceed 3 times the TLV-TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5 times the TLV-TWA, provided that the TLV-TWA is not exceeded."[14] The basic concept is that excursions above a substance's TWA exposure limit should be maintained within reasonable limits in well-controlled processes. Additionally, some chemicals have a skin notation to indicate that the substance may be absorbed through direct contact of the material with the skin and mucous membranes.

NIOSH RELs are based primarily on the prevention of occupational disease. In contrast, when developing PELs and other standards, OSHA must take into account the economic feasibility of reducing exposures in affected industries, public notice and comment, and judicial review. In evaluating worker exposure levels and NIOSH recommendations for reducing exposures, it should be noted that employers are legally required to meet OSHA standards.

An additional complication is that a Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in AFL-CIO v OSHA, 965F.2d 962 (11th cir., 1992).[16] OSHA now enforces the previous 1971 standards.[15] However, some states which have OSHA-approved state plans will continue to enforce the more protective 1989 OSHA PELs.[17] NIOSH encourages use of NIOSH RELs, ACGIH TLVs, or OSHA PELs, whichever are lower.

Methyl bromide

Methyl bromide (CAS number 74-83-9) is a broad-spectrum, restricted-use pesticide used to control insects, nematodes, weed seeds, and rodents.[18] Approximately 27,000 tons of methyl bromide are used annually in the United States for soil fumigation (87%), commodity and quarantine treatment (8%), and structural fumigation (5%).[5]

Human health effects

Methyl bromide is a colorless, nonflammable gas that is odorless and tasteless at air concentrations considered unsafe.[19,20] Odor thresholds reported for methyl bromide range from 20 to 1,000 ppm.[21] Methyl bromide is a severe pulmonary irritant and neurotoxin. Short-term inhalation exposure may cause headache, dizziness, nausea, vomiting, blurred vision, slurred speech, convulsions, and death. Short-term inhalation exposures to high concentrations may cause lung irritation resulting in congestion with coughing, chest pain, and shortness of breath. The onset of lung effects may be delayed.[22]

Prolonged or repeated exposures to methyl bromide may cause a variety of central nervous system symptoms including visual disturbances, slurred speech, numbness of the arms and legs, confusion, shaking, and unconsciousness.[22] The onset of neurological signs and symptoms may be delayed for several hours to a few days after exposure.[16]

Methyl bromide may be absorbed though the skin and cause systemic toxicity.[7,19] Skin contact with liquid methyl bromide may cause irritation.[18,20] Prolonged skin contact may cause burns and blistering.[7] To avoid prolonged skin contact, applicators are advised to not wear tight clothing, jewelry, gloves, or boots.[18]

Eye contact with liquid methyl bromide may cause severe corneal burns, but its vapors do not appear to be irritating.[20]

Occupational exposures

NIOSH considers methyl bromide a potential occupational carcinogen.[12,13] According to the previous NIOSH carcinogen policy, this meant occupational exposures to potential carcinogens should be controlled to the lowest feasible level. Based on the limit of quantitation of the NIOSH analytical method used at the time of this policy, the lowest feasible level was 4.7 ppm.[12] The NIOSH carcinogen policy was changed in 1995. According to the revised policy, NIOSH RELs will be adopted for potential occupational carcinogens, but one has yet to be adopted for methyl bromide.

Based on results from an inhalation study on laboratory rats, the ACGIH® TLV® for methyl bromide was reduced in 1997, to a TWA concentration of 1 ppm with a skin notation.[14] The previous TLV® was 5 ppm. The OSHA PEL for methyl bromide is a ceiling limit of 20 ppm with a skin notation.[15] The NIOSH immediately dangerous to life or health level is 250 ppm.[13]

The Environmental Protection Agency (EPA) requires that workers wear respiratory protection when methyl bromide exposures exceed 5 ppm.[18] When this air concentration is exceeded, at any time, an exposed worker must wear a self-contained breathing apparatus (SCBA) or a combination supplied-air respirator with auxiliary SCBA. ***For the purpose of this study, a safe waiting period before removing a spot-fumigation tarp was specified as the time needed for the methyl bromide air concentration under the tarp to reach 5 ppm or less.***

Though in disagreement with EPA's respirator requirement, air-purifying, organic vapor respirators have been recommended for use by workers exposed to methyl bromide during greenhouse fumigations[7,23] and plant quarantine activities in Japan.[24] Laboratory studies have shown that charcoal-containing, organic-vapor cartridges and canisters have brief breakthrough times when tested against methyl bromide.[24,25] Canisters containing activated carbon impregnated with triethylenediamine (TEDA) have shown longer breakthrough times than canisters containing activated carbon alone.[24] However, NIOSH-approved, air-purifying respirators with cartridges or canisters containing TEDA (i.e., MSA GMI-H, Scott 631-TEDA-H, and Survivair 1095-00) are not approved for methyl bromide. Because of methyl bromide's poor warning properties, an end-of-service-life indicator would be required as part of an air-purifying respirator submitted to NIOSH for certification testing, but presently none are certified for this use. Thus, only a SCBA or a combination device is recommended as protection against methyl bromide exposure.

Most published reports of human health effects following exposure to methyl bromide concern its use as an agricultural fumigant.[8,23,26-29] One author reviewed reports published between 1953 and 1981 describing 60 fatalities and 301 cases of systemic poisoning related to fumigant uses of methyl bromide.[26] A report was also published containing descriptions of six severe intoxications and four fatalities that occurred in California between 1957 and 1966 in the food processing industry. The products handled were nuts, fruits, and grains.[27] Air sampling for methyl bromide was not done in any work area. However, an exposure of 100 ppm was estimated from reconstructed conditions at two work sites.

Authors of two articles described exposure monitoring during soil fumigations in Belgian greenhouses.[23,28] Methyl bromide air concentrations ranged from 30 to 3,000 ppm. Soil injection of methyl bromide in closed areas (e.g., greenhouses) was prohibited in Belgium in 1979 after study results showed high exposures and severe poisoning symptoms in a dozen cases.[23]

A report was published describing the acute respiratory and neurologic symptoms of four unprotected workers who removed plastic tarps after a soil-injection application of methyl bromide.[8] The fumigant, 98% methyl bromide and 2% chloropicrin, had been applied ten days earlier to six acres at a rate of 350 pounds per acre. Though chloropicrin is meant to be a warning agent, the workers reported no immediate irritant symptoms or odor. The author concluded that 2% chloropicrin could not be relied on as a warning agent for methyl bromide. The report's author recommended that a SCBA be worn when methyl bromide exposures exceeded 5 ppm.

A report was published of a study of neurobehavioral functions in soil fumigators exposed to methyl bromide at an average air concentration of 2.3 ppm.[29] Soil fumigators reported a significantly higher prevalence of 18 symptoms consistent with methyl bromide toxicity than non-exposed workers. Also, fumigators did less well than non-exposed workers on 23 of 27 behavioral tests. They also did significantly less well on a finger sensitivity test and one of cognitive performance. The authors concluded that exposures to low levels of methyl bromide may produce slight neurotoxic effects.[29]

Replacement soil fumigants

Many of the world's atmospheric scientists believe that methyl bromide is an important ozone depleting chemical. The Montreal Protocol is an international treaty developed in the late 1980s to control world production and use of ozone-depleting chemicals. At the Ninth Meeting of the Parties to the Montreal Protocol in 1997, decisions were made that developed countries should stop using methyl bromide in 2005 and that developing countries should stop all use in 2015.[5] Under the Clean Air Act, EPA took steps to phase out methyl bromide use in the United States. In 1995, EPA froze U.S. production and importation at 1991 levels. Beginning in 1999, methyl bromide production and importation will be reduced gradually until 100 percent reduction occurs on January 1, 2005.[5] Quarantine, pre–shipment, and critical agricultural uses of methyl bromide are exempt from any control measures.

The approaching ban of methyl bromide caused PPQ management to evaluate replacement chemicals that will kill witchweed seeds. One soil fumigant considered was metam sodium (CAS number 137-42-8), also known by the trade names Vapam, Sectagon, and Arapam.[18] Most agricultural applications of metam sodium are classified as general use applications, except small area uses, which are classified as restricted use. Metam sodium exposure can cause skin, eye, and respiratory irritation.[18] Usually within a day after being injected into soil, metam sodium decomposes into hydrogen sulfide and methyl isothiocyanate, which diffuse to the surface and escape into the air.[30,31]

Both hydrogen sulfide and methyl isothiocyanate are chemical irritants.[31] Occupational exposure limits for hydrogen sulfide are a NIOSH REL 10-minute ceiling of 10 ppm, an OSHA PEL ceiling of 20 ppm with an acceptable maximum 10-minute peak of 50 ppm, and an ACGIH® TLV®-TWA of 10 ppm and a STEL of 15 ppm.[13,14,15] In 1998, ACGIH® proposed deleting the STEL and reducing the TLV®-TWA for hydrogen sulfide to 5 ppm.[14] Hydrogen sulfide's rotten egg odor can be smelled at concentrations of a few parts per billion.[21,32] Occupational exposure limits have not been determined for metam-sodium or methyl isothiocyanate. However, methyl isothiocyanate reportedly causes symptoms at concentrations below its odor threshold.[31]

Besides metam sodium, EPA's recommended alternatives to methyl bromide include 1,3-dichloropropene, dazomet, and chloropicrin.[5] NIOSH considers 1,3-dichloropropene a potential occupational carcinogen, and the NIOSH REL is 1 ppm with a skin notation.[12,13] Based on its irritation potential, the ACGIH® TLV-TWA for 1,3-dichloropropene is also 1 ppm with a skin notation.[14] OSHA does not have a PEL for 1,3-dichloropropene. No occupational exposure limits have been developed for dazomet.

EPA has reported that methyl iodide equals methyl bromide in controlling plant pathogens and weeds but that it would not adversely affect atmospheric ozone levels.[5] Though replacing methyl bromide with methyl iodide may benefit atmospheric ozone levels, the health risk to pesticide handlers may not change. Like methyl bromide, methyl iodide has poor warning properties.[19] Also, occupational exposure limits are lower for methyl iodide. Both the NIOSH REL and the ACGIH® TLV-TWA are 2 ppm with a skin notation.[12-14] NIOSH considers methyl iodide a potential occupational carcinogen.[12,13] The NIOSH immediately dangerous to life or health level is 100 ppm.[13] The OSHA PEL for methyl iodide is 5 ppm with a skin notation.[15] EPA has reported that an evaluation of methyl iodide's toxicity will be added to its methyl bromide phaseout web site when the information is available.[5]

Chloropicrin

Chloropicrin (CAS number 76-06-2) is a restricted use pesticide used as a soil and enclosure fumigant.[18] It is a colorless, oily liquid that is a severe irritant of the eyes, mucous membranes, skin, and lungs.[33] Chloropicrin causes eye irritation beginning at 0.3 to 0.4 ppm, and its odor threshold is approximately 1 ppm.[19,32,34] An air concentration as low as 1.3 ppm may cause respiratory irritation.[34] The NIOSH immediately dangerous to life or health level is 2 ppm.[13]

The NIOSH, OSHA, and ACGIH® exposure limits for chloropicrin are a TWA of 0.1 ppm.[12-15] EPA recommends that workers wear respiratory protection when chloropicrin exposures are 0.1 ppm or greater.[18] When this air concentration is exceeded, at any time, an exposed worker must wear an air-purifying, organic- vapor respirator, a SCBA or a combination supplied-air respirator with auxiliary SCBA.

Because chloropicrin is an irritant at low concentrations, it is added to odorless fumigants like methyl bromide to be a warning agent. However, "experience has shown that chloropicrin vapor may disappear before methyl bromide vapor and therefore the warning properties are lost."[20]

Table 1 was used by PPQ officers as guidance concerning the air concentrations of methyl bromide that equated to various air concentrations of chloropicrin and the expected responses to these chloropicrin exposures. The original source of this information is unknown, but the air concentrations of methyl bromide and chloropicrin are each exactly 98% and 2% of their total. This suggests that they may not have been determined by air sampling but that the methyl bromide values were back-calculated from those chloropicrin concentrations known to cause certain adverse responses.

RESULTS AND DISCUSSION

For the pilot study, two spot-fumigations were started on the morning of May 3, 1994, at a small farm near Evergreen, North Carolina. Air sampling was done on May 4 and 5, 1994. Ambient temperatures were cool, and temperatures under the two tarps ranged from 17°C (62°F) to 23°C (74°F). A light rain started on the evening of May 3 and ended the next morning. Despite the rain, soil under both tarps remained dry. Skies remained overcast through May 5.

Methyl bromide air concentrations under the pilot-study tarps were approximately 23,000 ppm and 26,000 ppm after 27 hours and 16,000 ppm and 18,000 ppm after 47 hours. All of the methyl bromide collected was on the first charcoal tube of each sampling train; none was found to have broken through to any of the backup tubes.

The six-tarp study began on August 25, 1994, at the Witchweed Methods Development Station in Little Rock, South Carolina. On most days of the 2-week study, the weather was sunny and hot with daytime temperatures in the 90s. A 2-hour thunderstorm brought a half-inch of rain on the evening of August 27, and an inch of rain fell during the ninth and tenth days of the study.

Because daytime temperatures under the tarps ranged from 49°C (120°F) to 60°C (140°F), air sampling results were corrected to a standard temperature of 25°C.[13,14] As with the pilot study air samples, all methyl bromide collected during the six-tarp study was on the first charcoal tube of each sampling train.

Table 2 shows the sampling results for the six-tarp study. Average methyl bromide air concentrations under the tarps range from 15,000 ppm, measured 24 hours after the start, to 50 ppm after 5 days. Average chloropicrin air concentrations range from 340 ppm, measured 15 minutes after the start, to 0.7 ppm after 5 days.

Data of Table 2 show that chloropicrin air concentrations declined steadily under intact tarps as the time after starting the spot fumigations increased. However, the methyl bromide air concentrations of Table 2 do not follow the same pattern. For example, the average methyl bromide air concentration after 6 hours (3,600 ppm) is less than the average concentration after 15 minutes (13,400 ppm), but the average concentration after 24 hours (15,000 ppm) is greater than either of these concentrations.

The most likely reason for the apparent discrepancy in the methyl bromide data concerns problems encountered with the shipment of the first set of samples. Methyl bromide samples collected on the first three days of the six-tarp study were collected on a Thursday, Friday, and Saturday. They were shipped together by express mail that Saturday evening for Sunday delivery. Unfortunately, they did not reach the NIOSH laboratory until Monday morning. By the time the cooler was opened, several tubes had warmed to room temperature. The problem caused by the delay in receiving the cooler was compounded by a leaking cold pack. The cold pack was apparently torn by the cooler's flip spout when the lid was screwed on. These problems demonstrate the importance of keeping methyl bromide samples cool and analyzing them as soon as possible after collection.

Because of sample-shipment problems, methyl bromide concentrations reported for 15 minutes, 6 hours, 24 hours, and 2 days after starting should be considered underestimates. When compared with the methyl bromide levels of the pilot study, the degree of underestimation may be the greatest for the samples collected at 15 minutes and 6 hours after the start.

Also shown in Table 2, methyl bromide measurements taken under three intact tarps at six days after starting are greater than any of those measured on the three previous days. Methyl bromide air samples taken at 5 and 6 days after the start were analyzed together as one set. The unexpectedly high concentrations may have resulted from a laboratory calculation error or an error in standard preparation. An unrecognized problem with the analytical method or some unusual field event is the least likely cause.

Plastic tarps having 6-mil thicknesses or greater meet the "high barrier" criterion of California EPA's Department of Pesticide Regulation.[35] To meet this criterion, a tarp "must have a permeability factor of less than 8 millimeters methyl bromide per hour, per square meter, per 1,000 ppm of methyl bromide under the tarp at 30°C."

Fifteen minutes after starting the six-tarp study, 30-minute methyl bromide measurements were taken directly above each of the six tarps, and the results ranged from none detected (one air sample) to 21 ppm. Like other methyl bromide measurements made on the study's first day, these air concentrations may also be underestimated. The limit of detection was 2 ppm.

After large-scale tarp applications of methyl bromide, California EPA requires that unprotected workers not enter an application area for a minimum of five days. After five days, workers are allowed to aerate a treated area by mechanically cutting tarps using a tractor-mounted cutting wheel. Twenty-four hours later, unprotected workers are allowed to remove the tarps.[35]

Twenty-four hours after cutting two spot-fumigation tarps, methyl bromide air concentrations of 80 ppm and 170 ppm were measured under sections of plastic. (Because of a problem with the methyl bromide samples collected six days after the start, these air concentrations may be overestimated.) Chloropicrin air concentrations under these tarps were 0.002 ppm and 0.003 ppm. These air concentrations were below the levels expected to warn that methyl bromide was present.

The day after removing a tarp, methyl bromide and chloropicrin were not detected directly above the soil. The limits of detection were 6 ppm for methyl bromide and 0.0002 ppm for chloropicrin. Using charcoal-tube air-sampling methods, methyl bromide and chloropicrin were also not detected under the three remaining intact tarps two weeks after starting the spot fumigations. The limits of detection for these samples were 7 ppm for methyl bromide and 0.0001 ppm for chloropicrin. However, detector tube sampling showed that low levels of methyl bromide were present at air concentrations less than 5 ppm.

CONCLUSIONS

After starting a spot fumigation, PPQ officers waited a minimum of 48 hours before removing a tarp. For the purpose of this study, a safe waiting period was specified as the time needed for methyl bromide air concentrations under a tarp to reach 5 ppm or less. Some of this study's methyl bromide measurements may have been affected by sample shipment or analysis problems. However, despite these problems, the results of methyl bromide measurements taken under tarps covering both packed and freshly-tilled sandy soil suggest that a level of 5 ppm or less will not likely be reached after 48 hours. Detector-tube measurements showed that methyl bromide levels did not decline to 5 ppm or less until two weeks had passed.

Methyl bromide measurements taken directly above tarps showed that the gas leaked through 6-mil plastic. This is unlikely to be an important health risk for PPQ officers, because they left a spot-fumigation site immediately after puncturing a can of methyl bromide. However, methyl bromide leakage through 6-mil tarps may be important to workers involved in large-scale tarp applications where acres of land are treated.

Workers have reported adverse health effects after removing spot-fumigation tarps, but they also reported no warning was received even though the fumigant contained chloropicrin.[8] During this study, residual air concentrations of methyl bromide were measured under tarps that had been cut 24 hours earlier. Thus, regardless of the size of the area treated, exposures to pockets of methyl bromide remaining under poorly aerated section of cut tarps should be considered a health risk for which no warning may occur.

RECOMMENDATIONS

The following recommendations are provided to improve the health and safety aspects of the PPQ spot-fumigation process:

• Because of a risk of exposure to methyl bromide and chloropicrin, PPQ officers should wait longer than 48 hours before removing spot-fumigation tarps. Because soil and environmental conditions encountered during spot fumigations will vary, a definite waiting period cannot be defined. However, a week or longer seems appropriate.

• Regardless of the time that has passed since starting a spot fumigation, PPQ officers should take detector tubes measurements before removing tarps to ensure that methyl bromide levels are less than 5 ppm.

• Chloropicrin should be relied upon as a warning agent for methyl bromide only at the start of a spot fumigation. This recommendation agrees with those of others who have reported that chloropicrin may not be detected or be present even though toxic levels of methyl bromide are present.[8,20,26]

• When evaluating other soil fumigants to replace methyl bromide, an important consideration should be the health risks associated with worker exposures to potential replacements and any warning agents.

REFERENCES

1. Anonymous [1991]. Witchweed overview. Gulfport, MS: U.S. Department of Agriculture, Animal and Plant Health Inspection Service.

2. Anonymous [1993]. Witchweed eradication: a cooperative effort. Raleigh, NC: North Carolina Department of Agriculture.

3. NIOSH [1996]. NIOSH health hazard evaluation report: U.S. Department of Agriculture, Animal and Plant Health Inspection Service, Plant Protection and Quarantine, Fayetteville, NC. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH Report No. HETA 94-0413-2560.

4. NIOSH [1992]. NIOSH health hazard evaluation closeout letter: Mr. Gary L. Clement, Regional Safety and Health Coordinator, U.S. Department of Agriculture, Animal and Plant Health Inspection Service, Gulfport, MS. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH Report No. HETA 92-0103.

5. EPA [1998]. Methyl bromide phaseout web site (http://earth1.epa.gov/ozone/mbr/mbrqa.html). U.S. Environmental Protection Agency.

6. Wheelwright J [1996]. The berry and the poison. Smithsonian. *27*(9):40–50.

7. Dead Sea Bromine Group [1992]. Methyl bromide for soil fumigation. Dead Sea Bromine Group, Makleff House, P.O. Box 180, Beer Sheva, Israel.

8. Herzstein J, Cullen MR [1990]. Methyl bromide intoxication in four field-workers during removal of soil fumigation sheets. Am J Ind Med *17*:321–326.

9. Gagnon Y, Ringenburg V, Fajen J [1994]. Problems with NIOSH method 2520 for methyl bromide. Appl Occup Environ Hyg *9*(3):165–167.

10. NIOSH [1996]. Methyl bromide: Method 2520. In Eller PM, Cassinelli ME, eds. First supplement to NIOSH manual of analytical methods (NMAM™). 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

11. National Draeger, Inc. [1992]. Dräger-tube handbook. Pittsburgh, PA: National Draeger, Inc.

12. NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) publication No. 92-100.

13. NIOSH [1997]. NIOSH pocket guide to chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 97–140.

14. ACGIH [1998]. 1998 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

15. 58 Fed. Reg. 35338 [1993]. Occupational Safety and Health Administration: Air contaminants; final rule.

16. 54 (12) Fed. Reg [1989]. Occupational Safety and Health Administration: Air contaminants; final rule.

17. de la Cruz PL, Sarvadi DG [1994]. OSHA PELs: Where do we go from here? Am Ind Hyg Assoc J *55*(10):894–900.

18. Sine C [1998]. Farm chemicals handbook. Vol. 84. Willoughby, OH: Meister Publishing Company, p. C 257.

19. ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

20. Torkelson TR, Rowe VK [1981]. Halogenated aliphatic hydrocarbons containing chlorine bromine and iodine. Chapter 48. In: Clayton GD, Clayton FE, eds. Patty's industrial hygiene and toxicology. 3rd rev. ed. Vol. IIB, Toxicology. New York, NY: Wiley-Interscience Publishers, pp. 3442–3446.

21. Ruth JH [1986]. Odor thresholds and irritation levels of several chemical substances: a review. Am Ind Hyg Assoc J *47*:A142–A151.

22. NIOSH [1978]. Occupational safety and health guidelines for chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 81-123.

23. Van Den Oever R, Roosels D, Lahaye D [1982]. Actual hazard of methyl bromide fumigation in soil disinfection. Br J Ind Med *39*:140–144.

24. Tanaka S, Abuku S, Imaizumi K, Ishizuka H, Seki Y, Imamiya S [1989]. Efficiency of respirator canisters with methyl bromide. Ind Health *27*:111–120.

25. Freedman RW, Ferber BI, Hartstein AM [1973]. Service lives of respirator cartridges versus several classes of organic vapors. Am Ind Hyg Assoc J *34*:55–60.

26. Alexeeff GV, Kilgore WW [1983]. Methyl bromide. Residue Rev *88*:101–153.

27. Hine CH [1969]. Methyl bromide a review of ten cases. J Occup Med *11*:1–10.

28. Roosels D, Van Den Oever R, Lahaye D [1981]. Dangerous concentrations of methyl bromide used as a fumigant in belgian greenhouses. Int Arch Occup Environ Health *48*:243–250.

29. Anger WK, Moody L, Burg J, Brightwell WS, Taylor BJ, Russo JM, et al. [1986]. Neurobehavioral evaluation of soil and structural fumigators using methyl bromide and sulfuryl fluoride. Neurotoxicology *7*:137–156.

30. van den Berg F [1993]. Measured and computed concentrations of methyl isothiocyanate in the air around fumigated fields. Atmospheric Environ. *27A*(1):63–71.

31. Kreutzer RA, Hewitt DJ, Sun R, Draper W, Mangiamele D, Goldman L, et al. [1996]. A community-based epidemiologic study of acute health effects from a metam-sodium spill on California's Sacramento River. Toxicol Environ Health *12*(2):267–275.

32. Amoore JE, Hautala E [1983]. Odor as an aid to chemical safety: odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. J Am Appl Toxicol *3*(6):272–289.

33. Hathaway GJ, Proctor NH, Hughes JP, Fishman ML, eds. [1991]. Proctor and Hughes' chemical hazards of the workplace. 3rd ed. New York, NY: Van Nostrand Reinhold Company, p. 174.

34. Ethyl Corporation. Methyl bromide. Baton Rouge, LA: Bromine Chemicals Division, Ethyl Corporation. (Publication date is unknown).

35. Andrews CM [1994]. Methyl bromide suggested soil injection fumigation permit conditions. Memorandum of May 2, 1994, from C.M. Andrews, California Environmental Protection Agency, to county agricultural commissioners.

Table 1. Information used by PPQ officers as guidance concerning the air concentrations of methyl bromide expected for various air concentrations of chloropicrin. (The source of this information is unknown.)

Air Concentration (ppm)			
Methyl Bromide	**Chloropicrin**	**Exposure Duration**	**Response**
15	0.3 - 0.4	3 - 30 seconds	eye irritation
54	1.1	----	odor detectable
64	1.3	----	respiratory irritation
196	4	a few seconds	unable to work
353	7.5	10 minutes	will not be tolerated
735	15	1 minute	will not be tolerated; injury to respiratory tract
5,880	120	30 minutes	lethal
14,700	300	10 minutes	lethal

Table 2. Methyl Bromide (CH_3Br) and chloropicrin (CCl_3NO_2) air concentrations (ppm) under the tarps of six spot-fumigation sites.

Time After Starting	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6		Average	
	CH_3Br	CCl_3NO_2	CH_3Br	CCl_3NO_2	CH_3Br	CCl_3NO_2	CH_3Br	CCl_3NO_2	CH_3Br	CCl_3NO_2	CH_3Br	CCl_3NO_2	CH_3Br	CCl_3NO_2
15 minutes(1)	14,800	270	17,100	360	8,200	------	11,800	210	13,500	220	15,200	660	13,400	340
6 hours(1)	2,900	84	4,000	120	3,400	57	4,300	60	3,900	62	3,300	26	3,600	68
24 hours(1)	13,900	24	16,400	26	16,500	21	15,800	18	14,700	26	12,800	14	15,000	22
2 days(1,2)	8,700	4.6	8,800	5.0	10,800	7.2	9,500	6.0	8,500	7.5	10,000	3.6	9,400	5.6
3 days	190	5.2	170	3.2	160	6.4	160	6.0	190	8.5	130	3.3	170	5.4
4 days	70	3.9	100	3.0	90	3.8	100	3.2	130	4.8	130	1.8	100	3.4
5 days	60	1.1	40	0.6	40	0.6	50	0.6	60	0.7	40	0.5	50	0.7
6 days(3)	ND(4,5)	ND(4,6)	800	1.0	80(7)	0.002(7)	640	0.9	170(7)	0.003(7)	610	0.05	680(8)	0.6(8)
2 weeks	-----	-----	ND(9)	ND(10)	------	-----	ND(9)	ND(10)	------	------	ND(9)	ND(10)	ND	ND

Notes:
ND means none detected.
1 - Because of sample-shipment problems, methyl bromide levels may be underestimates.
2 - One-half inch of rain fell between 7 and 9 PM.
3 - Because of a possible laboratory calculation error or an error in standard preparation, methyl bromide levels may be overestimated.
4 - Tarp removed completed 24 hours earlier. Samples taken directly above soil.
5 - Limit of detection was 6 ppm.
6 - Limit of detection was 0.0002 ppm.
7 - Tarp cut for aeration 24 hours earlier.
8 - Average of three intact tarps.
9 - Limit of detection for charcoal-tube sampling method was 7 ppm. Detector-tube sampling showed methyl bromide present at less than 5 ppm.
10 - Limit of detection was 0.0001 ppm.

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