ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA TO PESTICIDE PRODUCTS THAT CONTAIN CHLOROPICRIN

HS-1880

By

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ABBREVIATIONS AND ACRONYMS

ADD	Absorbed Daily Dosage
AADD	Annual Average Daily Dosage
AI	active ingredient
ARB	California Air Resources Board
CCR	California Code of Regulations
CFAC	California Food and Agriculture Code
CFR	Code of Federal Regulations
CV	coefficient of variation
DPR	California Department of Pesticide Regulation
EAD	Exposure Assessment Document
EC	emulsifiable concentrate
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
ISCST3	Industrial Source Complex Short Term model, Version 3
LADD	Lifetime Average Daily Dosage
LOD	limit of detection
LOQ	limit of quantification
OSHA	Occupational Health and Safety Administration
PISP	Pesticide Illness Surveillance Program
PPE	personal protective equipment
PUR	Pesticide Use Report
REI	restricted entry interval
RUP	Restricted Use Pesticide
SADD	Seasonal Average Daily Dosage
TWA	time-weighted average
U.S. EPA	U.S. Environmental Protection Agency
WPS	Worker Protection Standard

ABSTRACT

This document summarizes available information, data and calculations of exposures related to uses of chloropicrin in California. Exposure estimates reported in this document are used in the chloropicrin risk characterization document prepared by the California Department of Pesticide Regulation. Although individuals might potentially be exposed to a range of chloropicrin concentrations, for screening risk assessment purposes the highest realistic exposures are reported in this exposure assessment (if screening estimates lead to acceptable risk in the risk assessment, then lower exposures will as well).

Chloropicrin is a fumigant used in California for pre-plant soil fumigations and structural fumigations. It may be used alone or mixed with other fumigants such as methyl bromide, methyl iodide, and 1,3-dichloropropene. When mixed with other fumigants, chloropicrin may be considered either as an active ingredient (AI) contributing to pest control, or in smaller amounts as a warning agent to alert individuals in the area to the presence of other fumigants, some of which are odorless. Primary toxic effects that have been associated with exposure to chloropicrin vapor include irritation to eyes and respiratory tract.

Exposures were estimated for bystanders (individuals near an application site but not directly involved with the application), for individuals handling chloropicrin during a fumigation or breaching tarps to aerate a fumigated area, and for persons reentering a fumigated area. Exposure estimates are provided for short-term (defined as durations from a day or less, and up to one week) and, where appropriate, for seasonal (intermediate-term intervals, lasting from one week to one year), annual, and lifetime exposures. Short-term exposures were estimated for 1-hour durations because chloropicrin irritation occurs rapidly, and 1 hour is the shortest duration for which toxicity endpoints and concentrations can reasonably be estimated. The highest concentrations are associated with 1-hour durations.

Exposures of bystanders to soil fumigation were estimated from concentrations based on air dispersion modeling of direct flux measurements during application site monitoring. The 1-hour exposure estimate is 75,000 $\mu g/m^3$ (11,000 ppb). Exposures of bystanders adjacent to a structural fumigation with chloropicrin as a warning agent were based on monitoring conducted during structural fumigations. The 1-hour exposure estimate is 244 $\mu g/m^3$ (36.2 ppb).

Residential reentry exposures were estimated from indoor air monitoring following fumigation and aeration; exposure was estimated to be 3,060 $\mu g/m^3$ (456 ppb) for a 1-hour duration for individuals returning to fumigated structures.

Occupational exposure estimates were calculated from chloropicrin concentrations measured in exposure monitoring and air monitoring studies. Occupational exposure scenarios associated with soil fumigations were calculated separately for each application method, and further grouped into three categories: exposure to chloropicrin as an AI (involving products containing chloropicrin concentrations above 2%); exposure to chloropicrin as a warning

agent (involving products containing chloropicrin concentrations between 0.25% and 2.0%); and exposure to chloropicrin resulting from use of Methyl Bromide 89.5% (which contains 10.5% chloropicrin). Methyl Bromide 89.5% is considered separately because it was registered with chloropicrin labeled as a warning agent rather than an AI; however, exposure to chloropicrin associated with use of this product is anticipated to be greater than from use of other products containing chloropicrin as a warning agent.

Handlers involved in soil fumigation with chloropicrin as an AI had 1-hour exposure estimates ranging from 52.4 $\mu g/m^3$ (7.79 ppb) for tarp punchers associated with surface drip tarped irrigation applications to 15,500 $\mu g/m^3$ (2,310 ppb) for tarp removers finishing broadcast tarped shank applications. Reentry workers following applications of chloropicrin as an AI had 1-hour exposure estimates ranging from 49.9 $\mu g/m^3$ (7.42 ppb) for pipe layers following shallow non-tarped bedded shank applications to 279 $\mu g/m^3$ (41.4 ppb) for soil shapers following broadcast tarped shank applications.

Handlers involved in applications of Methyl Bromide 89.5% had 1-hour chloropicrin exposure estimates ranging from 4.60 $\mu g/m^3$ (0.684 ppb) for tarp punchers associated with tarped drip applications to 2,060 $\mu g/m^3$ (307 ppb) for tarp removers finishing broadcast tarped shank applications. Reentry workers had 1-hour exposure estimates ranging from 60.7 $\mu g/m^3$ (9.02 ppb) for soil shapers following broadcast tarped shank applications to 263 $\mu g/m^3$ (39.1 ppb) for soil shapers following non-tarped deep broadcast shank applications.

Handlers involved in soil fumigation with chloropicrin as a warning agent had 1-hour exposure estimates ranging from 0.800 $\mu g/m^3$ (0.119 ppb) for tarp punchers associated with tarped drip applications to 362 $\mu g/m^3$ (53.8 ppb) for tarp removers finishing broadcast tarped shank applications. Reentry workers following soil fumigation with chloropicrin as a warning agent had 1-hour exposure estimates ranging from 10.6 $\mu g/m^3$ (1.57 ppb) for soil shapers following broadcast tarped shank applications to 45.7 $\mu g/m^3$ (6.80 ppb) for soil shapers following non-tarped deep broadcast shank applications.

Occupational 1-hour exposures associated with structural fumigation in which chloropicrin was used as a warning agent ranged from 43.0 ppb for reentry following fumigation to 8,370 ppb for applicators pouring chloropicrin into a pan at the start of a fumigation. Exposures were based on air monitoring conducted in association with structural fumigations.

INTRODUCTION

Chloropicrin (trichloronitromethane) is used as either a fumigant or a warning agent. As a fumigant, chloropicrin is used alone or mixed with other fumigants (e.g., methyl bromide, 1,3-dichloropropene). In fumigation, pesticide gas completely fills an area, such as a building or soil in a field, and poisons targeted pests. Chloropicrin controls soil pathogens, certain weeds, and nematodes that adversely affect crops such as strawberries (Duniway, 2002).

As a warning agent, chloropicrin is combined in relatively low concentrations with a fumigant such as methyl bromide, methyl iodide, or sulfuryl fluoride. A warning agent is a chemical with good warning properties, including odor or irritation, that can be mixed with other chemicals to allow an average person with normal sensory perception to detect the presence of the warning agent at concentrations below which both chemicals produce adverse effects (NIOSH, 1987). Chloropicrin causes transient eye and mucous membrane irritation at relatively low concentrations. As a warning agent, chloropicrin is intended to protect individuals from potentially serious injuries that exposure to a less-detectable fumigant might cause.

The California Department of Pesticide Regulation (DPR) prepared this Exposure Assessment Document (EAD), its first addressing both occupational and bystander exposures to chloropicrin. This EAD estimates potential exposures to chloropicrin resulting from its use as a pesticidal active ingredient (AI). Additionally, it contains sections that discuss potential exposures due to chloropicrin use as a warning agent. An exposure assessment addressing bystander and other public exposures to chloropicrin was prepared earlier as part of the determination whether chloropicrin meets the criteria to be listed as a toxic air contaminant (Beauvais, 2010a). This EAD is intended to addresses occupational scenarios that as well as those included in Beauvais (2010a), using current product labels and approaches to estimating exposure. Product labels approved in California in Fall 2010 allow lower maximum application rates than previous labels, and some scenarios have been changed (e.g., potting soil fumigation and enclosed space fumigation are no longer allowed for 100% chloropicrin). The label changes are reflected in this EAD.

Previously, DPR has prepared EADs for four fumigants that are mixed with chloropicrin: 1,3-dichloropropene, sulfuryl fluoride, methyl bromide, and methyl iodide (Sanborn and Powell, 1994; Thongsinthusak and Haskell, 2002; Cochran and DiPaolo, 2005; Cochran and Frank, 2010). Exposure assessments for these other fumigants do not address exposures to chloropicrin.

DPR is charged with protecting individuals and the environment from potential adverse effects that may result from the use of pesticides in the State. This is codified in the California Food and Agricultural Code (CFAC), Sections 11501, 12824, 12825, 12826, 13121-13135, 14102, and 14103. As part of DPR's effort to meet this mandate, pesticide AIs are prioritized for assessment of exposure and risk potential. A description of the risk prioritization process can be found at DPR's website (http://www.cdpr.ca.gov/docs/risk/raprocess.pdf). When comprehensive risk assessments are initiated for particular AIs, the evaluations are conducted in accordance with California Code of Regulations Title 3, Section 6158 (3 CCR 6158).

Under California law, all pesticide products submitted for registration must be evaluated; the evaluation includes data submitted for acute and chronic health effects (3 CCR 6158). On October 16, 2001, DPR placed all products containing chloropicrin into reevaluation (Cortez, 2001), pursuant to California regulation (3 CCR 6220). The reevaluation decision was based on data suggesting that chloropicrin had the potential to cause adverse health effects at low doses.

The mode of toxic action of chloropicrin is not well characterized. Chloropicrin causes irritation and localized cellular lesions, and available data suggest that these might occur following reaction of chloropicrin with various thiol proteins (i.e., proteins with a sulfhydryl (–SH) functional group), including certain dehydrogenases that have critical sulfhydryl groups in their active sites (Sparks *et al.*, 2000).

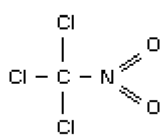
U.S. EPA STATUS

The U.S. Environmental Protection Agency (U.S. EPA) classified chloropicrin as a Toxicity Category I pesticide for acute oral, dermal, and inhalation toxicity (Reaves and Smith, 2008). Due to acute inhalation toxicity, all products containing more than 2% chloropicrin are classified by U.S. EPA as Restricted Use Pesticides (RUPs), which may only be used under the supervision of a certified applicator (Title 40 Code of Federal Regulations (40 CFR), Section 152.175). In July 2008, U.S. EPA released its final revised human health risk assessment and the Reregistration Eligibility Decision for chloropicrin (Reaves and Smith, 2008; U.S. EPA, 2008). An amended risk assessment and an amended Reregistration Eligibility Decision were issued in May 2009 (Smith and Reaves, 2009; U.S. EPA, 2009).

PHYSICOCHEMICAL PROPERTIES

Chloropicrin has a molecular weight of 164.38, and a molecular formula of CCl_3NO_2. Its CAS Number is 76-06-2. The chemical structure is shown in Figure 1.

Figure 1. Chloropicrin Chemical Structure.



Several physical and chemical properties of chloropicrin are listed in Table 1. The melting and boiling points indicate that chloropicrin is a liquid under typical use conditions. Chloropicrin is quite volatile (suggesting that inhalation is the major route of exposure) and highly water-soluble. It is non-flammable, and has a vapor density of 5.7, compared to the reference value of 1.0 assigned to air (Meister and Sine, 2003).

The log K_{ow} for chloropicrin is reported as 2.43 (Secara, 1991). Voliva (1987) reported a vapor pressure of 23.2 mm Hg at 25°C. The Henry's Law constant, based on these values, is 2.51×10^{-3} atm-m^3/mole (calculated by DPR's Environmental Monitoring Branch, internal database). Worthington and Wade (2007) reported an empirical Henry's Law constant of 2.1×10^{-3} atm-m^3/mole, measured with a stripping method in which nitrogen was bubbled through a saturated chloropicrin solution in deionized water maintained at 25°C.

Table 1. Physical and Chemical Properties of Chloropicrin

Chemical Property [a]	Value
Melting Point (°C)	-64
Boiling Point (°C)	112
Density (g/ml)	1.656
Water Solubility (mg/L, 25°C)	2,000
Octanol/Water Partition Coefficient	269
Vapor Pressure (mm Hg, 25°C)	23.2
Vapor Density	5.7
Henry's Law Constant (atm-m^3/mole, 25°C)	0.00251
Flash Point	None

[a] California Department of Pesticide Regulation's Pesticide Chemistry Database; Ariano (1987); Voliva (1987); Secara, 1991; Sparacino (1994); Meister and Sine (2003).

Chloropicrin concentrations reported in μg/m^3 can be converted to equivalent concentrations in parts per billion (ppb), expressed as ratio of volume of chloropicrin to volume of air, using the ideal gas law. At 1 atmosphere of pressure and a temperature of 25°C, the concentration in ppb is equal to the concentration in μg/m^3, multiplied by 24.45 liter-atm/mole and divided by the molecular weight of 164.38 g/mole. As 24.45/164.38 = 0.1487, this value can be multiplied by the concentration in μg/m^3 to obtain the concentration in ppb.

FORMULATIONS AND USES

As of December 2011, there are 55 registered products containing chloropicrin in California, including seven products intended solely for manufacturing or reformulation use and six products where chloropicrin is used as a warning agent (Table 2). Chloropicrin-containing products are available in both pressurized and non-pressurized containers, as compressed liquids in cylinders or liquid solutions containing emulsifiers. Many are mixtures with methyl bromide, methyl iodide, or 1,3-dichloropropene. Three products, including two mixtures with 1,3-dichloropropene (Telone C-17 CA, EPA Reg. No. 62719-12-ZB, and Telone C35 CA, EPA Reg. No. 62719-302-ZA) and a methyl bromide product with chloropicrin as a warning agent (Methyl Bromide 99.5%, EPA Reg. No. 8536-12-ZA), are in the process of being inactivated. With the exception of these three products, new labels were approved for all products in September through December 2010, and this EAD reflects the new labels.

Table 2 summarizes products available for agricultural and structural use in California. The seven products intended solely for manufacturer use are omitted from Table 2 because manufacturing uses are not regulated by DPR. In structural fumigations, chloropicrin is only used as a warning agent.

Pre-plant soil fumigation is done for many crops, using injection equipment or drip irrigation (six methyl bromide products, containing between 0.5% and 10.5% chloropicrin, have directions for hot gas fumigation; otherwise, chemigation is via cold gas methods). DPR (2004) describes three main types of pre-plant soil fumigation: broadcast fumigation (where the application of a pesticide occurs uniformly over the area to be treated without regard to arrangement of crops as in rows); strip fumigation (applications that have alternating fumigated and unfumigated areas, often with prior or subsequent fumigation of the unfumigated areas); and bed fumigation (where pre-formed beds are fumigated and the furrows are not). For both strip and bed fumigations, application rates refer only to treated areas; for example, if the maximum application rate is 350 lbs AI/acre (393 kg/ha), and a strip or bed fumigation of a field results in treatment of only 50% of a field in a particular application, then the rate to the field is decreased by 50% to 175 lbs AI/acre (DPR, 2004). This effective broadcast rate is calculated by dividing the mass of AI applied by the area of the entire field, including both treated and untreated areas.

Table 2. Chloropicrin-Containing Products in California as of December 2011

Active Ingredient [a]	Number of Products [b]	Chloropicrin Concentration Range (%)	Fumigation Type [c]	Number of Products with Greenhouse Uses [d]
Methyl Bromide	22	0.5 – 55	Soil/Structural [e]	22
Chloropicrin 0.5 – 2.0% [f]	(5)	0.5 – 2.0	Soil/Structural	(5)
Chloropicrin 10.5% [f]	(1)	10.5	Soil	(1)
Chloropicrin 19.8 – 67%	(16)	19.8 – 67	Soil	(16)
Methyl Iodide	4	2 – 67	Soil	0
1,3-Dichloropropene	13 [g]	15 – 60	Soil	1
Chloropicrin as sole AI	8	94 – 100	Soil/Structural [h]	7
Total	47			

[a] Active ingredient (AI) in addition to chloropicrin.
[b] Seven products intended for manufacture use only (i.e., no pesticidal uses) were omitted.
[c] Soil may be fumigated outdoors (e.g., pre-plant fields or replant tree holes), or indoors in greenhouses unless specifically prohibited.
[d] Includes products where greenhouse use is not specifically prohibited by product label. In most cases, specific instructions are provided for soil fumigation in greenhouses.
[e] One methyl bromide product, containing chloropicrin at 0.5% concentration, gives directions for structural, transport, and space fumigation. This product is in the process of being inactivated.
[f] In these products, chloropicrin is considered a warning agent, and is listed on the label as an "other ingredient" or an "inert ingredient." Chloropicrin at higher concentrations is listed as an active ingredient.
[g] Two of these products are expected to become inactive in 2011.
[h] Sulfuryl fluoride product labels provide instructions for using chloropicrin as a warning agent, which is required for sulfuryl fluoride structural fumigations. Four of the nine chloropicrin product labels contain a statement referring to sulfuryl fluoride labels for warning agent directions in structural fumigations.

Crops for which some chloropicrin-containing products are registered as pre-plant fumigants include asparagus, broccoli, cauliflower, eggplant, grapes, lettuce, melons, onions, peppers, pineapple, strawberries, tomatoes, floral crops, nursery crops, and fruit and nut crops. In addition, some products have instructions for fumigation of potting soil, mushroom casing soil, greenhouse beds, seedbeds and seed flats.

Chloropicrin as a Warning Agent

When used as a warning agent in a methyl bromide product, the chloropicrin concentration in the product is typically less than or equal to 2%. The exception is a product containing 10.5%

chloropicrin as a warning agent. When chloropicrin is used as a warning agent for sulfuryl fluoride in structural fumigation, the two chemicals are handled separately; chloropicrin may also be handled separately as a warning agent for structural fumigation with methyl bromide. Warning agents are not typically included when commodity fumigations are done with methyl bromide or sulfuryl fluoride, and no chloropicrin-containing products are registered for use in commodity fumigations (U.S. EPA, 2005a). Methyl bromide products containing chloropicrin as a warning agent are included in Table 2.

PESTICIDE USE AND SALES

California requires reporting of all agricultural applications of pesticides, as well as other uses when pesticides are applied by a licensed applicator. These data are collected in the Pesticide Use Report (PUR) database. In 2008, reported uses of all pesticide active ingredients in California totaled 161,531,202 pounds (73,423,274 kg; DPR, 2009). Chloropicrin accounted for 5,543,140 pounds (2,519,609 kg), or 3.4%, of the total. Table 3 summarizes PUR data for chloropicrin in the most recent 5-year interval available, based on pounds AI applied.

Table 3. Chloropicrin Use in California, 2004 – 2008

Use Site	Pounds Applied [a]				
	2004	2005	2006	2007	2008
Soil fumigation, pre-plant [b]	5,110,119	4,862,466	5,017,305	5,488,746	5,537,727
• Strawberries	3,258,348	3,182,417	3,236,844	3,408,331	3,643,946
• (Strawberry % of soil) [c]	(63.8%)	(65.4%)	(64.5%)	(62.0%)	(65.7%)
• Tree crops [d]	34,363	38,403	23,342	68,762	74,481
Commodity fumigation [e]	1,048	396	359	734	2,058
• Non-research commodity [f]	5	0	0	0	921
Turf/Sod	12,618	40,008	4,913	15,911	2,196
Structural Pest Control	6,540	2,093	1,126	4,316	1,260
Total Pounds Used	5,110,119	4,864,930	5,018,831	5,494,541	5,543,140
Soil fumigation % of total [g]	99.5%	99.9%	100%	99.9%	99.9%

[a] From DPR (2006a; 2006b; 2007; 2008; 2009). Multiply values by 0.455 to get use in kg applied. Average use during 5-year interval: 5,211,366 lbs (2,368,803 kg).
[b] Includes all use listed under specific crops, as well as non-specific pre-plant fumigations. Totals include applications to strawberries and tree crops, which are also listed separately for the reasons given below.
[c] Percent of chloropicrin use for pre-plant soil fumigation reported in strawberry beds or fields. Pre-plant soil fumigation for strawberries is the greatest single use of chloropicrin.
[d] Tree crops can be fumigated by handwand as well as by other soil fumigation methods.
[e] Includes commodity fumigation done for research purposes.
[f] Use reported for commodity fumigation, but not reported as research.
[g] Percent of total reported chloropicrin use that was due to pre-plant soil fumigation.

Table 3 shows that more than 99% of chloropicrin use is for pre-plant soil fumigation. The greatest use during these five years was identified as being in strawberry fields, which accounted for an average of about 64% of total chloropicrin use. Additionally, strawberry fields could account for some of the use reported simply as "pre-plant soil fumigation," in which no specific crop was identified. The top five counties in which chloropicrin was used in the 5-year interval 2004 – 2008 were Ventura, Monterey, Santa Barbara, Santa Cruz, and Siskiyou; together, they accounted for 78% of statewide use (DPR, 2010a).

California collects a fee for all pesticides sold in the state (Mill Assessment sales data). The 2008 Mill Assessment sales data indicate that a total of 11,257,576 pounds (5,117,080 kg) of chloropicrin was sold in California, compared to a total of 728,545,540 pounds (331,157,064 kg) of all AIs (DPR, 2010b). Thus, chloropicrin accounted for about 1.5% of pesticide sales in 2008. For many reasons, the amount of chloropicrin (or of any AI) sold in a single year would not necessarily equal the amount used. For example, pesticides sold in one year may be used in a later year or over multiple years, or might remain in storage. Between 2004 and 2008, annual sales of chloropicrin ranged from 4,301,992 pounds (1,955,451 kg) sold in 2005 to 12,664,972 pounds (5,756,805 kg) sold in 2006; an average of 6,978,012 pounds (3,171,824 kg) was sold during the 5-year interval. In contrast, average chloropicrin use reported during the interval was 5,211,366 pounds (2,368,803 kg).

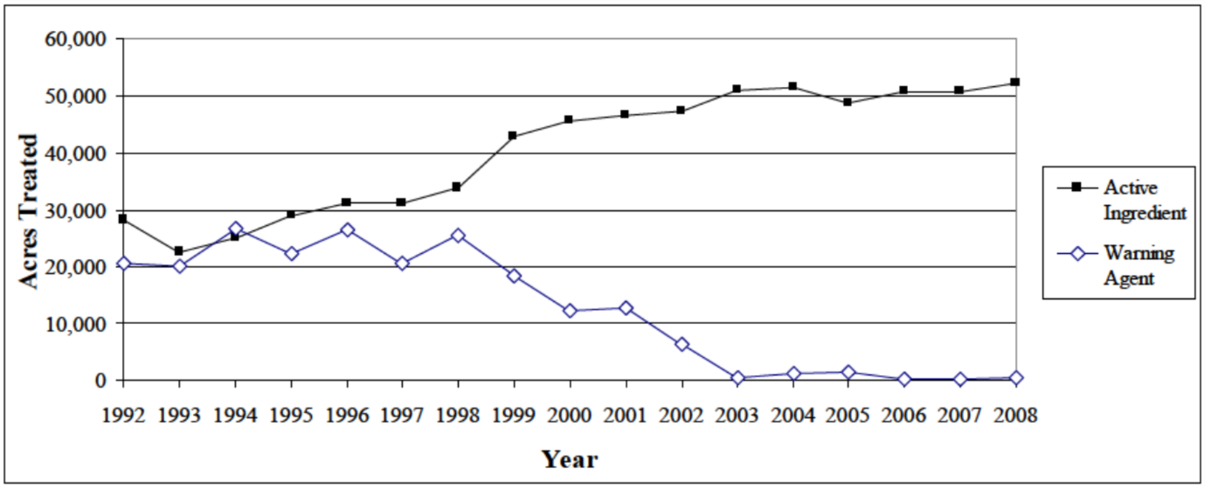
Chloropicrin as a Warning Agent

A query of the PUR database by percent chloropicrin in reported products allowed an estimate of how much agricultural chloropicrin use involved chloropicrin as a warning agent rather than as an AI (DPR, 2010a). Figure 2 summarizes PUR data for chloropicrin applied for agricultural uses. Only uses reported as agricultural (rather than non-agricultural) are included in Figure 2, which summarizes uses reported as acres treated (other uses, reported as square feet treated, or miscellaneous treatments such as bins or tree holes, were omitted). These uses include the majority of soil fumigant treatments involving chloropicrin. In Figure 2, applications of products containing 0.5 – 2.0% chloropicrin were classified as “warning agent” chloropicrin uses, and applications of products containing more than 2.0% chloropicrin were considered “active ingredient” uses. Both the decrease in warning agent uses and the increase in active ingredient uses are almost certainly related to the decrease of methyl bromide use occurring as a result of the federally-mandated phase-out of methyl bromide use (U.S. EPA, 1993).

REPORTED ILLNESSES

DPR’s Worker Health and Safety Branch (WHS) includes a Pesticide Illness Surveillance Program (PISP). PISP maintains a database of all reports of illness and injury potentially related to pesticide exposure in California. The PISP database contains information about the nature of the pesticide exposure and the subsequent illness or injury. DPR uses the database to identify high-risk situations and to evaluate the effectiveness of DPR's pesticide safety regulatory programs (WHS, 2007).

Figure 2. Chloropicrin Agricultural Uses in California Reported as Acres Treated [a]



[a] Acres treated annually, statewide, with chloropicrin-containing products in which chloropicrin is up to 2.0% of product formulation (warning agent) or more than 2.0% (active ingredient). Data summarized from the Pesticide Use Report (PUR) database (DPR, 2010a). Only agricultural uses are included, and only those uses reported in the PUR database by acres treated (pounds chloropicrin applied would vary between products). To convert acres to hectares (ha), multiply value by 0.405.

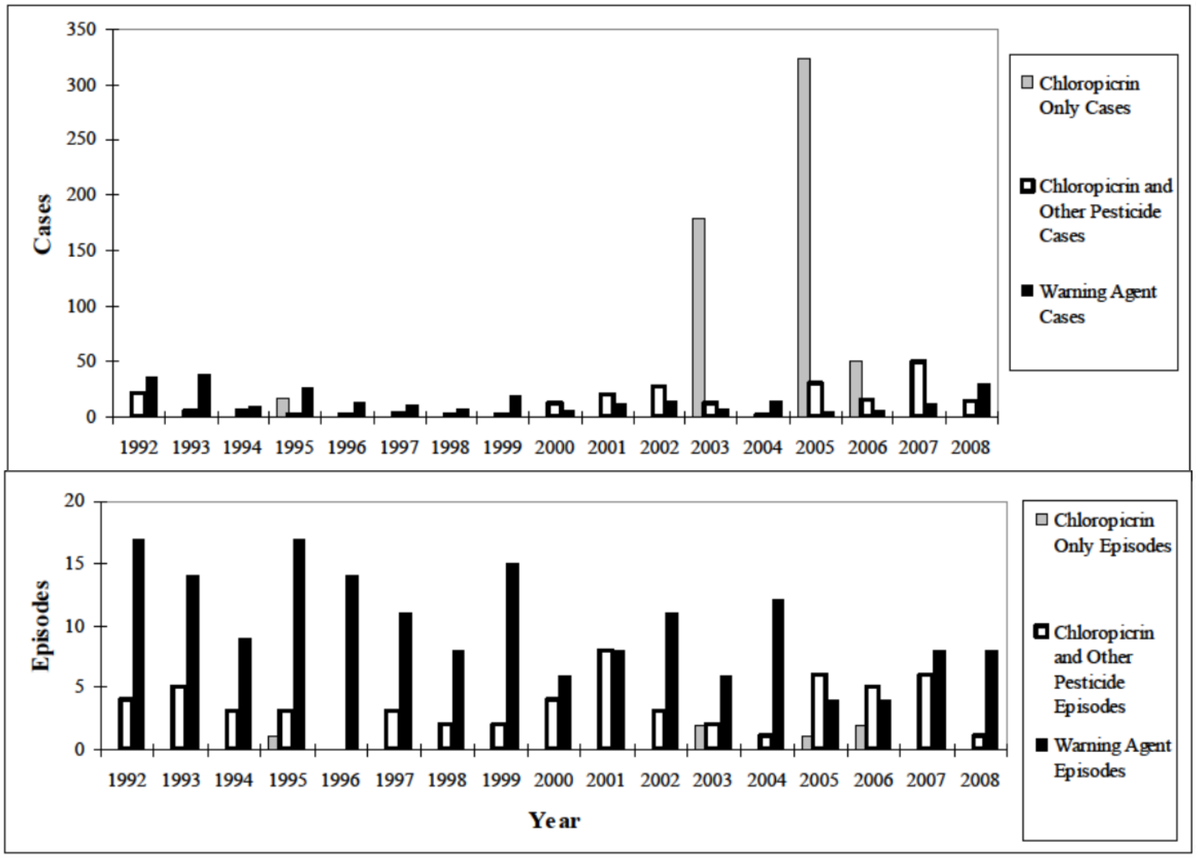
PISP defines a "case" as the program's representation of a pesticide exposure and its apparent effects on one individual's health (WHS, 2007). PISP scientists evaluate investigations of each case and record a qualitative assessment of the likelihood that pesticide exposure caused or contributed to the reported symptoms. Cases are considered to be associated with exposure to a pesticide as follows: they are evaluated as "definite" (both physical and medical evidence support exposure and consequent health effects), "probable" (incomplete or circumstantial evidence supports a relationship to pesticide exposure) or "possible" (available evidence neither supports nor contradicts a relationship). When the weight of evidence is against pesticide contribution to health effects, scientists may classify cases as "unlikely," "indirect," "asymptomatic," or "unrelated." They also have the option of declining to classify cases that lack critical information.

PISP defines an "episode" as an incident in which one or more people experience pesticide exposure from a particular source with subsequent development or exacerbation of symptoms. Occasionally, a single episode gives rise to a large number of cases.

Figure 3 summarizes numbers of chloropicrin-associated cases and episodes reported annually. The two largest chloropicrin-related episodes occurred in Kern County in 2003 and in Monterey County in 2005. The 2003 Kern County episode resulted in 165 illness reports (O'Malley *et al.*, 2004a; DPR, 2005b; Oriel *et al.*, 2009). In this incident, 100% chloropicrin was applied over two days to fallow land near a residential area, with a buffer zone of about 18 m; the chloropicrin was injected about 0.4 – 0.5 m into the soil. Applicators dragged a weighted board behind the tractor in an attempt to confine the fumigant without compacting the soil excessively. Each of the two evenings, nearby residents complained about eye and throat irritation, although the source of the irritation, was not located until the second evening.

Firefighters responding to the complaints also experienced eye irritation. The irritation ceased after the soil was compacted a second time.

Figure 3. Numbers of Illnesses (Cases) and Episodes Reported in California, 1992 –2008, Evaluated by the California Pesticide Illness Surveillance Program as Definitely, Probably, or Possibly Related [a] to Chloropicrin Exposure or That Were Associated with or Indirectly Related to Fumigants with Chloropicrin as a Warning Agent



[a] "Definite" means that both physical and medical evidence document exposure and consequent health effects, "probable" means that limited or circumstantial evidence supports a relationship to pesticide exposure, and "possible" means that evidence neither supports nor contradicts a relationship (Mehler, 2010). More than one case can be associated with each episode.

The 2005 Monterey County episode resulted in 324 cases (WHS, 2007). In this episode, following a tarped bedded application of a 94% chloropicrin product through a drip irrigation system, the system was flushed by an apparently inadequate amount of water. Additionally, chloropicrin was also emitted by the application itself (Barry *et al.*, 2010). In the evening, residents living near the application, and up to 2 or 3 miles away, complained of odor and eye irritation.

From 1992 through 2008, PISP identified chloropicrin as the sole implicated pesticide in six California episodes involving 571 people and as one of two or more fumigants that may have contributed to another 58 episodes that gave rise to 218 cases (Mehler, 2010). All of these episodes involved agricultural soil fumigations. The fumigant combinations included three episodes (13 cases) involving the product Methyl Bromide 89.5%, which contains chloropicrin 10.5% as a warning agent. Because the chloropicrin concentration in this product is >2%, illnesses associated with this product are considered to be potentially associated with chloropicrin for illness investigation and tracking purposes. This is consistent with U.S. EPA's designation of products containing more than 2% chloropicrin as Restricted Use Pesticides (40 CFR 152.175).

Exposure to chloropicrin used only as a warning agent was identified in 172 episodes that gave rise to 260 cases. Chloropicrin's function was not identified unequivocally in ten cases, each a separate episode; based on their circumstances, these cases were presumed to relate to warning agent use. Of these 270 cases, 57 involved agricultural use. All but seven of the other 213 cases related to structural fumigations. The seven cases involved (non-agricultural) commodity fumigations and transportation of used pesticide containers.

Of the 571 people exposed to chloropicrin alone, 557 (including four applicators) experienced airborne exposure and 14 entered chloropicrin-contaminated areas after the application concluded. The 218 people exposed to chloropicrin combined with other fumigants included 22 applicators and two people ("mechanics") working on pesticide-contaminated equipment. Eight of the pesticide handlers had direct contact with the fumigants. One "mechanic" and 44 applicators were among the 270 people exposed to chloropicrin used as a warning agent with other fumigants. All the other exposed people were essentially bystanders, including some who acted in a professional capacity (emergency responders, agricultural investigators), and some who traveled through the affected area in vehicles.

Table 4 summarizes the types of illnesses attributed to chloropicrin, to other fumigants used with chloropicrin, or evaluated as indirectly related to fumigant exposure. An indirect relationship indicates that protective measures required by pesticide regulations or a pesticide product label, rather than pesticide exposure, caused or contributed to health effects. (An example of an indirect relationship would be heat stress caused by wearing chemical resistant clothing while handling a pesticide for which such clothing is required.) When used as a warning agent, chloropicrin is considered a protective measure relative to the fumigants with which it is used. Table 4 suggests the prominence of eye effects among people exposed to chloropicrin. Figure 4 further clarifies the relationship between chloropicrin concentration and prevalence of eye effects.

Of the 1,059 cases summarized in Table 4, a total of 591 (or 56%) reported symptoms from more than one of the coded categories (eye, skin, respiratory, and systemic). Figure 4 summarizes the percentage of cases reporting each symptom type. The dominance of eye effects is especially notable in illnesses associated with chloropicrin alone. Eye effects, including irritation, burning, itching and watery eyes, were reported in 834 (79%) of all cases, but in 547 of 571 (96%) of chloropicrin-only cases. In contrast, eye effects were reported in just 160 of 218 (73%) cases associated with chloropicrin in combination with other fumigants, and only 127 of 270 (47%) cases associated with chloropicrin as a warning agent reported eye effects.

Table 4. Types of Illness Cases Reported in California (1992 – 2008) [a]

Illness Type [b]	Alone [c]	In Combination [d]	As Warning Agent [e]	Total
Eye only	246	50	21	317
Eye & Respiratory	126	46	26	198
Eye, Respiratory & Systemic	94	31	38	163
Eye & Systemic	75	24	18	117
Systemic	10	17	52	79
Respiratory & Systemic	4	19	40	63
Respiratory	10	16	17	43
Skin	0	4	25	29
Other combinations of types [f]	6	11	33	50
Total	571	218	270	1,059

[a] Illness cases that were potentially associated with chloropicrin exposure or that were associated with or indirectly related to fumigants with chloropicrin as a warning agent. "Definite" means that both physical and medical evidence document exposure and consequent health effects, "probable" means that limited or circumstantial evidence supports a relationship to pesticide exposure, and "possible" means that evidence neither supports nor contradicts a relationship (Mehler, 2010).

[b] Eye effects include irritation, burning, itching and watery eyes. Respiratory illnesses include irritation of nose, throat, and lungs; coughing; wheezing; lung congestion; asthma and other breathing difficulties. Systemic illnesses include symptoms such as nausea, dizziness, headache, numbness. Skin effects include itching, rashes, and burns.

[c] Chloropicrin was applied as a sole active ingredient.

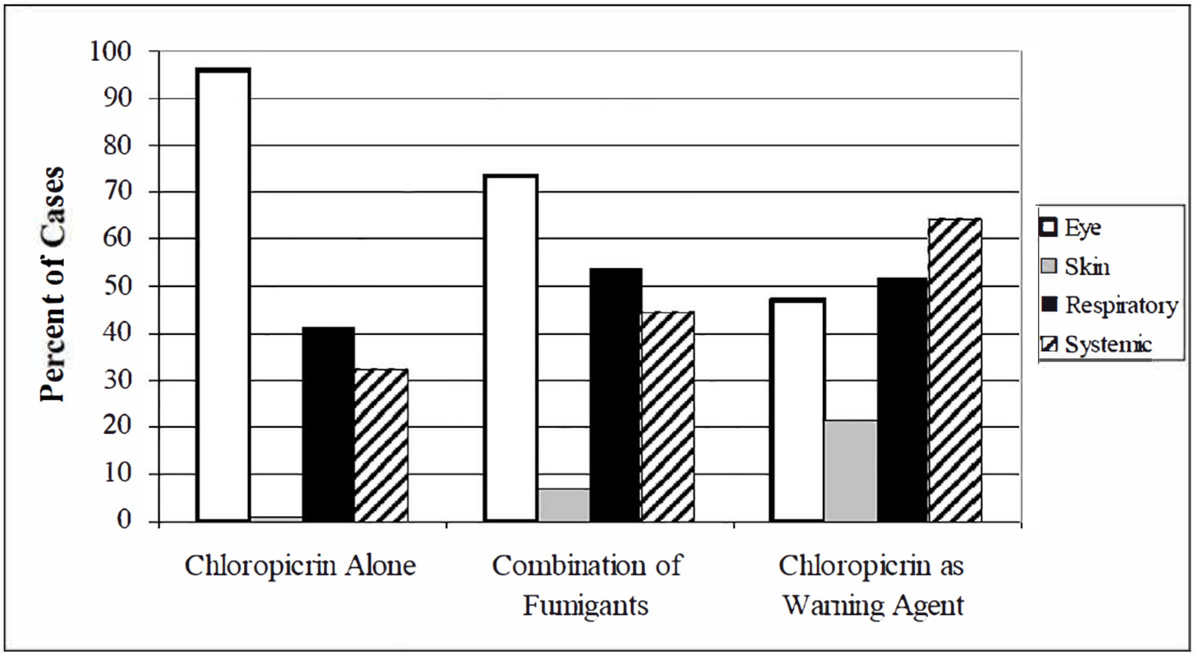
[d] Chloropicrin formulated in a product with 1,3-dichloropropene or methyl bromide in which the chloropicrin concentration is above 2%. Includes thirteen cases involving Methyl Bromide 89.5%, which contains chloropicrin 10.5% as a warning agent. Of these thirteen cases, seven reported effects to eyes along with respiratory illness, four reported only eye effects, one reported only skin effects, and one reported eye effects and systemic illness (see footnote *b* for explanation).

[e] Chloropicrin used in conjunction with sulfuryl fluoride, or formulated with methyl bromide in a product with chloropicrin concentration less than or equal to 2%.

[f] Includes seven less commonly reported combinations of eye, skin, respiratory, and systemic effects.

Reports of skin and systemic illnesses demonstrate the opposite trend. Of the 571 cases associated with chloropicrin alone, 6 (1%) reported skin effects; of the 218 cases associated with chloropicrin in combination with other fumigants, 15 (7%) reported skin effects; and of the 270 warning agent cases, skin effects were reported in 58, or 22%. Systemic effects were reported in 32% of cases associated with chloropicrin alone, 44% of the cases associated with chloropicrin in combination with other fumigants, and 64% of the warning agent cases. No clear trend was apparent for respiratory manifestations, which are recognized effects both of chloropicrin and of other fumigants.

Figure 4. Percent of Illnesses (Cases) Reporting Eye, Skin, Respiratory, and Systemic Symptoms in California, 1992 – 2008, Evaluated by the California Pesticide Illness Surveillance Program as Definitely, Probably, or Possibly Related [a] to Chloropicrin Exposure, Alone or in Combination with Another Fumigant, or That Were Associated with or Indirectly Related to Fumigants with Chloropicrin as a Warning Agent



[a] " Definite" means that both physical and medical evidence document exposure and consequent health effects, "probable" means that limited or circumstantial evidence supports a relationship to pesticide exposure, and "possible" means that evidence neither supports nor contradicts a relationship (Mehler, 2010). More than one type of symptom can be reported in each case.

Illnesses Reported in Open Literature

Additional incidents reported in California have been described in the literature (Goldman *et al.*, 1987; Prudhomme *et al.*, 1999). Goldman *et al.* (1987) summarized a complaint of illness following "off-gassing" of chloropicrin and methyl bromide from an episode occurring in 1984. In the introduction, four episodes the authors called "community exposures" were briefly described. The episodes occurred in Los Angeles County (1973; 3 cases), Ventura County (1980; 16 cases), Kern County (1984; 3 families affected), and Stanislaus County (1984; 32 cases). The fourth incident resulted in evacuation of 75 homes and three businesses, and 31 persons reported symptoms consistent with chloropicrin exposure (eye, nose, or throat irritation; noticing an unusual odor).

Prudhomme *et al.* (1999) reported respiratory damage to three men exposed in a 1995 episode to chloropicrin vapor in a truck trailer at a freight transportation company. Six weeks later, the men were seen at a clinic in San Francisco for follow-up of their persistent chest-wall pain, and were found to have elevated creatine phosphokinase levels, suggesting damage to skeletal muscle. The reason for the elevated creatine phosphokinase levels was unknown;

although earlier reports suggested that violent coughing could cause that sort of muscle damage, coughing was not a prevalent symptom of the exposed employees.

Chloropicrin concentrations during episodes are rarely reported, and exposure levels of persons reporting illnesses are almost never known. One exception is reported in a follow-up to an episode, which occurred in Minnesota, where chloropicrin was released into the basement of an empty home to (illegally) fumigate for bats (Teslaa *et al*., 1986). Three or four weeks later, a family moved into the house. A week after moving in, family members reported runny noses, lacrimation, and coughing. A family dog kept in the basement at night developed pneumonia. Six weeks after the chloropicrin application to the basement, air and cloth samples taken inside the house (upstairs, not in the basement) showed chloropicrin at concentrations of 30 - 48 ppb (202 - 323 $\mu g/m^3$) on the ground floor, and 3 ppb (20 $\mu g/m^3$) in an upstairs bedroom.

O'Malley *et al*. (2004a) used standard air-dispersion modeling to estimate 1-hour average chloropicrin air concentrations in areas south and west of the treated Kern County field during the 2003 episode. These estimates were as high as 200 ppb (1,340 $\mu g/m^3$). Similar techniques were applied to the Monterey episode (Barry *et al*., 2007), for which modeling also predicted 1-hour time-weighted average air levels in the range of 50 to 150 ppb (336 – 1,009 $\mu g/m^3$), with 3-minute concentrations as high as 600 ppb (4,035 $\mu g/m^3$).

LABEL PRECAUTIONS AND CALIFORNIA REQUIREMENTS

Label Precautions

Chloropicrin products are all Toxicity Category I pesticides and have the signal word DANGER (or DANGER POISON, with skull and crossbones) on the label. Due to acute inhalation toxicity, all products containing more than 2% chloropicrin are classified as RUPs according to U.S. EPA (40 CFR 152.175). Chloropicrin is listed as a Restricted Material under California regulation (3 CCR 6400). As a Restricted Material in California, chloropicrin may only be applied by, or under the supervision of, a certified applicator. The operator of the property must first obtain a permit from the County Agricultural Commissioner. Permit conditions may be required by the County Agricultural Commissioner.

Occupational reentry scenarios are considered differently depending on whether the reentry is regulated under the Worker Protection Standard (WPS). Federal WPS regulations are listed under 40 CFR 156 and 40 CFR 170, and California reentry WPS regulations are listed under 3 CCR 6760 – 6778. The WPS regulates "occupational exposures to pesticides used in the production of agricultural plants on farms or in nurseries, greenhouses, and forests, and also from the accidental exposure of workers and other persons to such pesticides" (40 CFR 170.1). Under the WPS, reentry into treated fields and other agricultural areas such as greenhouses is restricted for a specific interval (the restricted entry interval, or REI) following pesticide applications (40 CFR 170.112; 3 CCR 6770 - 6776). On chloropicrin product labels, no REI is specified following chloropicrin applications. However, an "entry restricted period" of 5 days is required instead. This includes entry following either tarped or non-tarped applications. Following tarped applications, tarps can be split after a minimum of 120 hours (5 days); tarp removal must wait an additional 2 hours after tarps are split.

Chloropicrin is available in 100% formulations, or it can be formulated with methyl bromide, methyl iodide, or 1,3-dichloropropene. Products containing methyl bromide, methyl iodide, or 1,3-dichloropropene have warning statements for these AIs. Typical precautionary statements for a product label (100% chloropicrin) are as follows:

> DANGER. Poisonous liquid and vapor. Inhalation of vapors may be fatal. Chloropicrin is readily identifiable by smell. Exposure to very low concentrations of vapor will cause irritation of eyes, nose, and throat. Continued exposure after irritation, or higher concentrations may cause painful irritation to the eyes or temporary blindness. Liquid will cause chemical burns to skin or eyes. Do not get on skin, in eyes, or on clothing. Harmful or fatal if swallowed.

Under Personal Protective Equipment (PPE), chloropicrin product labels state the following:

> Some materials that are chemical-resistant to this product are barrier laminate or viton $\geq$ 14 mils. For more options, follow the instructions for category H on an EPA chemical-resistance category selection chart.
>
> When not performing tasks with liquid contact potential, all handlers (including applicators) must wear:
> - Long-sleeved shirt and long pants, and
> - Shoes and socks.
> - Do not wear jewelry, gloves, goggles, tight clothing, rubber protective clothing, or rubber boots when handling. Chloropicrin is heavier than air and can be trapped inside clothing and cause skin injury.
>
> When performing tasks with liquid contact potential, all handlers (including applicators) must wear:
> - Long-sleeved shirt and long pants,
> - Chemical-resistant gloves,
> - Chemical-resistant apron,
> - Protective eyewear (Do NOT wear goggles), and
> - Chemical-resistant footwear and socks.

Under "Respiratory Protection and Stop Work Triggers," labels direct users as follows:

> The following procedures must be followed to determine whether an air-purifying respirator is required or if operations must cease for any person performing a handling task as stated in this label.

- ♦ If at any time any handler experiences sensory irritation (tearing, burning of the eyes or nose) then either:
  - o An air-purifying respirator must be worn by all handlers who remain in the application block, or
  - o Operations must cease and handlers not wearing air-purifying respirators must leave the application block.

Handlers can remove air-purifying respirators or resume operations if two consecutive breathing zone samples taken at the handling site at least 15 minutes apart show that levels of chloropicrin have decreased to less than 0.15 ppm, provided that handlers do not experience sensory irritation. During the collection of air samples, a full-face air-purifying respirator must be worn by the handler taking the air samples. Samples must be taken where the irritation is first experienced.

- ♦ When using monitoring devices to monitor air concentration levels, a direct reading detection device, such as a Matheson-Kitagawa, Dräger, or Sensidyne device must be used. The devices must have a sensitivity of at least 0.15 ppm for chloropicrin.
- ♦ When breathing zone samples are required, they must be taken outside respiratory protection equipment and within a ten inch radius of the handler's nose and mouth.
- ♦ When air-purifying respirators are worn, then air monitoring samples must be collected at least every 2 hours in the breathing zone of a handler performing a representative handling task.
- ♦ If at any time: (1) a handler experiences any sensory irritation when wearing an air-purifying respirator, or (2) an air sample is greater than or equal to 1.5 ppm, then all handler activities must cease and handlers must be removed from the application block. If operations cease the emergency plan detailed in the FMP must be implemented.
- ♦ Handlers can resume work activities without air-purifying respirators, if two consecutive breathing zone samples taken at the handling site at least 15 minutes apart show levels of chloropicrin have decreased to less than 0.15 ppm, provided that handlers do not experience sensory irritation. During the collection of air samples an air-purifying respirator must be worn by the handler taking the air samples. Samples must be taken where the irritation is first experienced.
- ♦ Work activities can resume if all of the following conditions exist provided that the appropriate air-purifying respirator is worn:
  - o Two consecutive breathing zone samples for chloropicrin taken at the handling site at least 15 minutes apart must be less than 1.5 ppm but are greater than 0.15 ppm,
  - o Handlers do not experience sensory irritation while wearing the air-purifying respirator, and
  - o Cartridges have been changed.
  - o During the collection of air samples an air-purifying respirator must be worn by the handler taking the air samples. Samples must be taken where the irritation is first experienced.

Product labels require that, whenever an air-purifying respirator is required, that handlers must wear at a minimum either a full-face respirator with an organic-vapor-removing cartridge with a prefilter approved for pesticides (NIOSH approval number prefix TC-23C), or a full-face respirator with a canister approved for pesticides (NIOSH approval number prefix TC-14G).

California Requirements

Under California regulation, field soil fumigation with chloropicrin and methyl bromide (excepting golf courses, tree holes, potting soil, raised-tarpaulin nursery fumigations of less than one acre (0.405 ha), and greenhouses and other similar structures) is regulated under 3 CCR 6447 – 6447.3 and 3 CCR 6780 – 6784. These regulations impose requirements for tarp use (if tarps are to be used) and limit the size of application blocks to 40 acres (16 ha; 3 CCR 6447(d)). These regulations do not apply to soil fumigations done with chloropicrin only (i.e., without methyl bromide).

California regulation places additional restrictions on fumigation of nursery potting soils or soil mixes, nursery stock, and other agricultural commodities, appliances, or equipment, with either chloropicrin or methyl bromide (or any mixture of the two chemicals) under 3 CCR 6453. This regulation specifies that fumigations of these types must be done in either "a properly sealed fumigation chamber, railroad car, or truck trailer, or under a gas confining tarp approved by the commissioner or director." DPR has also issued recommended permit conditions, with numerous additional requirements (DPR, 2010c).

Structural fumigations with mixtures of methyl bromide and chloropicrin are regulated under 3 CCR 6454. This regulation requires that chloropicrin be used as a warning agent whenever methyl bromide is used to fumigate a structure, unless prohibited by other regulations or by product labeling (the regulation does not specify the chloropicrin concentration). The regulation lists further requirements for tarps, buffer zones, and aeration based on application rates of methyl bromide.

In January 2008, California finalized regulations to control emissions of volatile organic compounds in certain parts of the state. Regulations for chloropicrin limit the application methods that are allowed in certain parts of the state at certain times of the year, and cap the allowed application rate to 400 lbs AI/acre (449 kg/ha; 3 CCR 6449 – 6449.1). As these restrictions do not apply to all areas of the state and all times of the year, they are not incorporated into exposure estimates reported in this EAD.

EXPOSURE SCENARIOS

An exposure scenario describes a situation where people may contact pesticides or pesticide residues, and in which the nature of the exposure as well as its magnitude (apart from variability among individuals and occasions) is relatively homogeneous. Several types of exposure scenarios were considered in the EAD, including occupational handlers exposed during chloropicrin applications (before aeration); occupational handlers conducting aeration activities; reentry scenarios; airborne exposures of bystanders (individuals who are not involved with the pesticide application but who may be exposed as a result of the pesticide's use); and ambient air exposures.

Screening (i.e., highest realistic) estimates are provided in this exposure assessment. Although individuals in each scenario might potentially be exposed to a range of chloropicrin concentrations, for quantitative risk assessment purposes the highest realistic exposures, based on available data, are determined; if these estimates result in acceptable risk, then lower exposures will, as well. Screening estimates are calculated using the maximum application rate allowed in California, along with any other conditions that would tend to increase exposure. Ideally, screening estimates provide the maximum realistic exposure. To achieve their purpose it is critical that estimates do not underestimate actual exposures.

This EAD is intended to address all significant exposure scenarios associated with chloropicrin use; however, exposure monitoring data are not available for all scenarios. In the absence of data, surrogate data were used in some cases. Otherwise, representative scenarios were selected to cover those with missing data. Scenarios grouped under a representative scenario are not all expected to have identical exposures; however, the representative scenario is anticipated to involve exposures similar to or greater than all scenarios covered by it.

Bystanders

Bystanders include individuals, working or not, who are not directly involved with a pesticide application but who may be exposed to airborne pesticide during or after the application, by drift or volatilized pesticide. Exposure scenarios include bystanders to a soil fumigation and to a structural fumigation. Both types of fumigations can use chloropicrin as a warning agent. Additionally, soil fumigations can use chloropicrin at higher rates as an AI, and screening estimates for these scenarios assume chloropicrin as an AI. As chloropicrin is used only as a warning agent in structural fumigations, screening exposure estimates associated with structural fumigation assume chloropicrin is used as a warning agent.

Bystanders are assumed to wear no protective clothing or equipment, as is required for handlers of chloropicrin-containing products during an application. Occupational bystanders may be handling other pesticides or they may be doing fieldwork such as harvesting, and are assumed to be present next to the chloropicrin application for an 8-hour workday. Residential bystanders are assumed to be in the vicinity of the chloropicrin application for 24-hour days.

Ambient Air

Air monitoring done in California (ARB, 2003a; 2003b) suggests that airborne exposures to chloropicrin are possible even in areas that are far from application sites. Ambient air monitoring was conducted by the California Air Resources Board (ARB) in three counties with relatively high chloropicrin use (Kern, Monterey, and Santa Cruz), during times when peak use was anticipated. Results of these studies suggest that airborne chloropicrin exposures to the public are possible in areas that are far from application sites.

Occupational Handler

Occupational (agricultural and commercial) handler activities associated with chloropicrin soil and structural fumigation are listed in Table 5. Occupational handler activities during soil fumigation with chloropicrin include operating tractor equipment (driving); assisting in the overall operation, ensuring proper tarpaulin placement and condition, and changing cylinders (copiloting); assisting with covering the tarpaulin (tarp) at the end of the rows (shoveling); operating equipment to compact soil in applications when a tarp is not used (soil sealer); and applicators using drip, structural or wand methods. Aeration scenarios associated with soil fumigation include slicing tarps lengthwise (tarp splitting); gathering tarps from a field (tarp removal); and punching a hole in a tarp through which planting may later be done (tarp punching). Separate exposure scenarios are assessed for each unique combination of application method and task. Scenarios are detailed in Appendix 1.

Table 5. Occupational Handler Scenarios for Chloropicrin

Fumigation Method	Scenario [a]
Shank Broadcast Tarped Shallow	Driver [b], Copilot [c], Shoveler [d], Tarp Splitter [e], Tarp Remover [e]
Shank Broadcast/Non-Tarped/Shallow	Driver, Soil Sealer [f]
Shank Broadcast/Non-Tarped/Deep	Driver
Shank Bedded Tarped Shallow	Driver, Copilot, Shoveler, Tarp Puncher [g]
Shank Bedded/Non-Tarped/Shallow	Driver
Surface Drip - Tarped	Applicator, Tarp Puncher
Buried Drip/Non-Tarped	Applicator
Hot Gas Drip [h]	Applicator, Tarp Puncher
Tree Replant Wand	Applicator
Potting Soil Fumigation [i]	Driver, Copilot, Shoveler, Tarp Splitter, Tarp Remover
Structural	Applicator, Fumigator [j], Tarp Remover, Aerator [k]

[a] Based on product labels, California regulations on field fumigation (3 CCR 6784), and descriptions from Beard *et al.* (1996) and Rotondaro (2004).

[b] Operator of tractor and attached or towed equipment.

[c] Worker who assists in the overall operation, ensuring proper tarpaulin placement and condition, as well as changing cylinders when needed. Copilots generally ride on the rear of the tractor.

[d] Worker who shovels soil onto tarp ends.

[e] Tarp splitting involves slicing a tarp lengthwise with a cutting disk, followed by tarp removal, which involves gathering tarps from field. Tarps covering mounds of potting soil are removed without splitting first.

[f] Soil sealer drives a tractor with a soil-moving or compacting device behind the application rig.

[g] Tarp punching refers to punching a hole in a tarp through which planting may later be done.

[h] Hot gas drip irrigation is allowed by methyl bromide product labels, and this method is considered along with tarped surface drip irrigation in the Exposure Assessment section.

[i] Potting soil fumigation is a representative scenario that covers fumigation of mushroom casing soil, seed flats and seedbeds. Potting soil is fumigated in mounds under tarps.

[j] Fumigators are licensed and certified to apply pesticides and to monitor aeration. They may perform tarp removal and other activities in addition to their certified/licensed activities.

[k] Aeration for non-tarped applications involves opening doors and windows, removing tape seals as needed. For tarped applications, aerators unfasten and remove tarps. Aerators from either tarped or non-tarped application may also set up and turn on fans.

Structural fumigation involves applicators and aerators. Some structural fumigations are non-tarped, and aeration following these applications involves removing any tape placed over openings and opening doors and windows. In structural fumigation, aeration is mechanically assisted with exhaust fans.

Handlers may be exposed to chloropicrin during structural fumigations with methyl bromide or sulfuryl fluoride. Handlers may also be exposed to chloropicrin during soil fumigations with methyl bromide products containing chloropicrin as a warning agent. For this reason, many of the scenarios listed in Table 5 require exposure estimates for warning agent use as well as for AI use of chloropicrin. Warning agent exposures are presented separately in the Exposure Assessment section.

Occupational and Residential Reentry Activities

Table 6 lists occupational and residential reentry scenarios following soil and structural fumigation. Exposure estimates generated for representative scenarios are anticipated to be the best available for covered scenarios as indicated in Table 6, although any data available for covered scenarios are also reported in the Exposure Assessment section. In some cases, aeration activities were considered to best represent reentry; aeration scenarios are listed in Table 5.

Table 6. Representative Reentry Scenarios for Chloropicrin

Fumigation Method	Representative Scenario [a]	Covered Scenarios [b]
Shank Broadcast Tarped Shallow	Soil Shaper	Pipe Layer, Planting [d]
Shank Broadcast Non-Tarped Shallow	Soil Shaper	Pipe Layer, Planting [d]
Shank Broadcast Non-Tarped Deep	Soil Shaper	Pipe Layer, Planting [d]
Shank Bedded Tarped Shallow	Pipe Layer	Planting
Shank Bedded Non-Tarped Shallow	Pipe Layer	Planting [d]
Surface Drip - Tarped	Tarp Puncher [c]	All activities following tarped and non-tarped drip applications
Potting Soil Fumigation	Tarp Remover [c]	All post-application activities for potting soil, mushroom casing soil, seed flats and seedbeds.
Structural Fumigation	Reentry	All reentry into treated structure

[a] Based on product labels registered by DPR, California regulations on field fumigation (3 CCR 6784), and descriptions from Beard *et al.* (1996) and Rotondaro (2004).
[b] All scenarios covered by the representative scenarios are anticipated to have exposure equivalent to or less than that of the representative scenario.
[c] This activity is listed with handler scenarios in Table 5. No reentry exposure data were available.
[d] Planting covers all cultivation activities for crops planted following soil fumigation.

PHARMACOKINETICS

Dermal and Inhalation Absorption

Dermal Absorption

Critical toxic effects from exposure to chloropicrin vapor are primarily due to contact with eyes and respiratory tract, causing irritation (OEHHA, 1999; OEHHA, 2001; U.S. EPA, 2008). For chemicals such as chloropicrin where the primary toxic effect is localized irritation, the effect is related to concentration in air rather than absorbed dose (Pauluhn, 2003). As exposure estimates are appropriately reported as concentrations rather than as absorbed doses, no dermal absorption estimate is required.

Inhalation Absorption

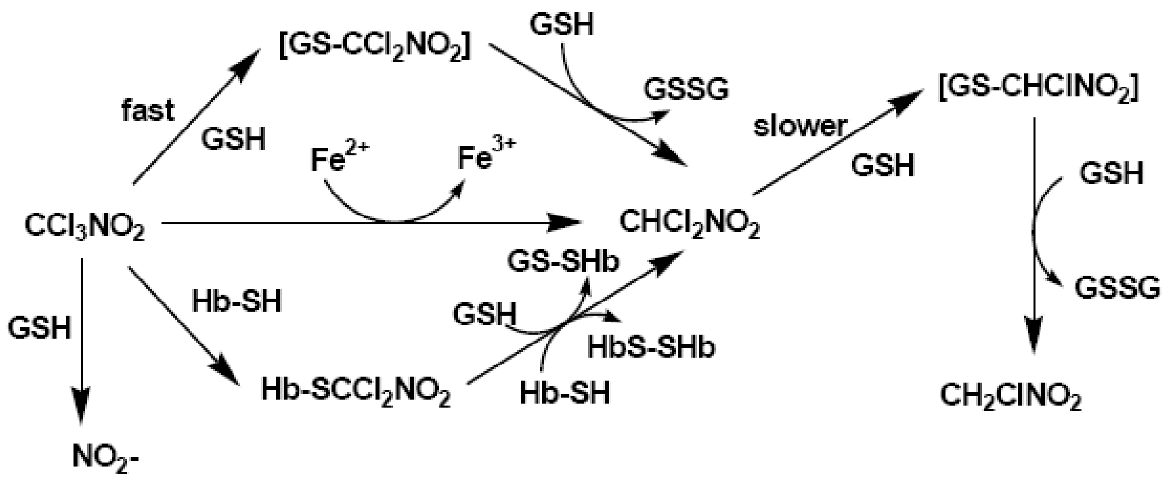
Critical toxic effects from exposure to chloropicrin vapor are primarily due to contact with eyes and respiratory tract, causing irritation (OEHHA, 1999; OEHHA, 2001; U.S. EPA, 2008). For chemicals such as chloropicrin where the primary toxic effect is localized irritation, the effect is related to concentration in air rather than absorbed dose (Pauluhn, 2003). As exposure estimates are appropriately reported as concentrations rather than as absorbed doses, no inhalation absorption estimate is required.

Metabolism

Limited data are available on the metabolism of chloropicrin. Metabolism in mammals was investigated in only two *in vivo* studies, both using male albino Swiss-Webster mice weighing 20 – 25 g (Sparks *et al.*, 1997; Sparks *et al.*, 2000). Both studies also included *in vitro* components to investigate specific reactions, which will be briefly discussed below following discussion of the *in vivo* data. Together, these studies suggest that most absorbed chloropicrin is eliminated through urine, and that the chief metabolic pathway for chloropicrin is through dechlorination reactions with biological thiols, followed by formation of multiple metabolites which are mostly excreted in urine. Figure 5 summarizes the metabolic pathways proposed by Sparks *et al.* (1997).

Alwis *et al.* (2008) developed an analytical method for quantifying nitromethane in human blood as a potential biomarker for exposure to chloropicrin. In a series of in vitro studies, blood samples spiked with chloropicrin were extracted with solid-phase microextraction and quantitated by gas chromatography/high resolution mass spectrometry. Nitromethane was the major product formed by reactions in the blood samples; it formed gradually over a 48-hour interval. Dichloronitromethane and chloronitromethane also were detected. No pathway was proposed for the reactions. Alwis *et al.* (2008) also found variable background nitromethane in blood drawn from individuals with no known exposure to either nitromethane or chloropicrin.

Figure 5. Proposed pathways for reaction of chloropicrin with glutathione and hemoglobin (Sparks et al., 1997)



<u>*In Vivo* Studies</u>

Sparks *et al*. (1997) administered ^{14}C-radiolabeled chloropicrin in a triethylene glycol vehicle, both orally (two mice) and via intraperitoneal injection (four mice), at doses in the range of 1-3 mg/kg. Of the four mice treated intraperitoneally, two were euthanized at one hour and two at 48 hours post-dose. Both orally-dosed mice were euthanized 48 hours post-dose. Most of the administered radiolabel was recovered from urine, feces, and expired gases; the total eliminated by these routes averaged 81% following the intraperitoneal dose and 65% of the oral dose. In mice dosed by either route, about 43 – 47% of the radiolabel was recovered in urine excreted during the first 24 hours post-dose; an additional 8% was recovered from urine excreted between 24 and 48 hours post-dose. Another 2.5 – 13% was recovered from feces through 48 hours post-dose, and 0 – 15% was recovered from expired gases. The radiolabeled compounds recovered after dosing were not identified, although thin-layer chromatography showed that some compounds recovered from urine were polar.

Sparks *et al*. (2000) administered non-radiolabeled chloropicrin in a dimethylsulfoxide vehicle via intraperitoneal injection to four mice at a dosage of 5 mg/kg. All four mice were euthanized at 24 hours post-dose. Urine collected from the mice during that interval was assayed for 2-thioxothiazolidine-4-carboxylic acid (also called, "raphanusamic acid"). This metabolite, a cyclic cysteine adduct with thiophosgene ($CSCl_2$), was detected in an amount equivalent to about 1% of the administered chloropicrin dose. Excretion of this metabolite suggests that at least one metabolic pathway for chloropicrin proceeds via formation of thiophosgene intermediates.

Interactions of chloropicrin with blood proteins were investigated in groups of three mice intraperitoneally injected with doses of 5, 14, 25, and 50 mg/kg chloropicrin (Sparks *et al*., 2000). Mice were euthanized 1 hour post-dose. Blood samples were collected from each mouse using cardiac puncture, and the liver was removed, rinsed with phosphate buffer, homogenized, and centrifuged to yield cytosolic samples for assay. Assays conducted on liver cytosol samples included total hemoglobin, oxyhemoglobin, and hemoprotein levels. All three assays showed dose-dependent increases, suggesting that chloropicrin interacts with these proteins in the liver during the first hour post-dose. Whole blood samples were lysed with deionized water and assayed for percent methemoglobin. Percent methemoglobin ranged 0-3, suggesting that chloropicrin and its metabolites did not substantially produce methemoglobin, at least within an hour after dosing.

In Vitro Studies

When mixed in a phosphate buffer with each of several biological thiols (including glutathione, cysteine, N-acetylcysteine, coenzyme A, and reduced lipoic acid), chloropicrin reacted rapidly (Sparks *et al*., 1997). These reactions resulted in both the dechlorination of chloropicrin to dichloronitromethane, and production of the disulfide of each thiol. Chloropicrin reacted completely when mixed in a phosphate buffer with two proteins containing free thiols, hemoglobin (from dog and human) and alcohol dehydrogenase (from yeast), forming both dichloronitromethane and protein adducts. In contrast, a protein with no sulfhydryl group (myoglobin) and one with partially blocked sulfhydryl groups (albumin), did not take up the radiolabel when mixed in a phosphate buffer with chloropicrin (Sparks *et al*., 1997). These data suggest that chloropicrin could be anticipated to react most readily with free thiols and thiol proteins.

In one of four *in vitro* studies to investigate reactions potentially resulting in mammalian toxicity, chloropicrin was incubated in a phosphate buffer with either pyruvate dehydrogenase (30 minutes) or succinate dehydrogenase (5 minutes). Following the incubation period, the enzyme activity was assayed for each of these thiol proteins; chloropicrin was a potent inhibitor of both (Sparks *et al*., 2000). These data further confirm the reactivity of chloropicrin with thiol proteins. Sparks *et al*. (2000) suggested a metabolic pathway that proceeds to either phosgene or raphanusamic acid. Phosgene was proposed to be formed via two pathways, with intermediates thiophosgene and trichloromethanol. Formation of phosgene, via a trichloromethanol intermediate that spontaneously dechlorinates, has been established as a major metabolic pathway for chloroform (Mansuy *et al.*, 1977; Meek *et al*., 2002), providing support for the pathway suggested by Sparks *et al*. (2000). However, it is unclear whether this is the dominant pathway for chloropicrin, as it is for chloroform.

ENVIRONMENTAL FATE

DPR released an Environmental Fate Review for chloropicrin in 1990 (Kollman, 1990). This section briefly summarizes and updates information from that review. Following application to soil, chloropicrin rapidly diffuses through the soil in all directions, then dissipates quickly, with half-lives ranging from approximately an hour to several days. Volatilization is the major pathway through which chloropicrin dissipates from soil, but chloropicrin is also degraded through biotic and abiotic reactions. In water, chloropicrin can persist for several days in the absence of light, but it degrades rapidly when subjected to light of suitable wavelengths, with half-lives ranging from 6 hours to 3 days. Under reducing conditions, chloropicrin also reacts quickly, undergoing reductive dechlorinations. In air, chloropicrin is reactive, undergoing photodegradation to products such as phosgene, ozone, nitrogen dioxide, chlorine nitrate, and nitryl chloride, with an estimated half-life in the range of 3 – 18 hours under constant illumination in the laboratory.

Persistence in Soil Environment

As a soil fumigant, chloropicrin is applied to soil via either injection with shank or similar equipment, or via drip irrigation. After application to soil, chloropicrin rapidly diffuses through the soil in all directions, although it moves less rapidly than the more volatile methyl bromide (Wilhelm, 1960; Youngson *et al.*, 1962; Gan *et al*., 2000; Desager *et al*., 2004). Volatilization from soil is the major off-site loss pathway, followed by chemical degradation and microbial decomposition (Gou *et al*., 2003). Chloropicrin disappearance from treated soils is well-described by first-order kinetics (Gan *et al*., 2000; Ibekwe *et al.*, 2004; Zhang *et al*., 2005).

Volatilization from Soil

Both the vapor pressure and Henry's Law Constant for chloropicrin are relatively high, 23.2 mm Hg and 2.5 x 10^{-3} atm-m^3/mole, respectively, at 25°C (See Table 1). Field volatility data suggest that substantial proportions of applied chloropicrin are emitted from soil. Field volatility studies reported by Beard *et al.* (1996) and Rotondaro (2005) are summarized below in the Environmental Concentrations section. As summarized in Table 12 in the Environmental Concentrations section, over 2-week intervals, on average 61 – 69% of the chloropicrin applied by shank fumigation volatilized, while 15% of chloropicrin applied by tarped drip fumigation volatilized over 2 weeks.

Abiotic and Microbial Reactions with Chloropicrin in Soil

Chloropicrin is rapidly degraded in soil under both aerobic and anaerobic conditions (Olson and Lawrence, 1990a and 1990b; Wilhelm *et al*., 1996; Gan *et al.*, 2000). Field dissipation studies reported degradation half-lives between 1 and 8 days, depending on the formulation, application method and soil type (Ivancovich *et al*., 1990). Studies of soil repeatedly treated with chloropicrin suggest that enrichment can occur of the microorganisms capable of degrading chloropicrin (Ibekwe *et al.*, 2004; Zhang *et al*., 2005).

Laboratory soil metabolism studies also report chloropicrin degradation half-lives in the range of a few hours to several days. The estimated half-life when 250 ppm of ^{14}C-radiolabeled chloropicrin was incubated with sandy loam under aerobic conditions was approximately 5 days; about 70% of the applied radiolabel was recovered by the 90th day of the study as CO_2, while most of the rest was volatilized chloropicrin (Olson and Lawrence, 1990a). In an anaerobic soil metabolism study, Olson and Lawrence (1990b) incubated 250 ppm chloropicrin with sandy loam under aerobic conditions for 5 days post-application (i.e., the aerobic half-life); the soil was then made anaerobic by flushing with nitrogen gas 5 days post-application. Although a half-life was not calculated for chloropicrin under anaerobic conditions because the only sampling intervals were 30 and 60 days after the soil was made anaerobic, Olson and Lawrence (1990b) reported that dissipation was "rapid." The anaerobic half-life was assumed to be shorter than 10 days, as no parent chloropicrin was recovered 35 days post-application (Lawrence, 1990). As with the aerobic soil metabolism study, the radiolabel was predominantly recovered in CO_2 and the parent compound, with CO_2 averaging up to 16.4% of the total applied. However, total recovery of the radiolabel was poor, ranging from an average of 50.2% immediately following treatment to an overall mean total recovery of 74.3% on the 30^{th} and 60^{th} days post-application. Olson and Lawrence (1990b) concluded that losses occurred during the sampling procedure.

In a laboratory study, chloropicrin degraded rapidly when incubated in 100-g samples of Wooster sandy loam collected from Ohio (Craine, 1985b). Aliquots of a chloropicrin solution consisting of 11.35 mg in 1 ml ethanol were pipetted into flasks containing 100 g of soil. Flasks were incubated in the dark at 25°C under aerobic conditions and sampled hourly for 24 hours; concentrations of chloropicrin and inorganic chloride were determined in the samples. Within the first hour, the chloropicrin was reduced to 48.7% of the initial dose, yielding an estimated half-life of about 1 hour. After 24 hours, approximately 91% of the chloropicrin had degraded. Conversion of chloropicrin to inorganic chloride had an estimated half-life of 9.9 hours. Craine (1985b) also investigated anaerobic metabolism of chloropicrin; water was added to the flasks to induce anaerobic conditions. The mean chloropicrin degradation half-life was reported to be 17 hours in the soil-water slurries.

Wilhelm *et al.* (1996) reported on an aerobic soil metabolism study in which 50-g sandy loam soil samples were treated with ^{14}C-chloropicrin at a rate equivalent to 500 lbs AI/acre (562 kg AI/ha), then incubated in the dark at 25°C. Samples were collected after 4.5 hours, and at 1, 2, 3, 6, 14, 21, and 24 days post-dose. Overall recovery was 97.2% of the applied radiolabel. The estimated half-life for chloropicrin was 4.5 days. After 24 days, up to 75.2% of the applied radiolabel was recovered as ^{14}C-CO_2.

Gan *et al*. (2000) investigated the aerobic metabolism of chloropicrin in 10-g samples of three soils, including Arlington sandy loam from California, Carsitas loamy sand from California, and Waukegen silt loam from Minnesota, with respective organic matter content of 0.92%, 0.22%, and 3.1%. In all three soils (with initial water content adjusted to 10%), chloropicrin degradation increased 7- to 11-fold as soil temperatures increased in the range 20°C – 50°C. In contrast, variation of soil moisture content, which was tested only in Arlington and Carsitas soils, had little effect. With soil temperatures held at 20°C, and soil moisture ranging 1.8% – 16%, degradation in chloropicrin doubled from the high to low moisture contents in Arlington sandy loam, but did not change across the same moisture range in Carsitas loamy sand. In a laboratory study with loamy sand from a Wisconsin nursery, Zhang *et al.* (2005) found no change in chloropicrin degradation rates when moisture ranged 0.5% – 10%, but the degradation was significantly lower at a moisture content of 15%.

Gan *et al*. (2000) found that degradation was slower in sterile soil: in untreated, air-dried soil, the half-life was 1.5, 4.3, and 0.2 days for the Arlington, Carsitas and Waukegen soils respectively, while in autoclaved soils the respective half-lives were 6.3, 13.9, and 2.7 days. Based on the difference in the degradation between the sterile and non-sterile soils, Gan *et al*.

(2000) estimated that microbial degradation accounted for 68 – 92% of the chloropicrin degradation. In similar studies, Zheng *et al.* (2003) estimated that microbial degradation of chloropicrin in a sandy loam from California accounted for 84% of the total chloropicrin degradation, and Zhang *et al.* (2005) estimated the microbial contribution to chloropicrin degradation in loamy sands from Wisconsin and Georgia to range between 40% and 80%.

Chloropicrin is degraded in soil by *Pseudomonas* bacteria via a metabolic pathway involving dehalogenated intermediates dichloronitromethane, chloronitromethane, and nitromethane, apparently formed in sequence (Castro *et al.*, 1983):

$$CCl_3NO_2 \Rightarrow CHCl_2NO_2 \Rightarrow CH_2ClNO_2 \Rightarrow CH_3NO_2$$

Alternately, Cervini-Silva (2000) found evidence that formation of dichloronitromethane and chloronitromethane can occur simultaneously via abiotic oxidation-reduction reactions in the presence of strong electron donors such as those found in iron-bearing soils.

Other reaction products of chloropicrin in soil have been documented as well. Spokas and Wang (2003) noted increased emissions of nitrous oxide (N_2O) following soil fumigation with chloropicrin, in both laboratory and field studies; in the field, daily N_2O emissions increased 7-fold during the first 10 days post-fumigation before decreasing to background levels. Follow-up laboratory studies using radiolabels and microbial inhibitors caused Spokas *et al.* (2006) to conclude that in the Georgia loamy sand treated in their studies, about 20% of the increased N_2O production could be attributed to microbes sensitive to tetracycline and streptomycin, while 70% – 80% was due to fungi sensitive to cycloheximide and benomyl. Following studies in which chloropicrin was incubated with steam-sterilized soil, Spokas *et al.* (2006) concluded that at most 18% of the increase in N_2O was from abiotic reactions, although they could not verify that sterilized soil did not have residual biotic activity. ^{15}N-labeled chloropicrin yielded a significant increase of ^{15}N-N_2O, yet only about 12% of the ^{15}N-N_2O was calculated to come from chloropicrin mineralization; most of the ^{15}N came from other pools in the treated soil (Spokas *et al.*, 2006). Increasing the oxygen content in the headspace of the incubation vials to 30% further increased N_2O, to about 5-fold greater than amounts occurring when chloropicrin was incubated at ambient oxygen concentrations. Although chloropicrin increases production of N_2O, no increased production of nitrogen, CO_2 or methane occurred in soils incubated with chloropicrin in comparison to soils incubated without chloropicrin (Spokas *et al.*, 2005; Spokas *et al.*, 2006).

Adsorption and Leaching in Soil

The soil/water adsorption coefficient (K_d; ratio of chemical concentrations in soil and water) of chloropicrin was investigated in a series of laboratory experiments with 50-g samples of four soil types, including commercially purchased agricultural sand, Canfield sandy loam, Wooster sandy loam, and Holly sandy loam (Craine, 1985c). Other than the purchased sand, soils were collected from several locations near Ashland, OH, and sifted through 0.25-inch (0.64-cm) mesh. The sandy loams were misidentified by Craine (1985c) as silt loams, but the correct soil texture can be determined using a nomogram in USDA (2007). The organic matter content of the soils was 0.3% for the agricultural sand, 5.5% for the Canfield sandy loam, 7.2% for the Wooster sandy loam, and 7.4% for the Holly sandy loam. Chloropicrin in an ethanol solution was added in amounts ranging from 9 to 127 mg/kg soil. A soil-free control bottle containing the same amount of chloropicrin as the soil samples was used to determine loss of chloropicrin during the sampling procedure, which ranged 26% – 50% of the amount applied, and the amount of chloropicrin that degraded in soil samples, which ranged 10% – 61%. After the 1-hour incubation period, 200 ml water was added to flasks, and the amount of chloropicrin in water and soil was determined. The estimated chloropicrin adsorbed to soil ranged from 2.8% – 16.2%. The mean K_d ranged from 0.179 to 0.311 for the sandy loam soils and was 0.273 for the agricultural sand; the mean soil absorption coefficient (K_{oc}; soil adsorption normalized to soil organic matter content) was 25 cm^3/g (calculated by DPR's Environmental Monitoring Branch, internal database). In a subsequent communication, Craine (1986) noted that because of the "rapid rate at which chloropicrin is metabolized in soil," no equilibrium between adsorption and desorption could be established in the 1-hour interval monitored in this study.

Kenaga (1980) calculated a K_{oc} of 62 for chloropicrin, based on a reported water solubility of 2,270 ppm. The calculation used a regression of K_{oc} on water solubility for 170 chemicals. The regression equation was $K_{oc} = 3.64 – 0.55$(log water solubility).

Although chloropicrin rapidly dissipates from soil under many conditions, in some cases residual amounts can persist. For example, Guo *et al.* (2003b) report a case in which soil beneath a facility in Maine that had formerly manufactured several chemicals, including chloropicrin, contained residues as high as 500 mg/kg 7 years after manufacturing ceased and the facility was abandoned. Chloropicrin concentrations in groundwater beneath the facility ranged 10 – 150 mg/l (Guo *et al.*, 2003b).

To investigate chloropicrin's persistence in soil, Guo *et al.* (2003a) conducted a laboratory study with triplicate 10-g samples of sandy loam, loam, and silt loam soils from California and Pennsylvania. Samples were mixed with chloropicrin at an initial concentration of 1,690 mg/kg (i.e., 10 µl chloropicrin in 10 g soil) and incubated in the dark at 20°C for 30 days. Following incubation, soils were thinly spread onto foil sheets in a fume hood, and residues were allowed to evaporate for 20 hours, after which the remaining residues were extracted. The average residues extracted from the incubated soil ranged from 0.7% in the sandy loam to 4.0% in the silt loam. Extending the evaporation from 20 hours to 120 hours had little effect on the persistent residues, nor did shortening the incubation time to 10 days. Soils incubated for less than 10 days had lower persistent residue levels.

Laboratory data suggest that under some conditions chloropicrin residues could leach into ground water. Guo *et al.* (2003b) investigated the leaching potential of persistent chloropicrin residues in silt loam from Pennsylvania. Triplicate samples of soil were mixed with chloropicrin at an initial concentration of 845 mg/kg (i.e., 150 µl chloropicrin in 330 g soil) at 20°C for 35 days. Following incubation, soils were thinly spread onto foil sheets in a fume hood, and residues were allowed to evaporate for 48 hours. Aliquots of this treated soil were mixed with deionized water (10 g soil, 8 ml water). After an additional 24 hours, the mixtures were centrifuged (at 956 x gravity for 15 minutes), and an average of 2.10 mg/l chloropicrin was quantitated in the supernatant. Follow-up soil column studies by Guo *et al.* (2003b) suggested that under conditions of high water movement through soil and limited microbial activity, substantial amounts of chloropicrin could potentially leach into ground water.

Persistence in Water Environment

Chloropicrin persists in water for several days in the absence of light, but degrades rapidly when subjected to light of suitable wavelengths, with half-lives ranging from 6 hours to 3 days (Castro and Belser, 1981; Chang, 1989; Moreno and Lee, 1993). Under reducing conditions, chloropicrin undergoes a series of reductive dechlorinations (Zheng *et al*., 2006; Lee *et al*., 2008). In addition to leaching from pesticide applications, chloropicrin is also formed in water with high organic content as a byproduct of certain disinfection chemicals, although environmental concentrations are invariably low. The potential for chloropicrin to bioconcentrate in aquatic organisms is also anticipated to be low.

<u>Hydrolysis and Photohydrolysis</u>

Craine (1985a) investigated chloropicrin hydrolysis in 250-ml aliquots of aqueous solutions at pH 5, 7 or 9. The solutions, with initial chloropicrin concentrations of 110 mg/l, 42.1 mg/l, and 205 mg/l, respectively, were incubated in sealed 550-ml Erlenmeyer flasks in the dark at either 25°C or 35°C for 29 days. Preliminary experiments without water showed that flasks would retain chloropicrin for 29 days, although "inconsistent" chloropicrin losses occurred during headspace sampling. Samples of headspace gases and of solution were collected at 0, 2, 4, 9, 14, 21, and 29 days. Chloroform was detected in trace amounts in several flasks, at all three pH levels. No other organic degradation products were detected by gas chromatography with either ^{63}Ni or flame ionization detectors; reference standards of chloropicrin, chloroform, methane, methanol, and nitromethane were used to calibrate the detectors. Inorganic chloride in the solutions was quantitated with an ion-specific electrode, and was corrected for amounts initially present in the buffered solutions. Recognizing that each chloropicrin molecule contains three chlorine atoms, the theoretical maximum inorganic chloride concentration in each solution could be calculated from the initial chloropicrin concentration. The highest measured amount of inorganic chloride in each solution ranged from 0.8% of the theoretical maximum at pH 5 and 25°C to 63.3% of the theoretical maximum at pH 7 and 35°C. Craine (1985a) calculated rates of hydrolysis at each pH and temperature; in general, rates increased with temperature and pH, with the slowest rate at pH 5 and 25°C (0.8 µmol/liter/day) and the highest at pH 9 and 35°C (165.2 µmol/liter/day).

In contrast to Craine (1985a), Chang (1989) found limited hydrolysis of chloropicrin in 100-mg/l aqueous solutions at pH 5, 7 and 9. To prevent volatilization, all vials were filled to the top, without any headspace, and capped tightly. The foil-wrapped vials were incubated in that dark at 25°C. Three vials were sampled at 0, 2, 4, 9, 14, 21, and 28 days. Inorganic chloride in the solutions was quantitated with an ion-specific electrode, and chloropicrin was quantitated by gas chromatography with a flame ionization detector. In all solutions, final chloropicrin concentrations were at least 90% of initial, and inorganic chloride never exceeded the detection limit of 1.5 mg/l.

Jeffers and Wolfe (1996) investigated chloropicrin hydrolysis at elevated temperatures (85 – 166°C) in aqueous 0.0003 μmol/l solutions sealed in Pyrex glass bulbs. Detectable hydrolysis occurred only at temperatures greater than 140°C, and Jeffers and Wolfe (1996) concluded that "homogeneous hydrolysis is a completely negligible process for chloropicrin." However, in another set of experiments, chloropicrin in an aqueous 0.0006 μmol/l solution was incubated with 0.5 g of an aquatic plant, parrot feather, and degraded via reduction to dichloronitromethane then chloride ion, with a half-life that was less than 20 hours. Jeffers and Wolfe (1996) concluded, based on this experiment and others with halogenated compounds, that "plant dehalogenases will degrade chloropicrin readily and completely, within 20 hours, as 'reasonable' concentrations."

Castro and Belser (1981) investigated photohydrolysis of an aqueous, 0.01-M (1,640 mg/l) chloropicrin solution in a tube-shaped quartz photoreactor irradiated with a small, low-pressure quartz lamp at 254 nm. The photoreactor contained 100 ml solution and 115 ml headspace. Inorganic chloride was quantitated with an ion-specific electrode, chloropicrin was quantitated by gas chromatography with a flame ionization detector, nitrate was quantitated spectrophotometrically as nitrotoluene following reaction with toluene, and carbon dioxide was quantitated by gravimetric determination of barium carbonate after reaction with barium hydroxide. Following a 24-hour incubation at 25°C, no detectable chloropicrin remained in solution or in the headspace. Inorganic chloride was present at 0.003 M, nitrate at 0.00105 M, and carbon dioxide (in gas and solution) at 0.00097 M. Kinetics experiments with this apparatus showed that chloropicrin dissipated completely after 6 hours in light at 254 nm.

Additional kinetics experiments conducted by Castro and Belser (1981) investigated chloropicrin hydrolysis in solution under ambient light conditions, under a 150-watt flood lamp, and exposed to sunlight in a quartz cuvette in August. The latter two conditions yielded identical decay curves, with a half life of 3 days. Under ambient light, however, negligible hydrolysis occurred after 10 days. Castro and Belser (1981) concluded that photohydrolysis was proportional to the light available in the blue and ultraviolet regions of the electromagnetic spectrum. Furthermore, Castro and Belser (1981) concluded the fact that inorganic chloride was not formed at the expected rate of three times the disappearance of chloropicrin indicated the presence of chlorinated intermediates, which their analyses were not able to identify.

The hydrolysis of chloropicrin in a pH 7 aqueous 0.001-M solution was investigated by Moreno and Lee (1993); this study was also described by Wilhelm *et al.* (1996). Aliquots of the solution were injected with a syringe into 12-ml Teflon®-sealed vials, leaving no headspace, and incubated at 25°C under both dark and simulated-sunlight conditions (Suntest CPS photomachine with xenon lamp, 12-hour light/dark cycles). Three to five vials were sampled at 12, 24, 36, 48, 60, 72, 84 and 108 hours. Chloropicrin was quantitated by gas chromatography with a flame ionization detector, carbon dioxide was quantitated by gas chromatography/mass spectrometry, and a combination pH/ion analyzer was used to measure pH and to quantitate nitrate, nitrite, and chloride concentrations. There was no measurable hydrolysis of chloropicrin after 10 days under dark conditions. However, chloropicrin underwent significant photodegradation with simulated sunlight. The estimated half-life was 31.1 hours. After 10 days, the chloropicrin concentration had declined to 91% of its initial concentration. The degradation products identified included carbon dioxide (a portion of which would ionize in solution to bicarbonate at the pH tested), chloride, nitrate and nitrite.

Oxidation-Reduction Reactions

Under reducing conditions, chloropicrin undergoes a series of dechlorinations (Zheng *et al.*, 2006; Lee *et al*., 2008). To investigate reactions with reduced sulfur compounds, 50-ml aliquots of a deoxygenated 0.0005-M chloropicrin stock solution were mixed with a deoxygenated sulfide solution in 55-ml serum bottles capped with Teflon®-faced butyl rubber stoppers, and incubated in the dark at 25°C (Zheng *et al.*, 2006). Hydrolysis controls contained only chloropicrin solution. Chloropicrin was quantitated by gas chromatography with an electron capture detector, and transformation products were analyzed by gas chromatography/mass spectrometry. Chloropicrin reacted completely with the sulfide solution, and was non-detectable in less than 1 hour; decay was exponential. The reaction was increased more than 20-fold when pH was increased from 5.8 to 8.9. In contrast, no discernable hydrolysis occurred in the chloropicrin-only controls. Transformation products from the chloropicrin-sulfide reactions included dichloronitromethane and chloronitromethane. These products formed simultaneously in kinetics experiments, suggesting that the reactions involve formation of radicals. Zheng *et al.* (2006) suggest that such reactions may be a significant pathway for chloropicrin dissipation in the environment, especially after drip irrigation applications where the saturated soil becomes anoxic.

Laboratory experiments by Lee *et al.* (2008) suggest that reduced iron species, like the reduced sulfur species used by Zheng *et al.* (2006), quickly and quantitatively react with chloropicrin to form dichloronitromethane and nitromethane. In their study, Lee *et al.* (2008) determined the half-life of such reactions to be less than 5 minutes.

Chloropicrin as a Disinfection Byproduct in Drinking Water

In addition to its presence in water following pesticide applications, chloropicrin concentrations occur as a byproduct of reactions between organic matter and certain water treatment chemicals used in chlorination, as well as other oxidative treatments used to disinfect drinking water (Merlet *et al*., 1985). Chloropicrin is a minor disinfectant byproduct, as it is formed at a rate that is at least 10-fold slower than major byproducts of disinfection such as chloroform. It is present in drinking water only at low concentrations (< 10 µg/L) under all conditions that have been investigated (Hoigne and Bader, 1988; Lee *et al.*, 2007; Yang *et al.*, 2007).

Chen and Weisel (1998) monitored several disinfection byproducts at three locations in a drinking water distribution system in New Jersey, in which free chlorine levels were maintained at 0.5 mg/L to prevent regrowth of microorganisms. Chloropicrin concentrations ranged from below the LOD of 0.05 µg/L to 0.9 µg/L. Mean chloropicrin concentrations were 0.1 µg/L in winter and 0.5 µg/L in summer. However, chloropicrin concentrations decreased with residence time in the distribution system, suggesting that chloropicrin was formed during treatment then dissipated following treatment; in contrast, most other byproducts continued to be formed during distribution of drinking water from the treatment plant (Chen and Weisel, 1998). Wells *et al.* (2001) found that grab samples of Seattle tap water contained chloropicrin at a mean concentration of 0.249 μg/L (n = 3), but that boiling tap water samples for 5 minutes decreased chloropicrin concentrations to below the LOD of 0.009 μg/L.

Krasner *et al.* (1989) collected quarterly water samples, from spring 1988 through winter 1989, at 35 utilities across the U.S. (ten of which were in California). These samples were analyzed for a number of disinfection byproducts, including chloropicrin. Results were reported as quarterly means across all 35 utilities; the quarterly mean for chloropicrin ranged 0.10 μg/L to 0.16 μg/L. Krasner *et al.* (1989) selected utilities operating under a wide variety of conditions. In a later study, Krasner *et al.* (2006) selected ten utilities with water sources high in organic carbon or bromide. Results were aggregated across all ten plants; the maximum chloropicrin concentration reported was 2.0 μg/L, and the median concentration was 0.2 μg/L.

<u>Bioconcentration in Aquatic Organisms</u>

Bioconcentration/bioaccumulation is defined by U.S. EPA (1996) as "the increase in concentration of the test substance in or on an organism (specified tissues thereof) relative to the concentration of test substance in the surrounding medium." Bioconcentration refers specifically to uptake of a substance solely from water. The bioconcentration factor (BCF) is the ratio of concentrations in fish tissues (expressed as wet weight of the fish) and surrounding water. A high BCF suggests a potential for a compound to segregate into body lipids rather than be excreted, and might be predicted from a high K_{ow} (Franke, 1996).

The relatively low K_{ow} and high water solubility of chloropicrin suggest that bioconcentration in aquatic organisms is likely to be low. Kenaga (1980) calculated a BCF of 8, based on a reported water solubility of 2,270 ppm. The calculation used a regression of BCF on water solubility for 170 chemicals. The regression equation was log BCF = 2.791 – 0.564(log water solubility).

Using the Estimation Program Interface, a software package available from U.S. EPA that relies on K_{ow} to predict the BCF, Sanderson *et al.* (2007) predicted a BCF of 8.1 for chloropicrin. U.S. EPA considers substances having a BCF exceeding 1,000 bioaccumulative, although actual bioaccumulation or bioconcentration is affected by pharmacokinetic differences between species (U.S. EPA, 2000).

Persistence in Air Environment

Chloropicrin is reactive and has a relatively short half-life in sunlight. The importance of photolysis as a primary mechanism for degradation of chloropicrin vapor is emphasized by a laboratory study conducted by Moilanen *et al.* (1978), in which negligible chloropicrin loss occurred in the dark over 70 days at 25°C – 30°C. Under laboratory conditions with simulated sunlight, chloropicrin vapor undergoes photodegradation to products such as phosgene, ozone, nitrogen dioxide, chlorine nitrate, and nitryl chloride, with an estimated half-life in the range of 3 – 18 hours under constant illumination (Allston *et al*., 1978; Carter *et al.*, 1997; Hatakeyama *et al.*, 1999; Wade *et al*., 2007). Carter *et al.* (1997), citing reviews of atmospheric reactions of halogenated and nitro compounds by Atkinson (1989 and 1994), stated that the only significant reactions of chloropicrin in air are due to photolysis rather than reaction with radical species such as OH, ozone, and NO_3.

Photolysis

The photodegradation of chloropicrin in the vapor phase was analyzed by Moilanen *et al.* (1978) in the laboratory under simulated sunlight (275-W RS Sunlamp). Chloropicrin was vaporized in a photoreactor at 0.1, 1.4 and 14 g/ml and irradiated at sunlight wavelengths (> 290 nm) continuously for 70 days at 25°C – 30°C. Control flasks incubated at the same temperature but in the dark showed little chloropicrin loss over the 70-day study. The photodegradation half-life was 20 days for all three concentrations tested. The initial photodegradation products were phosgene ($COCl_2$) and nitrosyl chloride (NOCl) resulting from the photochemical oxygenation of chloropicrin, with the following overall equation:

$$CCl_3NO_2 \Rightarrow COCl_2 + NOCl$$

Moilanen *et al.* (1978) concluded that this reaction required the presence of oxygen (Moilanen *et al.*, 1978), for two reasons. First, chloropicrin was stable when irradiated in a nitrogen atmosphere or in a flask from which oxygen was excluded. Second, when irradiated in the presence of $^{18}O_2$, a labeled oxygen atom appeared on newly-formed phosgene. Moilanen *et al.* (1978) proposed a mechanism with trioxazole intermediates to account for these results. Following its formation as an initial product of chloropicrin photolysis, nitrosyl chloride underwent photodegradation to nitric oxide (NO) and chlorine (Cl_2), the former oxidized further to yield nitrogen dioxide (NO_2). The accumulation of phosgene during the experiment indicated that it was relatively stable in the flasks under these experimental conditions, but Moilanen *et al.* (1978) predicted that in the atmosphere it would "be subject to rapid dissipation," hydrolyzing to yield carbon dioxide and hydrogen chloride. Helas and Wilson (1992) estimated phosgene's lifetime to be a few days at ground level, based on laboratory data.

Carter *et al.* (1997) measured chloropicrin absorption across the spectrum ranging 190 – 800 nm, and identified two maxima in the ranges 216 – 220 nm and 274 – 276 nm. Although Carter *et al.* (1997) observed no significant absorption at wavelengths above 370 nm, sufficient absorption occurred in the range 300 – 360 nm to suggest that photolysis will occur in ambient sunlight. Chloropicrin photodegradation was measured in two environmental chambers consisting of 4' x 4'x 8' interconnected Teflon reaction bags. The chambers were mounted side-by-side in a room with reflective walls, and irradiated with four xenon arc lamps at the opposite end of the room. The half-life was estimated at 18 hours, and with assumptions that 0.87 $\pm$ 0.26 moles of chloropicrin will photodegrade per mole of photons absorbed and that their chamber conditions closely approximate daytime conditions (except with higher light intensity from sunlight), Carter *et al.* (1997) predicted that in ambient sunlight the half-life would range 3.4 – 7.6 hours. These values are considerably less than the 20-day half-life reported by Moilenen *et al.* (1978), probably due to differences in light intensity at the locations of the spectrum where chloropicrin absorption occurs (Carter *et al.*, 1997). Furthermore, Carter *et al.* (1997) found that photolysis occurred in a nitrogen atmosphere; they suggested that the fact the photolysis did not need oxygen in their experiments, along with the much faster reaction rate in their experiments than reported by Moilenen *et al.* (1978), might indicate that different wavelengths favored different mechanisms, with the trioxazole mechanism dominating only at wavelengths longer than 360 nm. Carter *et al.* (1997) concluded that at wavelengths in the range of 300 – 360 nm, their data were more consistent with initial cleavage of the C-N bond with formation of a trichloromethyl radical (•CCl_3) and an electronically excited species of nitrogen dioxide (NO_2^*) as the major mechanism:

$$CCl_3NO_2 \Rightarrow \bullet CCl_3 + NO_2^*$$

Chloropicrin reactivity with several organic compounds was also monitored in the photoreactors by Carter *et al.* (1997). Chloropicrin reacted with the organic compounds, and catalyzed formation of ozone, but at a much slower rate than chlorine.

A preliminary study, with only a limited description of experimental conditions, suggests a photolysis half-life of 3.3 hours for chloropicrin. Allston *et al.* (1978) analyzed a total of 19 absorption spectra of chloropicrin over the wavelength range 190 – 400 nm. In that range, chloropicrin absorbed light between 190 nm and 375 nm, with absorption maxima at 202 $\pm$ 1 nm and 272 $\pm$ 2 nm. Assuming photolysis of 1 mole of chloropicrin per mole of photons absorbed, Allston *et al.* (1978) calculated a photodissociation lifetime at ground level of 4.8 hours. A lifetime for an exponential decay process is the amount of time for a concentration to decrease to 1/e times the initial concentration. As 1/e is approximately 0.3679, a photolysis lifetime is approximately 1.443 times a photolysis half-life, and a lifetime of 4.8 hours corresponds to a half-life of 3.3 hours.

Hatakeyama *et al.* (1999) monitored photodissociation of chloropicrin in air at 1 atm in a 6-m^3 reaction chamber irradiated with nineteen 1-kW xenon arc lamps; light intensity, expressed as NO_2 photolysis rate, was 0.2/min. Concentrations of chloropicrin and its reaction products were monitored with Fourier transform infrared emission spectroscopy; a total of 64 repeat scans were run at 1 cm/min resolution (neither reaction time nor scan time were reported). Hatakeyama *et al.* (1999) estimated a first-order photodecomposition rate of 9.6 x 10^{-4}/min, which corresponds to a half-life of 12 hours. They identified the following photoproducts in the chamber: phosgene, ozone, nitrogen dioxide, chlorine nitrate, and nitryl chloride. Nitrosyl chloride was not observed; Hatakeyama *et al.* (1999) suggested that it would photolyze too rapidly to be detected in their system. Phosgene was formed at almost a 1:1 ratio with the amount of chloropicrin added, which ranged from 500 – 2,000 ppb. Hatakeyama *et al.* (1999) agreed with Carter *et al.* (1997) with regard to the primary mechanism of chloropicrin photolysis.

Wade *et al.* (2006) conducted detailed studies of chloropicrin photodissociation at room temperature using a series of unfocused lasers to specifically excite chloropicrin at wavelengths of 193 nm (argon fluoride laser), 248 nm (krypton fluoride laser), and 266 nm (neodimium:yttrium aluminum garnet laser). Emission spectra were monitored for 1 – 2% chloropicrin vapor in helium buffer gas using step-scan Fourier transform infrared emission spectroscopy. Wade *et al.* (2006) concluded that the primary response of chloropicrin to light at these wavelengths was to form $\bullet CCl_3$ and NO_2^*, the mechanism supported by Carter *et al.* (1997) and Hatakeyama *et al.* (1999). Both compounds rapidly react to form other products, such as nitric oxide. The evidence suggested that phosgene and nitrosyl chloride are secondary products of subsequent reactions (Wade *et al*., 2006).

Vera *et al.* (2010) conducted photolysis experiments under laboratory conditions, and also using ambient sunlight. Laboratory experiments used a 171-cm^3 Pyrex reaction vessel maintained at a temperature of 25 $\pm$ 2°C. Infrared spectra were recorded before the start of each experiment and also during the reaction phase, using a Fourier Transform infrared spectrometer with a mercury cadmium telluride detector. The light source was a 500-watt medium pressure mercury lamp. Chloropicrin was added to the vessel at a pressure ranging 5 – 10 mm Hg, with nitrogen diluent gas with 100 – 400 mm Hg pressure. Vera *et al.* (2010) reported that phosgene was the only carbon-containing reaction product in this anaerobic system, and its yield was essentially 1:1.

Photolysis in ambient sunlight was monitored in the spring and summer of 2006 and 2007 using a chamber in an outdoor photoreactor named "EUPHORE," located in Valencia, Spain. The two dome-shaped EUPHORE chambers each have a volume of 200 m^3, and are covered by a Teflon foil that is at least 75% transparent to solar radiation in the 290- to 500-nm wavelength range. A non-reactive tracer gas, SF_6, was added to chloropicrin to allow tracking of gas diffusion through the chamber wall; the chamber was slightly over-pressurized to minimize inward diffusion, and concentrations of chloropicrin and reaction products were corrected for SF_6 loss. The reaction procedure was as follows: gases were introduced into the chamber and allowed to mix for 30 minutes, then the chamber's cover was opened to allow sunlight to enter, and "middle of the day" sunlight exposure under "relatively clear" skies occurred for 4 – 7 hours. Infrared spectrometry was used to monitor chloropicrin decay and phosgene formation during the 30-minute dark mixing interval, as well as during the sunlight exposure interval; ozone formation was monitored using ultraviolet absorption. Negligible chloropicrin loss occurred during the 30-minute dark interval. The initial chloropicrin concentration was in the range of 137 – 353 ppb. Vera *et al.* (2010) reported photolysis lifetimes ranging from 5.4 – 7.1 hours, corresponding to a half-life range of 3.7 – 4.9 hours, with phosgene as the major product having a 1:1 yield.

ENVIRONMENTAL CONCENTRATIONS

Air

California has laws intended to limit ambient air concentrations of pesticides, including the Toxic Air Contaminants Act (California Health and Safety Code, Sections 39650-39761), which codified the state program to evaluate and control toxic air contaminants. Chloropicrin is listing as a toxic air contaminant (3 CCR 6860(a)). In California, chloropicrin concentrations have been monitored in the air surrounding application sites and in the ambient air during peak application season. These studies are discussed below. Additionally, numerous studies have monitored chloropicrin concentrations during occupational activities. Occupational monitoring is summarized in the Exposure Assessment section.

Ambient Air

Chloropicrin concentrations have been monitored by ARB in ambient air, not associated with specific applications. Samplers in each case consisted of duplicate sampling tubes containing XAD-4 resin. Information about all three studies is summarized in Table 7, including reported detection and quantification limits and the maximum concentration reported in each study. The limit of detection (LOD), also called the method detection limit, is "...the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero..." (Segawa, 1995). The limit of quantification (LOQ), sometimes called the "estimated quantitation limit," is a threshold above which results are generally considered reliable (Helsel, 2005).

Ambient air monitoring was conducted by ARB and DPR in areas and at times when chloropicrin use was anticipated to be high. However, actual locations and timing of applications can vary relative to monitoring, and although general information about applications in an area is available through the PUR, applications are reported in the PUR in 1-mi^2 sections and distances of applications from ambient air samplers are unknown. Furthermore, applications spanning multiple days in a single field can be reported in PUR as occurring on a single date; thus, there is no way to exactly relate applications to ambient air monitoring data. Even with these caveats, examination of Table 7 suggests that the reported concentrations may underestimate actual ambient air concentrations for short-term exposures. For example, the earliest ambient air study (ARB, 1987) was unable to detect chloropicrin in most samples. Limited ambient air monitoring was conducted by DPR in 2000, with just five samplers collecting samples for a total of 72 hours in association with two nearby soil fumigations with methyl bromide/chloropicrin products (Wofford *et al*., 2003). Chloropicrin was not detected in any of the 60 samples; method detection limits were 0.111 $\mu g/m^3$ for 8-hour samples and 0.056 $\mu g/m^3$ for 16-hour samples. Of the two studies done by ARB in 2001, the one in Kern County reported mostly non-detects; just five of 162 samples contained chloropicrin above the LOQ (ARB, 2003a). And in the other study conducted in 2001, 129 of 157 samples contained chloropicrin above the LOQ; this study also reported the highest 24-hour chloropicrin concentration measured in any ambient air study, 14.3 $\mu g/m^3$ (ARB, 2003b).

Table 7. Ambient Air Monitoring for Chloropicrin in California Counties

County [a]	Dates	No. Samples	LOD [b] (µg/sample)	LOQ [c] (µg/sample)	Samples ≥ LOQ	Maximum (µg/m^3) [d]
Monterey [e]	8/26/86 – 9/18/86	71	0.02	not given	20 [f]	5.18
Santa Barbara [g]	10/7/00 – 11/19/00	60	0.016	0.200	0	No detects
Kern [h]	6/30/01 – 8/31/01	162	0.00396	0.0198	5	0.75
Monterey, Santa Cruz [i]	9/08/01 – 11/8/01	157	0.00396	0.0198	129	14.3

[a] Monitoring conducted by the Air Resources Board (ARB) and the Department of Pesticide Regulation (DPR).
[b] Limit of Detection. In some study reports, this is called the "method detection limit," or MDL. It was set in the three most recent studies as 3.14 x the standard deviation following analysis of seven replicate cartridges spiked at a level near the anticipated LOD (ARB, 2003a; ARB, 2003b; Wofford *et al.*, 2003). ARB (1987) did not describe the method used to determine the LOD.
[c] Limit of Quantification. In some study reports, this is called the "estimated quantitation limit," or EQL. It is set as 5 times the LOD. ARB (1987) did not report an LOQ; number of results ≥ LOD are reported in the next column. Wofford *et al.* (2003) did not specify how the LOQ was determined, other than to say it was the level above which results could be quantitated, and that it was rounded to 0.2 µg/tube.
[d] For duplicate (collocated) samples, the higher of the two measured concentrations is reported here. Multiply concentrations in µg/m^3 by 0.1487 to get concentrations in parts per billion (ppb).
[e] ARB (1987). Three sites plus background. Samples were each collected over 4 hours, with a reported LOD of 0.085 µg/m^3. Sample sites and dates were selected to coincide with pre-plant applications for strawberries.
[f] Results above the LOD were reported by ARB (1987) in 20 of 96 samples; no LOQ was given.
[g] Wofford *et al.* (2003). Five sites in the city of Lompoc were monitored by DPR. Samples were collected in 8- to 16-hour intervals for a total of 72 hours beginning with each of two nearby soil fumigations. No chloropicrin was detected in any sample; the LODs for 8- and 16-hour samples were 0.111 and 0.056 µg/m^3, respectively (sample volumes were 0.144 and 0.288 m^3: 0.016/0.144 = 0.111, and 0.016/0.288 = 0.056).
[h] ARB (2003a). Five sites plus background. Samples were each collected over 24 hours, with a 24-hour LOD of 0.028 µg/m^3. Sample sites and dates were selected to coincide with pre-plant applications for carrots.
[i] ARB (2003b). Four sites in Monterey County (including one background site) and two sites in Santa Cruz County; three of the six sites did not have strawberry fields within a 3-mile radius, while the other three sites had strawberry fields within 360 feet to 1 mile. Samples were each collected over 24 hours, with an LOD of 0.028 µg/m^3. Sample sites and dates were selected to coincide with pre-plant applications for strawberries.

Chloropicrin concentrations reported in these ambient air monitoring studies are lower than those reported during application site monitoring (see the next section). This is consistent with studies showing that the highest airborne pesticide concentrations occur adjacent to an application (Siebers *et al.*, 2003; Garron *et al.*, 2009). As insufficient information is available to determine how concentrations measured in ambient air monitoring relate to the range of concentrations actually encountered by the public, and to assure health-protective estimates, concentrations reported in ambient air monitoring were not used to estimate airborne chloropicrin exposures.

Application Site Air – Soil Fumigation

Two types of data have been collected during air monitoring associated with chloropicrin applications: air concentration samples taken on-site for direct estimation of chloropicrin field volatility (emission rate or flux), and off-site concentrations of chloropicrin in air. Results are reported as time-weighted average (TWA) concentrations.

Off-site concentrations are reported below. Measured air concentrations can fluctuate throughout a sampling interval, with the environmental conditions that affect measured air concentrations being specific to a particular application. Measurements taken during one particular application cannot be directly generalized to applications occurring under different environmental conditions (Johnson *et al*., 1999). Consequently, it is unlikely that the measurements from one particular study will capture the highest possible air concentrations for an application method.

Field volatility data for chloropicrin, and concentration estimates based on these data, are summarized following the discussion of measured off-site concentrations. Flux, or emission rate, is the rate at which a chemical's mass moves out of the ground into the air, and is expressed in units such as $\mu g/m^2/sec$. Direct estimation of flux uses air concentrations measured by multiple samplers attached at different heights to a sampling mast in the center of the field. Regression of the logarithm of sampler height against the wind speed, air temperature, and TWA concentrations at each height yields the flux estimate for each time interval; an example of this type of calculation was provided by Majewski *et al.* (1990). All chloropicrin flux estimates reported in this EAD were obtained by using direct flux estimation.

Flux data are used, together with an appropriate air dispersion model, to estimate off-site concentrations associated with a fumigation. Air dispersion models use mathematical equations to simulate how air molecules, and volatilized chemicals mixed with them, move away from the chemicals' source (a fumigated field in this case). DPR uses the Industrial Source Complex Short Term model, Version 3 (ISCST3), to estimate off-site concentrations. ISCST3 is based on a steady-state Gaussian plume dispersion equation, which means that the chemical is assumed to have a normal (or Gaussian) distribution of concentrations within the plume, with the concentration peak occurring at the plume's centerline and concentrations decreasing along the edges of the plume. The model is "steady-state" in that TWA concentrations are calculated assuming constant emission rate and meteorological conditions for each hour; conditions may vary from one hour to the next (U.S. EPA, 1995). ISCST3 assumes that off-site concentrations are proportional to flux. DPR analysis imposes the additional assumption that flux is proportional to application rate (Johnson *et al.*, 1999).

Chloropicrin concentrations were modeled using the "screening" mode in ISCST3. As explained by Barry (2008a), "screening mode produces a single air concentration estimate at a receptor (a point location at a specified distance from the source) using a single set of worst-case meteorological conditions. This means that a single downwind centerline set of air concentration estimates at various distances is the result of the analysis." Barry (2008a) mentions other ISCST3 modes, which use historical meteorological data "to produce multiple air concentration estimates at each receptor. This produces a distribution of air concentrations at a given receptor over the span of the meteorological data." In the screening mode, DPR first simulates generic downwind centerline concentrations using a default flux of 100 $\mu g/m^2/sec$. Next, the generic downwind centerline concentrations are adjusted for the flux estimated during the study, and for application rate. The adjusted concentrations are used to estimate bystander exposures.

Off-Site Concentrations

Preliminary monitoring studies of off-site concentrations in air of methyl bromide and chloropicrin were conducted by DPR during three shallow shank tarped broadcast applications in 1982 and 1983 in Orange County (Maddy *et al.*, 1983; 1984). Neither the application rate of the methyl bromide/chloropicrin mixture nor the proportion of chloropicrin in the mixture was reported, precluding the use of these data in estimating exposure. Maximum chloropicrin concentrations reported were 713 $\mu g/m^3$ (106 ppb) at 25 ft (7.6 m) downwind and 545 $\mu g/m^3$ (81 ppb) at 50 ft (15 m) downwind.

Monitoring of off-site chloropicrin concentrations in conjunction with soil fumigations has been conducted by ARB (2003a; 2004; 2006) as well as in studies submitted by registrants (Beard *et al.*, 1996; Rotondaro, 2004). With the exception of ARB (1987), these data sets are summarized in Table 8, and briefly described below. ARB (1987) monitored off-site concentrations during a 2-day tarped broadcast application to a strawberry field of an unspecified methyl bromide/chloropicrin mixture using three samplers, one 902 ft (275 m) NW of the field, and two 220 ft (67 m) and 574 ft (175 m) SE of the field. No information was reported about the field size or the application rate, precluding the use of these data in estimating bystander exposure. The maximum chloropicrin concentration reported in this study was 160 $\mu g/m^3$ (24 ppb) during a 3-hour sample collected on the second application day at the sampler located 574 ft (175 m) SE of the field edge.

Off-site concentrations of chloropicrin were monitored adjacent to bed fumigations by ARB in three studies conducted between 2001 and 2005 (ARB, 2003c; 2004; 2006). Two of these were associated with applications of methyl bromide/chloropicrin mixtures, and applications and monitoring were impacted by regulatory requirements for soil fumigations with methyl bromide, including buffer zone requirements. The third study (ARB, 2006) involved monitoring during and following an application of a 94% chloropicrin product. Samplers consisted of 8 mm x 150 mm adsorbent tubes containing 400 mg XAD-4 resin, with a back-up section of 200 mg of XAD-4 resin to verify that no breakthrough occurred, connected to sampling pumps with Teflon tubing and fittings. The pump flow rate was 90 standard cubic centimeters per minute (i.e., flow rate is referenced to a standard temperature of 25°C and standard pressure of 760 mm Hg, rather than actual temperature and pressure during study, but it is approximately 0.1 liters per minute). The flow rate was calibrated with a digital mass flowmeter at the start and end of each sampling interval. The sampler flow rate was increased to 100 standard cubic centimeters per minute in the second and third studies (ARB, 2004; ARB, 2006). The optimal sampler flow rate was determined during method validation; chloropicrin breakthrough occurred readily at flow rates $\geq$ 0.2 liters per minute, but not at 0.1 liters per minute (ARB, 2003c).

Table 8. Studies Monitoring Off-Site Chloropicrin Concentrations Associated with Soil Fumigation

Application Method	Rate (lbs AI/acre) [a]	Sampler Distance (m) [b]	Total Samples	LOQ [c] (µg/sample)	Samples ≥ LOQ	Maximum Concentration (µg/m³) [d]	Maximum Concentration (hours) [e]
Broadcast non-tarped [f]	171	18 – 55	398	0.07	209	1,820	6.52
Broadcast tarped [f]	332	18 – 55	444	0.07	242	968	6.00
Broadcast tarped [g]	343	18 – 55	444	0.07	438	677	6.00
Broadcast tarped [h]	346	18 – 55	444	0.07	243	868	13.0
Bedded non-tarped [f]	86	18 – 55	264	0.07	106	1,760	6.00
Bedded tarped [i]	125	265	64	0.150	22	39	14.8
Bedded tarped [j]	150	50	44	0.0198	43	270 [k]	10.6
Bedded tarped [f]	189	18 – 55	420	0.07	196	1,810	6.10
Bedded tarped drip [l]	188	20	62	0.0198	62	415	8.4
Bedded tarped drip [m]	156	15	255	0.1	81	349	3.82
Greenhouse drip [n]	13.6	1.5	224	0.1	4	14.9	5.58
Greenhouse drip [n]	166	1.5	256	0.1	203	577	4.00
Greenhouse drip [n]	174	1.5	224	0.1	30	108	4.02

[a] For bedded applications, the reported rate is for the total acres, including furrows as well as beds. Beds reduce treated acres by 50 – 58%. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[b] Sampler distance from edge of greenhouse, otherwise from edge of treated plot.
[c] LOQ: Limit of Quantification. In some study reports, this is called the "estimated quantitation limit," or EQL.
[d] Highest measured concentration associated with the application. Multiply value by 0.1487 to get result in parts per billion (ppb).
[e] Time interval for sample with highest reported concentration associated with the application (i.e., the concentration in the previous column).
[f] Fumigant consisting of 99.4% chloropicrin was applied to plots near Phoenix, Arizona (Beard *et al*., 1996).
[g] Fumigant consisting of 99.4% chloropicrin was applied to a field in Washington (Beard *et al*., 1996).
[h] Fumigant consisting of 99.1% chloropicrin was applied to a field in Florida (Beard *et al*., 1996).
[i] Fumigant consisting of 50:50 chloropicrin:methyl bromide was applied over three days at 250 lbs product/acre (125 lbs chloropicrin/acre), to a 22-acre (8.9-ha) field in Monterey County, California (ARB, 2003c).
[j] Fumigant consisting of 50:50 chloropicrin:methyl bromide was applied at 300 lbs product/acre (150 lbs chloropicrin/acre), to a 4.8-acre (1.9-ha) field in Santa Cruz County, California (ARB, 2004).
[k] This concentration occurred during background sampling. Nearby applications were documented on days preceding the monitored application.
[l] Fumigant consisting of 94% chloropicrin was applied to an 8.2-acre (3.3-ha) field in Santa Barbara County, California (ARB, 2006).
[m] Fumigant consisting of 99.1% chloropicrin was applied to a California field (Rotondaro, 2004).
[n] Fumigant consisting of 99.1% chloropicrin was applied to beds in a California greenhouse (Rotondaro, 2004).

Quality assurance in ARB monitoring consisted of co-located replicate sampling at one sampler; a laboratory solvent blank, a laboratory spike, a laboratory method blank and a laboratory control sample with each set of samples analyzed; trip blanks; and trip, field, and laboratory spikes. Samples were analyzed via gas chromatography with a mass selective detector operating in selective ion mode and a Restek Rtx-200 column.

In 2001, ARB monitored off-site chloropicrin concentrations during and following a shallow shank tarped bed application of a methyl bromide/chloropicrin 50:50 mixture in Monterey

County (ARB, 2003c). The application was to a 22-acre (8.9-ha) field, and the application rate was 125 lbs AI/acre (140 kg/ha). Because of restrictions on the methyl bromide application, the application occurred over three days. Background samples were collected from 1500 hour on October 29 to 1000 hour on October 30; chloropicrin was detected in all of the background samples, at concentrations up to 2.0 $\mu g/m^3$ (0.3 ppb). Air monitoring around the treated field was conducted from October 31 to November 4. Eight air samplers, one on each side and one at each corner, were positioned 850 to 1,665 ft (259 to 507 m) from the field edge (two samplers were collocated on the north side of the field). The highest concentration detected was 39 $\mu g/m^3$ (5.8 ppb). Mean recovery of field spikes was 94%; sample results were not corrected for field spike recoveries.

In 2003, ARB monitored off-site chloropicrin concentrations during and following a shallow shank tarped bed application of a methyl bromide/chloropicrin 50:50 mixture in Santa Cruz County (ARB, 2004). The application was to a 4.8-acre (1.9-ha) field, and the application rate was 150 lbs AI/acre (168 kg/ha). Eight air samplers, one on each side and one at each corner, were positioned 160 ft (49 m) from the field edge (two samplers were collocated on the north side of the field). Mean recovery of field spikes was 91%. Background samples were collected from 0630 hour to 1700 hour (daytime) and 1700 hour to 0600 hour (nighttime) on November 12 to 13. Chloropicrin was above the LOQ in all of the background samples, at concentrations up to 270 $\mu g/m^3$ (40 ppb); in fact, the highest concentrations reported in the study occurred in the background samples. ARB (2004) advised caution in using results from this study because of known nearby applications, and because rain occurred during sampling, confounding interpretation of study results.

In 2005, ARB monitored off-site chloropicrin concentrations during and following a drip tarped bed application of chloropicrin 94% in Santa Barbara County (ARB, 2006). The application was to an 8.2-acre (3.3-ha) field, and the application rate was 188 lbs AI/acre (211 kg/ha). The beds were covered with a single clear tarp, 1.34 mil thickness, with a double layer at the ends; ARB (2006) noted that the doubled tarp deviated from typical practice. Eight air samplers, one on each side and one at each corner, were positioned 60 ft (18 m) from the field edge (two samplers were collocated on the southeast corner of the field). Background samples were collected prior to the application, as usual. Chloropicrin was detected in all of the background samples, at concentrations up to 5.04 $\mu g/m^3$ (0.749 ppb); this is in the range of concentrations reported during ambient air sampling. Mean recovery of field spikes was 95%; sample results were not corrected for field spike recoveries.

In the studies conducted by Beard *et al.* (1996) and Rotondaro (2004), off-site movement of chloropicrin was monitored at sites in three states in association with soil fumigations using four different application methods. In all cases, air samples were collected with XAD-4 sorbent tubes connected to pumps calibrated at 50 ml/min. Tubes had 400 mg sorbent in the front section and 200 mg in the back section; to determine breakthrough back sections were analyzed in 10% of the field and travel spikes, and in any samples in which the amount of chloropicrin recovered from the front section exceeded approximately 0.4 µg. Breakthrough was below the level of concern (Beauvais, 2009). Chloropicrin was analyzed by gas chromatography with a nickel-63 electron capture detector.

Beard *et al.* (1996) monitored off-site chloropicrin concentrations associated with applications to fields in Washington (broadcast tarped application), Florida (broadcast tarped application), and Arizona (broadcast tarped, broadcast non-tarped, bedded tarped, and bedded non-tarped applications). Samplers were located at 60, 120, and 180 feet (18, 37, and 55 m) from the four edges of each field (north, south, east and west). Sampling intervals were 6 hours per sample during the first 48 hours, and 12 hours per sample over the following 12 days (14 days total). The non-tarped bedded application was monitored for 7 rather than 14 days. The highest concentration during any sampling interval was 1,820 $\mu g/m^3$ (271 ppb), measured 0 – 6 hours following the non-tarped broadcast application in Arizona.

Rotondaro (2004) monitored off-site chloropicrin concentrations associated with two types of applications in California, field (outdoor) surface drip and greenhouse (indoor) surface drip. Samplers were located at a single distance, 50 feet (15 m) from the field application and 5 feet (1.5 m) from the edge of the greenhouse, at four sides and four corners of the field or greenhouse. Sampling intervals were 4 hours per sample during the first 48 hours, and 12 hours per sample for an additional 8 – 10 days (10 - 12 days total). The highest concentration from the field drip irrigation was 349 $\mu g/m^3$ (51.9 ppb), measured 4 – 8 hours following the application. Rotondaro (2004) monitored off-site concentrations 1.5 m from the outside of three greenhouses during and following drip applications. At two of the three greenhouse sites, most concentrations were below the LOQ. At the third site, the maximum concentration was 557 $\mu g/m^3$ (82.8 ppb), measured 4 – 8 hours following the application.

Off-site concentrations are proportional to application rate. For all of the studies summarized in Table 8, higher application rates are allowed on current product labels than were used in the studies. Table 9 summarizes the maximum concentration in each study, adjusted for the maximum rate allowed in California. Four of the data sets summarized in Table 8 were omitted from Table 9: 1) the bedded tarped application monitored by ARB (2003c), with samplers positioned 265 m from the treated field; 2) the bedded tarped application monitored by ARB (2004), in which the highest concentration occurred in background samples; 3) and 4) two of the three greenhouse drip applications monitored by Rotondaro (2004), in which most samples were below the LOQ.

The distance from the application edge to the sampler where the highest concentration occurred is included in Table 9, as is the field size; higher concentrations would be anticipated if samplers had been positioned closer to the treated fields or if larger fields had been treated (Barry, 2005b). Sampling intervals associated with the maximum concentration are also listed in Table 9, and ranged from 4.0 to 13.0 hours. Shorter sampling intervals under the same conditions (size, application method, rate) would result in higher concentrations (Barry, 2000).

Table 9. Off-Site Chloropicrin Concentrations Associated with Soil Fumigation, Adjusted for Maximum Application Rate

Application Method	Sampler Distance (meters) [a]	Field Size (acres) [b]	Study Application Rate (lbs/acre) [c]	Maximum Application Rate (lbs/acre) [c]	Sample Interval (hours)	Reported Maximum Concentration (µg/m³) [d]	Adjusted Maximum Concentration (µg/m³) [e]
Broadcast non-tarped [f]	18	8.01	171	500	6.5	1,820	5,322
Broadcast tarped [f]	35	7.97	332	500	6.0	968	1,458
Broadcast tarped [g]	18	8.35	343	500	6.0	677	987
Broadcast tarped [h]	18	8.18	346	500	13.0	868	1,254
Bedded non-tarped [f]	18	8.46 [i]	86	250	6.0	1,760	5,116
Bedded tarped [f]	18	5.92 [j]	189	500	6.1	1,810	4,788
Bedded tarped drip [k]	20	8.2 [l]	188	300	8.4	415	622
Bedded tarped drip [m]	15	8.67 [n]	156	300	4.0	349	671
Greenhouse drip [o]	1.5	0.831 [p]	166	300	6.0	577	1,043

[a] Sampler distance from edge of treated plot; greenhouse drip distance from edge of greenhouse.
[b] For bedded applications, the total acres are reported, including furrows as well as beds; where available, treated acres are listed in footnotes below. Multiply value by 0.405 to get area in hectares (ha).
[c] For bedded applications, the reported rate is for the total acres, including furrows as well as beds. Beds reduce treated acres by 50 – 58%. The maximum application rate is the highest allowed for that method on any current product label in California. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[d] Highest measured concentration associated with the application. Multiply value by 0.1487 to get result in parts per billion (ppb).
[e] Calculated by multiplying highest reported concentration by ratio of maximum application rate to study application rate (assumes that concentration is proportional to application rate).
[f] Fumigant consisting of 99.4% chloropicrin was applied to plots near Phoenix, Arizona (Beard *et al*., 1996).
[g] Fumigant consisting of 99.4% chloropicrin was applied to a field in Washington (Beard *et al*., 1996).
[h] Fumigant consisting of 99.1% chloropicrin was applied to a field in Florida (Beard *et al*., 1996).
[i] 4.86 acres treated.
[j] 2.96 acres treated.
[k] Fumigant consisting of 94% chloropicrin was applied to a California field (ARB, 2006).
[l] No information given about bed width or acres treated.
[m] Fumigant consisting of 99.1% chloropicrin was applied to a California field (Rotondaro, 2004).
[n] 4.5 acres treated.
[o] Fumigant consisting of 99.1% chloropicrin was applied to beds in a California greenhouse (Rotondaro, 2004).
[p] 0.0741 acres treated.

Field Volatility (Flux)

In the field volatility studies available to DPR, flux of chloropicrin was estimated by a direct measurement method using a central gradient sampling mast supporting multiple samplers (Beard *et al*., 1996; Rotondaro, 2004). Air samples were collected with XAD-4 solid sorbent tubes having 400 mg sorbent in the front section and 200 mg in the back section; tubes were connected to pumps calibrated at 50 ml/min. Chloropicrin was analyzed by gas chromatography with a nickel-63 electron capture detector.

Beard *et al.* (1996) characterized flux during four types of applications to fields in Arizona: broadcast tarped, bedded tarped, broadcast non-tarped, and bedded non-tarped. Flux was also profiled during broadcast tarped applications to fields in Washington and Florida; the flux was lower following these applications, and they are not considered further in this EAD other than in comparison with results from the Arizona application. In the center of each treated plot, a gradient sampling mast supported six air samplers at 15, 33, 55, 90, and 150 cm above the treated soil surface; two samplers were collocated at 150 cm. Two masts were located near each other, and alternated in sequential sampling intervals; this allowed continuous monitoring when samplers were changed. Monitoring lasted 6 hours per sample during the first 48 hours, and 12 hours per sample for an additional 12 days (14 days total). The non-tarped bedded application was monitored for 7 rather than 14 days.

Quality assurance consisted of laboratory and field spikes (sampling tubes fortified with known amounts of chloropicrin), solvent blanks, and controls. Field spikes were fortified at the start of each monitoring period by injecting 1-5 µL of chloropicrin dissolved in hexane; after the solvent was evaporated, tubes were attached to sampling pumps and air was drawn through them throughout the monitoring periods. During analysis, each batch of samples was co-analyzed with a solvent blank, control tube, and laboratory spikes that were fortified before analysis (but not connected to a sampling pump). Laboratory spikes are included as a check on the analytical procedure, and field spikes are checks on environmental conditions and potential interferences during sample collection, transport, storage, and analysis. The mean percent recovery $\pm$ standard deviation (SD) of recoveries from laboratory spikes were 87 $\pm$ 17%, 93 $\pm$ 24%, and 85 $\pm$ 21% for analyses of samples collected in Arizona, Washington, and Florida, respectively. Data from the three sites were considered separately because monitoring was conducted at different times; additionally, at the Arizona site data from non-tarped and tarped applications are considered separately, as monitoring of the two types of applications occurred at different times.

For the purpose of adjusting results for field spike recoveries, data from the three sites were considered separately because monitoring was conducted at different times; additionally, at the Arizona site data from non-tarped and tarped applications were considered separately, as monitoring of the two types of applications occurred at different times. Field spike recoveries were generally acceptable at the Arizona and Florida sites, where mean recoveries ranged 78 – 107%. At the Washington site, mean field spike recoveries were acceptable for the mid- and high-level spikes, at 118% and 109%, respectively. Mean $\pm$ SD of low-level field spikes at the Washington site was 164 $\pm$ 65, and the range was 79.5 – 384%. Ranges of mid- and high-level spikes at the Washington site were 44.2 – 193% and 39.4 – 223%, respectively. Beard *et al.* (1996) adjusted sample residues for field spike recoveries that were < 100%, with residue range intervals defined by mid-points between spike levels. This approach is similar to DPR policy for adjusting data used in estimating exposure, which is in general agreement with U.S. EPA policy, in which samples are corrected for field fortification recoveries below 90% (U.S. EPA, 1992; U.S. EPA, 1998). At the Arizona sites, the flux ranged from 114 to 222 $\mu g/m^2/sec$ during the highest 6-hour period, corresponding to 12 to 25 percent of the chloropicrin applied.

These three broadcast non-tarped applications represent the only flux data that are replicated. The replication allows calculation of a coefficient of variation (CV) for flux associated with this application method. The CV is calculated using this equation: CV = 100% x SD/mean (also called the Relative Standard Deviation). Calculations are detailed in Appendix 2. The CVs for 6-hour daytime flux, 6-hour nighttime flux, and 24-hour flux were 48.2%, 116%, and 80.8%, respectively.

Rotondaro (2004) characterized flux during two types of applications, field (outdoor) surface drip and greenhouse (indoor) surface drip. Barry (2005a) evaluated this study and found that, for multiple reasons, the chloropicrin measurements associated with the greenhouse drip applications were not suitable for use in estimating flux. For example, samplers were essentially located at the same distance from the application (1.5 m from the edge of the greenhouse), a distance that was also too close for effective back-calculation. Additionally, the majority of the results at one of the sites were non-detects; at that site, six of eight samplers were not near the treated area. Monitoring during the field drip application was conducted with a pair of masts, each of which supported six air samplers at 15, 33, 55, 90, and 150 cm above the treated soil surface; two samplers were collocated at 150 cm. Rotondaro (2004) reported that an estimated 15.2% of the applied chloropicrin mass was lost through field volatility during the 2-week monitoring interval. The highest flux, 70.1 $\mu g/m^2/sec$, occurred during the first 4-hour interval following the application.

Barry (2008a) calculated from the submitted studies the maximum estimated 6-hour TWA and 24-hour TWA chloropicrin soil flux densities (during both day and night sampling intervals); the highest flux values for each interval duration (6 hour and 24 hour), application method and application rate are summarized in Table 10. The 6-hour day and night intervals are considered separately because flux differs under day and night conditions. The 24-hour interval, of course, includes both day and night.

Table 10. Chloropicrin Flux Estimates Used to Estimate Off-Site Air Concentrations for Short-Term Exposures

Application Method [a]	Study Location	Study Application Rate (lbs/Acre) [b]	Study Effective Broadcast Application Rate (lbs/Acre) [c]	24-Hour Flux ($\mu g/m^2/sec$)	6-Hour Flux, Day [d] ($\mu g/m^2/sec$)	6-Hour Flux, Night [d] ($\mu g/m^2/sec$)
Broadcast non-tarped	Arizona	171	171	86	50	180
Bedded non-tarped	Arizona	149	86	66	114	113
Bedded tarped	Arizona	377	189	111	211	30
Broadcast tarped [e]	Arizona	332	332	108	132	142
Bedded drip tarped	California	300	156	22	47 [f]	5 [f]

[a] From Barry (2008a). Data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004).
[b] This application rate is the "treated acre" rate. For broadcast application methods the Study Application Rate and the Study Effective Broadcast Application Rate will be the same. For bedded applications an adjustment must be made to the Study Application Rate to account for the portions of the field that are untreated, because the treated area is the top of the bed only; the furrow area between the beds is untreated. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[c] The effective broadcast application rate is found by dividing the total amount of chloropicrin applied to the field by the whole area of the field, including untreated areas interspersed with the treated areas. In the case of bedded applications, the treated area is the top of the bed only, and the furrow area between the beds is untreated.
[d] The 6-hour flux is used to estimate both 6-hour and 1-hour TWA air concentrations. Then a peak-to-mean adjustment is made to the 6-hour TWA air concentrations to derive the 1-hour air concentrations (Barry, 2000).
[e] Data were available from multiple sites. Washington and Florida sites had lower flux and concentrations and are not included.
[f] These two flux estimates are 8-hour TWA due to the sampling intervals in the study.

For short-term bystander exposures, Barry (2008a) calculated rate-adjusted chloropicrin air concentrations at a point 1.2 m above ground (assumed breathing zone) and 10 feet (3.0 m) from the edge of the treated area. These estimates were derived using the ISCST3 model together with "screening mode" inputs. The treated field is modeled as a square 40-acre (16-ha) area source. Barry (2008a) used the following screening level meteorological conditions for each interval: 1 m/s wind speed and Pasquill-Gifford Class D stability (maximum daytime atmospheric stability) to estimate daytime 6-hour flux; 1.0 m/s and Class F stability (moderately stable atmospheric stability) to estimate nighttime 6-hour flux; and 1.4 m/s and Class C stability (slightly unstable daytime atmospheric stability) for 24-hour flux. The model yielded downwind centerline estimates of reasonable worst-case concentrations at any pre-determined distance from the edge of the field. Table 11 reports concentrations adjusted for the maximum application rates allowed on product labels currently registered in California.

Table 11. Chloropicrin Concentrations for Estimating Short-Term Bystander Exposures [a]

Application Method	Study Location	Maximum Application Rate (lbs/Acre) [b]	1-Hour, Day (μg/m^3) [c]	1-Hour, Night (μg/m^3) [c]	6-Hour, Day (μg/m^3)	6-Hour, Night (μg/m^3)	24-Hour (μg/m^3)
Broadcast non-tarped	Arizona	350	13,000	**75,000**	5,300	**31,000**	5,400
Bedded non-tarped	Arizona	175	29,000	47,000	12,000	19,000	3,500
Bedded tarped	Arizona	350	31,000	54,000	13,000	22,000	**5,200**
Broadcast tarped	Arizona	350	28,000	6,500	12,000	2,600	3,000
Bedded drip tarped	California	300	11,000	2,100	4,700	840	1,100

[a] From Barry (2008a), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, assuming a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre treated area, and have been rounded to two significant figures. Bolded values represent the highest concentration for the exposure duration. Multiply value by 0.1487 to get result in parts per billion (ppb).
[b] The application rate is the maximum allowed for that method on any product label currently registered in California for that use. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[c] 1-hour concentrations were estimated from the 6-hour concentrations by employing a peak-to-mean ratio as described in text (Barry, 2000).

Measurements of air concentrations are known to be sampling duration-dependent (Csanady, 1973; Pasquill, 1974). This is because real-time concentrations of an airborne chemical are heterogeneous and fluctuating. When a sample is collected, the final value is an average of all the variations in air concentration over the continuous period of sample collection. With shorter sampling durations, any extreme values will have a greater impact on the value of the final concentration than with longer sampling durations. Health-protective estimates will thus be higher for shorter durations. The shortest monitoring interval for flux in any chloropicrin study was 6 hours, and 1-hour concentrations were estimated from the 6-hour concentrations by employing a peak-to-mean ratio using the following equation (Barry, 2000):

$$C_p = C_m(t_p/t_m)^{-1/2}$$

Where:

C_p = peak concentration over period, t_p, of interest
C_m = mean concentration over measurement period, t_m
t_p = duration of peak period of interest
t_m = duration of mean measurement period

Due to equipment limitations, during pre-plant soil fumigations approximately 40 acres (16 ha) can be treated by one application rig and crew in a single workday. Larger fields may be treated on consecutive days (a practice commonly referred to as “rolling applications”). When this occurs, a bystander can potentially be located downwind of an application occurring that day, as well as another area treated the previous day. Barry (2008b) provided estimates of concentrations a bystander might be anticipated to encounter when downwind of a field currently being treated, with another field upwind having been treated the previous day. These estimates are summarized in Appendix 3.

The 24-hour TWA concentrations in Table 11 assume that an individual is located downwind throughout the exposure interval. For repetitive exposures over longer intervals of weeks or months, that assumption is not realistic, however. For seasonal and annual bystander exposure estimates, concentrations are needed that reflect the reality of changing wind directions. Furthermore, over longer intervals a bystander is unlikely to be consistently adjacent to 40-acre applications. As summarized in Appendix 4, over a recent 5-year interval (2004 – 2008), reported application sizes ranged from less than one acre to as many as 277 acres (larger acreages likely were treated over multiple days), and 40 acres was about the 80th or 85th percentile each year. The median application size is a better approximation of what bystanders are likely to encounter over longer intervals, and based on the use data summarized in Table A4-1 in Appendix 4 the typical application size was assumed to be 15 acres.

Assuming a 15-acre application, Barry (2010) estimated 2-week TWA concentrations that were used in estimating seasonal and annual bystander exposures. The approach was described by Barry (2008c), and involved first calculating an average 24-hour flux over 2 weeks, then adjusting with a time-scaling factor derived using peak-to-mean theory based on both empirical and theoretical studies. These concentrations are summarized in Table 12. The highest concentration, 230 $\mu g/m^3$ associated with bedded tarped applications, was assumed for seasonal and annual bystander exposures. This concentration was selected, rather than an average across all application methods, because no data are available on how often different application methods are used and it is possible that someone could be adjacent to multiple bedded fumigations over a period of time.

For long-term exposures application rates that are considered typical were assumed instead of the maximum rates allowed on current product labels. Table A4-2 in Appendix 4 summarizes cumulative percentile application rates, calculated from pounds chloropicrin applied and acres treated in chloropicrin applications as reported in the PUR (DPR, 2010a). Applications reported in the PUR do not include information about the application method, and tarped and non-tarped, broadcast and bedded, etc., applications are aggregated into a single distribution. Over the 5-year interval 2003-2007, the annual 50th percentile ranged between 111 and 188 lbs AI/acre, while the 95th percentile was 200 – 235 lbs AI/acre. For seasonal and annual exposure estimates, an application rate of 190 lbs AI/acre was assumed, corresponding to the high end of the range of median values as described in Appendix 4. An exception to this assumption was made for bedded non-tarped applications, which have a maximum application rate of 175 lbs AI/acre. As this rate is lower than the median application rate, and as no data are available to estimate the typical application rate for a single method, seasonal and annual exposures associated with non-tarped bedded applications assume the maximum rate of 175 lbs AI/acre.

Barry (2008c) also provided estimates of the proportion of applied mass that was lost through volatilization in the 2 weeks following fumigant introduction. These mass-loss estimates are listed as percentages in Table 12.

Table 12. Chloropicrin Concentrations Used to Estimate Seasonal and Annual Bystander Exposures [a]

Application Method	Study Location	Study Effective Broadcast Application Rate (lbs/Acre) [b]	Assumed Typical Application Rate (lbs/Acre) [c]	2-Week Flux ($\mu g/m^2/sec$) [d]	Percentage of Applied Mass Lost Over 2-Week Interval [e]	2-Week Average Concentration ($\mu g/m^3$)
Broadcast non-tarped	Arizona	171	190	10.39	62	120
Bedded non-tarped	Arizona	86	175	5.39	61	120
Bedded tarped	Arizona	332	190	21.45	69	**230**
Broadcast tarped	Arizona	189	190	12.37	63	74
Bedded drip tarped	California	156	190	2.24	15	29

[a] From Barry (2008c; 2010), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, assuming a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 15-acre treated area, and have been rounded to two significant figures. Bolded value represents the highest concentration for this exposure duration.

[b] This is the application rate used in the study; for bedded applications the effective broadcast application rate is found by dividing the total amount of chloropicrin applied to the field by the area of the entire field, rather than just the area treated, because the treated area is the top of the bed only, and the furrow area between the beds is untreated. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] An application rate of 190 lbs chloropicrin/acre is assumed to be a typical rate for seasonal and annual exposure estimates, based on the 50th percentile rate used in recent applications as summarized in Appendix 4. Because the maximum allowed rate for bedded non-tarped applications is 175 lbs chloropicrin/acre, that rate is also used for estimating season and annual exposures.

[d] This is the average 24-hour flux over the 2-week flux profile, adjusted for variation in weather conditions.

[e] This is the mass projected to be emitted over a 2-week interval, reported as percent of applied mass (Beard *et al*., 1996; Rotondaro, 2004).

<u>Application Site Air – Structural Fumigation</u>

ARB monitored off-site concentrations of chloropicrin during three structural fumigations with sulfuryl fluoride, in which chloropicrin was used as a warning agent (ARB, 2003d; 2005a; 2005b). These studies are summarized in Table 13.

In addition to the ARB studies, a registrant-submitted study measured off-site chloropicrin air concentrations during structural fumigation of four houses in Ventura, Riverside, and Fresno counties (Barnekow and Byrne, 2006). Chloropicrin exposures of bystanders to structural fumigation are based on data from this study. In two ARB studies (ARB, 2003d; ARB, 2005a) indoor air samples were collected for 48 hours following aeration. Exposures of individuals entering fumigated structures are based on monitoring by Barnekow and Byrne (2006) that was conducted a total of 36 hours post-aeration.

In all four studies, samplers consisted of 8 mm x 140 mm adsorbent tubes containing 400 mg XAD-4 resin, with a back-up section of 200 mg of XAD-4 resin to verify that no breakthrough occurred, connected to sampling pumps with Teflon tubing and fittings. The pump flow rate was 90 standard cubic centimeters per minute in the first ARB study (ARB, 2003d), and 100 standard cubic centimeters per minute in all other studies (ARB, 2005a; ARB, 2005b; Barnekow and Byrne, 2006). Pump rates were calibrated with a digital mass flowmeter at the start and end of each sampling interval. Sampler intakes were approximately 1.5 m above ground.

Table 13. Chloropicrin Off-Site Air Concentrations Measured by the Air Resources Board (ARB) During Structural Fumigations in California

Study Location (County)	Dates	Sampler Distances (m) [a]	Total Samples [b]	LOQ (µg/sample) [c]	Samples ≥ LOQ	Maximum Concentration (µg/m^3) [d]
Sacramento [e]	10/28/02 – 11/3/02	1.5 – 18	140	0.0198	65	29
Nevada [f]	7/18/04 – 7/24/04	1.5 – 12	178	0.0198	97	43
Placer [g]	6/24/04 – 7/4/04	1.5 – 12	132	0.0198	42	21

[a] Sampler distance from edge of tarped house. In each study, samplers were placed in three concentric rings with four samplers in each ring.
[b] Includes four background samples collected before fumigation; all background results were < LOQ.
[c] LOQ: Limit of Quantification. In the study reports, this is called the "estimated quantitation limit," or EQL.
[d] Highest measured chloropicrin concentration associated with the application; results have not been corrected for spike recoveries. Multiply value by 0.1487 to get result in parts per billion (ppb).
[e] From ARB (2003d). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of a 22,000-ft^3 house; total amount chloropicrin 1.5 ounces for a nominal indoor concentration of 68 µg/m^3. Fumigation duration was 48 hours, followed by a 45-minute mechanical venting interval and 22-hour aeration.
[f] From ARB (2005a). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of an 81,000-ft^3 house; total amount chloropicrin 6 ounces for a nominal indoor concentration of 74 µg/m^3. Fumigation duration was 71 hours, followed by an 83-minute mechanical venting interval and 72-hour aeration.
[g] From ARB (2005b). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of a 45,000-ft^3 house; total amount chloropicrin 3 ounces for a nominal indoor concentration of 65 µg/m^3. Fumigation duration was 43.5 hours, followed by a 50-minute mechanical venting interval and 72-hour aeration.

The first ARB study was conducted in 2002 in Sacramento County, and monitored off-site chloropicrin concentrations during fumigation of a single-story, 1,375-square-foot house (ARB, 2003d). The estimated volume for fumigation was 22,000 ft^3 (620 m^3). Quality assurance consisted of replicate sampling, a single trip blank, and four trip, field, and laboratory spikes. Collocated duplicate samples were collected at a sampler 1.5 m east of the house during each sampling interval. In the seven sample pairs with results > LOQ, the collocated samples differed 5 – 63%, with an average difference of 20%. No chloropicrin was detected in the background samples or the trip blank. The mean recovery of four 0.225-µg field spikes was 83%. The highest reported concentration was 29 µg/m^3, occurring during the mechanical ventilation interval; the sampling interval was 1.5 hours. Corrected for the mean field spike recovery of 83%, this result would be 35 µg/m^3.

The second ARB study was conducted in 2004 in Nevada County, and monitored off-site chloropicrin concentrations during fumigation of a two-story house (ARB, 2005a). The estimated volume for fumigation was 81,000 ft^3 (2,300 m^3). Quality assurance consisted of replicate sampling, a single trip blank, and four trip, field, and laboratory spikes. Collocated duplicate samples were collected at a sampler 1.5 m north of the house during each sampling interval. In the nine sample pairs with results > LOQ, the collocated samples differed 0 – 36%, with an average difference of 11%. No chloropicrin was detected in the background samples or the trip blank. The mean recovery of four 0.228-µg field spikes was 79%. The highest reported concentration was 43 $\mu g/m^3$, occurring during the mechanical ventilation interval; the sampling interval was 1.5 hours. Corrected for the mean field spike recovery of 79%, this result would be 54 $\mu g/m^3$.

The third ARB study was conducted in 2004 in Placer County, and monitored off-site chloropicrin concentrations during fumigation of a two-story house (ARB, 2005b). The estimated volume for fumigation was 45,000 ft^3 (1,300 m^3). Quality assurance consisted of replicate sampling, a single trip blank, and four trip, field, and laboratory spikes. Collocated duplicate samples were collected at a sampler 1.5 m north of the house during each sampling interval. In the seven sample pairs with results > LOQ, the collocated samples differed 2 – 15%, with an average difference of 9.9%. No chloropicrin was detected in the background samples or the trip blank. The mean recovery of four 0.228-µg field spikes was 77%. The highest reported concentration was 21 $\mu g/m^3$, occurring during the mechanical ventilation interval; the sampling interval was 1.25 hours. Corrected for the mean field spike recovery of 77%, this result would be 27 $\mu g/m^3$.

Barnekow and Byrne (2006) monitored chloropicrin concentrations during eight fumigations; in this study four houses in California were each fumigated twice by professional fumigators. The study was reviewed and all calculations documented by Beauvais (2009). All houses were tarped prior to fumigant introduction, and tarps were removed following aeration. Clearance testing was done after tarp removal. Replicates 1 and 2 were conducted at a one-story 32,000-ft^3 house (the fumigation volume was estimated from the amount of chloropicrin used, 3.2 ounces in both replicates, and from the reported use rate of 1 oz per 10,000-ft^3) in Ventura County in November 2004. Replicates 3 and 4 were conducted at an L-shaped, 53,000-ft^3 house (one-story, other than an attached garage beneath a game room) in Riverside County in November 2004. Replicates 5 and 6 were conducted at a one-story 25,000-ft^3 house in Fresno County in December 2004 (estimated from chloropicrin amounts of 2.6 and 2.4 ounces, respectively). Replicates 7 and 8 were conducted at a two-story, approximately 40,000-ft^3 house in Fresno County in February 2005; the amount of chloropicrin used was 3.6 and 4.1 ounces, respectively. No explanation was given for the fact that about 14% more chloropicrin was used in Replicate 8 than in Replicate 7, such as whether house was tarped to include more area in Replicate 8 than in Replicate 7. The amount of sulfuryl fluoride used in Replicate 8 was also 14% greater than that used in Replicate 7, suggesting the possibility that the fumigation volume was greater in Replicate 8. However, no dimensions were provided for any of the houses.

Following a fumigation lasting approximately 20 hours, each house was aerated for 12 hours (replicates 1 through 6) or 24 hours (replicates 7 and 8). At the end of the aeration period, sulfuryl fluoride concentrations in all eight replicates were less than 5 ppm, and the houses were considered to be cleared for reentry (Barnekow and Byrne, 2006). During fumigation, outdoor samples were collected at one 4-hour interval followed by two 8-hour intervals (Intervals 1 – 3). During aeration, outdoor samples were collected at four 1-hour followed by two 4-hour intervals (Intervals 4 – 9). Following clearance, four indoor samplers were used to monitor chloropicrin concentrations in the attic, crawl space, utility area and either the living room or a bedroom for four 1-hour intervals, followed by four 8-hour intervals (Intervals 10 – 17). Quality assurance samples consisted of unfortified control samples (blanks), laboratory spikes, travel spikes, and field spikes. Ten sets of 12 travel blanks and spikes and ten sets of 12 field blanks and spikes were used. Each set of 12 tubes contained three blanks, three tubes spiked at 1 µg, three tubes spiked at 50 µg, and three tubes spiked at 200 µg. All blanks had results below the LOQ. Mean field spike recoveries ranged from 45.2% (1 µg spike in Replicate 1) to 131% (200 µg spike in Replicate 2).

Data from Barnekow and Byrne (2006) were used to estimate exposures of bystanders to a structural application, as well as residential reentry following a structural fumigation. The outdoor sampling portion of the study is summarized in Table 14.

The highest reported concentrations at outdoor samplers occurred in Replicate 2. The ambient temperature, measured in 5-minute increments, at Replicate 2 ranged 5.1 – 17.3°C during fumigation, and 4.7 – 22.5°C during aeration. The highest concentration reported by Barnekow and Byrne (2006) was 177 $\mu g/m^3$, occurring during aeration in Replicate 2; the sampling interval was 1 hour. All concentrations reported by Barnekow and Byrne (2006) had been corrected for the "average study" spike recovery of 86.7%, which was based on the mean of 138 spikes analyzed in the study. However, DPR practice is to correct samples for site-specific and fortification-level specific field spike recoveries below 90%; this is in general agreement with U.S. EPA policy (U.S. EPA, 1992; U.S. EPA, 1998). Corrected for the mean field spike recovery of 62.7% for the 1 µg field spike in Replicate 2, the 1-hour concentration is 244 $\mu g/m^3$ (36.2 ppb).

The highest outdoor concentration measured during an interval approximating an 8-hour workday also occurred in Replicate 2; it was 41.2 $\mu g/m^3$ (6.12 ppb). This was a 7-hour sample, collected in Interval 2, during fumigation. However, higher concentrations occurred during Intervals 4 – 8 in Replicate 2, which together span 8 hours. The rolling time-weighted average concentration from these samplers were used to estimate occupational bystander exposure as follows (the first three results were from samplers with < LOQ chloropicrin, which were not adjusted for field spike recovery):

$[11.8 + 13.4 + 13.8 + 244 + (4 \times 64.6)]/8 = 67.7\ \mu g/m^3$ (10.1 ppb).

Table 14. Chloropicrin Off-Site Air Concentrations Reported by Barnekow and Byrne (2006) During Structural Fumigations in California

Replicate [a]	Study Location (County)	Dates	Estimated Volume (m^3) [b]	Total Samples [c]	Samples ≥ LOQ	Duration of Maximum Concentration [d]	Maximum Concentration ($\mu g/m^3$) [e]
1	Ventura [f]	11/8/04 – 11/11/04	32,000	288	16	8 (Fum)	30.5
2	Ventura [f]	11/11/04 – 11/14/04	32,000	288	31	1 (Aer)	244
3	Riverside [f]	11/15/04 – 11/18/04	53,000	287	47	7 (Fum)	50.3
4	Riverside [f]	11/18/04 – 11/21/04	53,000	287	37	4 (Aer)	129
5	Fresno [f]	12/13/04 – 12/16/04	25,000	288	12	4 (Aer)	21.4
6	Fresno [f]	12/16/04 – 12/19/04	25,000	288	14	8 (Fum)	16.4
7	Fresno [g]	2/14/05 – 2/17/05	40,000 [h]	287	27	1 (Aer)	54.7
8	Fresno [g]	2/17/05 – 2/20/05	40,000 [h]	288	13	1.75 (Aer)	33.5

[a] All fumigations involved tarped houses; two replicates were conducted at each house. A total of 32 samplers around each house at distances of 5 – 100 ft (1.5 – 30 m) were sampled for intervals ranging 1 – 8 hours. The limit of quantification (LOQ) was 0.153 µg/sample for all samples.
[b] Fumigation volume estimated from the amount of chloropicrin used and from the reported use rate of 1 oz per 10,000-ft^3. Amount of chloropicrin used was reported to 2 significant figures, and volumes are reported at the same resolution unless otherwise indicated.
[c] Excludes four background samples collected before fumigation; all background results were < LOQ.
[d] Duration in hours of the sample interval containing the highest concentration associated with the application. Notation in parenthesis identifies whether the maximum concentration was measured during fumigation (Fum) or aeration (Aer).
[e] Highest measured chloropicrin concentration associated with the application; results corrected for spike recoveries. Multiply value by 0.1487 to get result in parts per billion (ppb).
[f] Fumigation duration was 17 – 21 hours, followed by a 20-hour aeration.
[g] Fumigation duration was 16 – 21 hours, followed by a 24-hour aeration.
[h] Fumigation volume estimated with one significant figure, because the amount of chloropicrin used in the two replicates was 3.6 and 4.1 ounces, a difference of 14%.

The longest sampling interval in this study was 8 hours. No 24-hour samples were collected, and a 24-hour concentration for residential bystander exposure was estimated as a rolling time-weighted average. The 24-hour concentration for occupational bystanders was estimated from Intervals 2 – 8 in Replicate 2; these intervals total 23 hours:
$[(7 \times 41.2) + (8 \times 39.1) + 11.8 + 13.4 + 13.8 + 244 + (4 \times 64.6)]/23 = 49.7\ \mu g/m^3$ (7.39 ppb).

Table 15 summarizes the short-term concentrations used to estimate bystander exposures associated with structural fumigation. The highest use rate of chloropicrin as a warning agent for sulfuryl fluoride, 1 oz per 10,000-ft^3 (equivalent to 0.0107 lbs/1,000 ft^3), was used by Barnekow and Byrne (2006). One methyl bromide product containing chloropicrin, Methyl Bromide 99.5% (EPA Reg. No. 8536-12-ZA) has directions on the product label for structural fumigation. This product is in the process of becoming inactive; exposure estimates associated with its use are given in Appendix 5.

Table 15. Concentrations Used to Estimate Exposure of Bystanders to Chloropicrin from Structural Fumigation

Duration	Sample Interval (Hours)	Chloropicrin in Sample (µg/sample) [a]	Volume Sampled (m^3)	Measured Concentration (µg/m^3) [b]	Corrected Concentration (µg/m^3) [c]
1 Hour	1.0	0.919	0.006	177	244
8 Hours [d]	8.0	1.29	0.0237	54.4	67.7
24 Hours [e]	23.0	3.90	0.114	34.2	49.7

[a] Off-site samples collected during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent (Barnekow and Byrne, 2006).
[b] Time-weighted average of-site concentration with 86.7% "study average" spike correction as reported by Barnekow and Byrne (2006).
[c] Concentrations above the limit of quantification corrected for 62.7% field spike recovery after reversing correction applied by Barnekow and Byrne (2006).
[d] Highest rolling 8-hour concentration, calculated from consecutive 1- to 4-hour concentrations as follows: [11.8 + 13.4 + 13.8 + 244 + (4 x 64.6)]/8 = 67.7 µg/m^3 (10.1 ppb).
[e] Highest rolling 24-hour concentration, calculated from consecutive 1- to 8-hour concentrations as follows: [(7 x 41.2) + (8 x 39.1) + 11.8 + 13.4 + 13.8 + 244 + (4 x 64.6)]/23 = 49.7 µg/m^3 (7.39 ppb).

Water

Chloropicrin is on the list of pesticides that are considered to have the potential to contaminate ground water (Clayton, 2005). Chloropicrin is on this list based on its fairly high water solubility, its low soil adsorption coefficient (K_{oc} = 25 cm^3/g), and the relatively long half-life reported for hydrolysis, which data suggest exceeds 191 days (Clayton, 2005).

Although chloropicrin has certain physicochemical properties that might predispose it to leach into ground water, in extensive monitoring there have been no verified detections of chloropicrin in California's ground water. DPR has not conducted any monitoring of well water for chloropicrin in California; however, DPR has included in its groundwater monitoring database results from sampling conducted by other agencies. The database, including criteria for selection of wells and sampling and analytical methods, is described by Troiano *et al.* (2001). Between 1984 and 1996, a total of 1,719 wells sampled in 34 California counties (out of 58 counties total) were tested for the presence of chloropicrin (Schuette *et al*., 2003; Nordmark, 2009), and chloropicrin was not detected in any of these samples. Detection limits ranged from 0.01 to 5 µg/liter; most limits were at 1 µg/liter (Nordmark, 2009). No well water sampling in California for chloropicrin has been reported since 1996.

EXPOSURE ASSESSMENT

Exposure estimates are provided for representative exposure scenarios described in the Exposure Scenarios section. For each scenario, estimates are provided for short-term (defined in this EAD as durations from a day or less, and up to one week) and, where appropriate, for seasonal (intermediate-term intervals, lasting from one week to one year), annual, and lifetime exposures. Short-term exposures were estimated for 1-hour durations because chloropicrin irritation occurs rapidly, and 1 hour is the shortest duration for which toxicity endpoints and concentrations can reasonably be estimated. Short-term estimates of 8-hour and 24-hour durations are included to address occupational and residential exposures, respectively.

For short-term exposures, DPR estimates the highest exposure an individual may realistically experience during or following legal chloropicrin uses (Frank, 2009). To estimate seasonal, annual, and lifetime exposures, the average daily exposure is of interest because over these periods of time, an individual is expected to encounter a range of daily exposures (i.e., DPR assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely). Typical exposure conditions are assumed for seasonal and annual exposure estimates. An annual exposure is a time-weighted average concentration that integrates concentrations of chloropicrin generated by use throughout the year, and a lifetime exposure estimate averages daily exposure to chloropicrin over a lifetime.

Bystander Exposure

Bystanders include individuals, working or not, who are not directly involved with a pesticide application but who may be exposed during or after the application by drift or volatilized pesticide. Most bystanders are assumed to wear no protective clothing or equipment, such as that required for handlers of chloropicrin-containing products. Individuals involved in chloropicrin applications can be adjacent to fields where chloropicrin was previously applied; product labels require handlers either to wear appropriate respiratory protection or to stop work and leave the area whenever they experience sensory irritation. Occupational bystanders may be handling other pesticides, or they may be doing fieldwork such as harvesting. Occupational bystanders are assumed to be present next to the chloropicrin application for an 8-hour workday. Residential bystanders are assumed to be in the vicinity of the chloropicrin application for 24-hour days. This representative worst case assumption includes individuals who may be unable to leave, for illness or other reason, as well as individuals who are present for shorter intervals. While bystanders might potentially be exposed to a range of chloropicrin concentrations, for screening risk assessment purposes the highest realistic exposures to bystanders are reported in this exposure assessment.

Although buffer zones can be imposed on individual applications on a case-by-case basis, neither product labels nor state regulations impose consistent buffer zones on all chloropicrin uses. Consequently, individuals could be immediately adjacent to an application. Chloropicrin air concentrations were estimated at a point 1.2 m above ground, which is the assumed breathing zone.

<u>Soil Fumigation</u>

Table 16 summarizes screening estimates of chloropicrin exposure of bystanders to soil fumigations. Short-term exposure estimates, including 1-hour, 8-hour, and 24-hour, are concentrations taken from Table 11.

Table 16. Estimated Exposure of Bystanders to Chloropicrin from Soil Fumigation

Duration	Concentration (µg/m³) [a]	Concentration (ppb) [a]
1 Hour [b]	75,000	11,000
8 Hours [c]	31,000	4,600
24 Hours [d]	5,400	800
Seasonal [e]	230	34
Annual [f]	96	14
Lifetime [g]	96	14

[a] Reasonable worst case exposure estimates for bystanders were generated using the Industrial Source Complex—Short Term, Version 3 (ISCST3) air dispersion model and flux data from application site monitoring studies in Arizona (Beard *et al.*, 1996) and California (Rotondaro, 2004), adjusting for the appropriate application rate and assuming the bystander was downwind, 10 ft (3.0 m) from the edge of a square field and the breathing zone was 1.2 m (4 ft) above ground (Barry, 2008a). Estimates for 1-, 8-, and 24-hour exposures assume a 40-acre field and a maximum application rate of 350 lbs AI/acre. Seasonal, annual, and lifetime exposures assume a 15-acre field and a typical application rate of 190 lbs AI/acre. Estimates have been rounded to 2 significant figures.

[b] The 1-hour exposure was estimated from the highest 6-hour concentration for the different application methods (using the peak-to-mean ratio: $C_p = C_m(t_p/t_m)^{1/2}$ where C_p is the peak concentration over the peak period of interest, t_p, and C_m is the mean concentration over mean measurement period, t_m.

[c] The highest 6-hour concentration was used for the 8-hour exposure. The 6-hour concentration was highest for broadcast non-tarped application at night.

[d] The 24-hour concentration was highest for the bedded tarped application.

[e] Seasonal exposure was estimated by calculating an average 24-hr flux over 2 weeks, then adjusted using a time-scaling factor based on the peak-to-mean theory to account for changing wind directions expected to occur during longer intervals (Barry, 2008c). Assumes a 5-month high-use season.

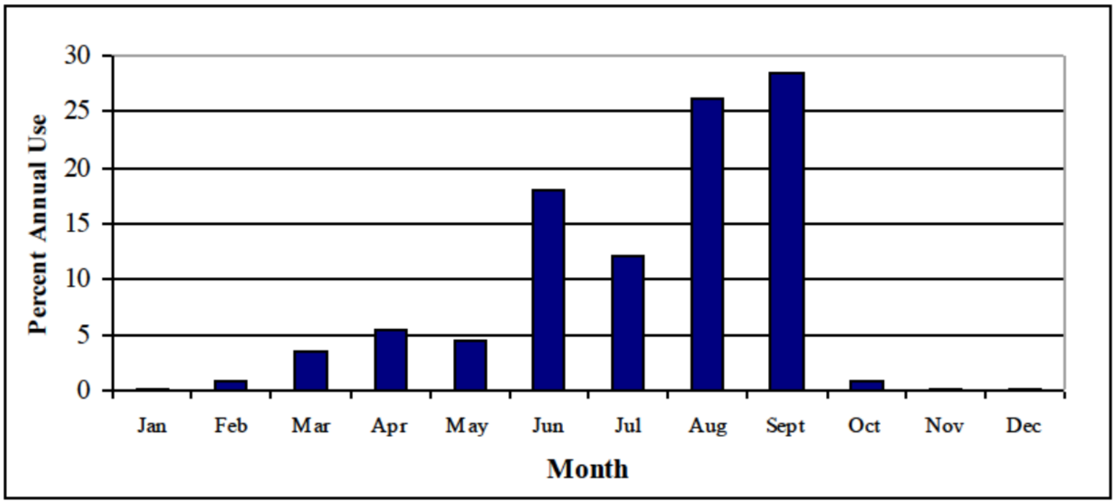
[f] Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[g] Lifetime concentrations assume average annual exposures occur each year.

Seasonal, annual, and lifetime estimates in Table 16 are based on the highest 2-week concentration reported in Table 12, assuming a typical application rate of 190 lbs AI/acre and a typical field size of 15 acres. Surrogate data from the PUR were used to estimate intervals for seasonal and annual exposures. Chloropicrin is registered for pre-plant use for several different crops, and some crops with shorter growing seasons may be replanted multiple times a year, suggesting that bystanders in high-use areas may potentially be exposed throughout the year. However, PUR data show that in many parts of the state chloropicrin use does not occur throughout the year, and that at other times relatively few applications are made. It is reasonable to assume that an individual bystander is less likely to be exposed to chloropicrin during these relatively low-use intervals. Thus, rather than assume that bystanders are exposed throughout the year, annual use patterns are plotted based on monthly PUR data from the county with the highest use. Annual exposure to chloropicrin is assumed to be limited to the months when use is relatively high (defined as 5% or more of annual use each month).

Figure 6 summarizes monthly applications of chloropicrin in Ventura County during a recent 5-year interval. Among the counties with high chloropicrin use, Ventura has the longest use season. Examination of Figure 6 shows that in April and between June and September, monthly chloropicrin use was at least 5% of the annual total use, and that 90% of annual use occurred during these 5 months. Seasonal and annual exposure estimates for bystanders to soil fumigation assumed exposure durations of 5 months.

Figure 6. Applications of Chloropicrin in Ventura County, 2004 – 2008 [a]



[a] Percent calculations based on pounds applied (DPR, 2010a; queried August 19, 2010).

For bystanders in active growing areas, such as in strawberry growing regions, exposures can potentially occur each year, as fields are fumigated before every crop. For a residential bystander with lifelong residency at the same location in one of these areas, average lifetime exposures are assumed to approximate annual exposures.

Structural Fumigation

Table 17 summarizes screening estimates of chloropicrin exposure of bystanders to structural fumigations. Short-term exposure estimates, including 1-hour, 8-hour, and 24-hour, are concentrations taken from Table 15, and are all from the same study (Barnekow and Byrne, 2006). Barnekow and Byrne (2006) monitored chloropicrin concentrations associated with fumigation of sulfuryl fluoride; in that study, chloropicrin was used at the maximum allowed rate of 1 oz per 10,000-ft3 (equivalent to 0.0107 lbs/1,000 ft3). One methyl bromide product containing chloropicrin, Methyl Bromide 99.5% (EPA Reg. No. 8536-12-ZA), allows a higher rate for chloropicrin, 0.01875 lbs/1,000 ft3 This product is in the process of becoming inactive; exposure estimates associated with its use are given in Appendix 5.

Table 17. Estimated Exposure of Bystanders to Chloropicrin from Structural Fumigation

Duration	Concentration (µg/m^3) [a]	Concentration (ppb) [a]
1 Hour [b]	244	36.2
8 Hours [c]	67.7	10.1
24 Hours [d]	49.7	7.39

[a] Exposure estimates were based on the highest off-site concentrations measured during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent (Barnekow and Byrne, 2006). Concentrations were measured in Ventura County during the fumigation of a structure with an estimated fumigation volume of about 32,000 ft^3 (900 m^3), and were corrected for 62.7% field spike recovery.
[b] The 1-hour exposure was based on the air concentration during the 1-hour sample.
[c] The 8-hour exposure was based on the time-weighted average of consecutive concentrations. Calculations shown in Table 15.
[d] The 24-hour exposure is based on the average of consecutive concentrations.

Residential Reentry

Because chloropicrin can be used as a warning agent in structural fumigation, individuals can potentially be exposed to chloropicrin in indoor air following fumigation of their residence if chloropicrin was used as a warning agent in that fumigation. The sulfuryl fluoride product Vikane (EPA Reg. No. 62719-4-ZA) has directions for use of chloropicrin as a warning agent during structural fumigation. Following fumigation with sulfuryl fluoride, aeration is required until a certain level of fumigant AI is reached, but no monitoring of chloropicrin concentrations is required during or following fumigation.

Air monitoring of structural fumigations conducted by ARB (2003d), ARB (2005a), and Barnekow and Byrne (2006) included post-clearance indoor air concentrations. The highest concentrations in any study were reported by Barnekow and Byrne (2006); full results are summarized by Beauvais (2009). Following clearance, four indoor samplers were used to monitor chloropicrin concentrations in the attic, crawl space, utility area and either the living room or a bedroom for four 1-hour intervals, followed by four 8-hour intervals (Barnekow and Byrne, 2006). The highest indoor concentration during a 1-hour interval occurred in Replicate 4 and was 3,060 µg/m^3 (456 ppb). The highest indoor concentration during an 8-hour interval (needed for occupational reentry exposure) was measured in the living room in Replicate 5 and was 1,230 µg/m^3 (183 ppb). Although no 24-hour indoor samples were collected for residential reentry exposure estimates, a 24-hour concentration was estimated as a rolling time-weighted average spanning intervals that approximate 24 hours. The highest concentration estimated this way is from Intervals 10 – 15 in the living room of Replicate 5, which span 20 hours:

[1,340 + 13.0 + 2,040 + 1,750 + (8 x 1,230) + (8 x 1,040)]/20 = 1,160 µg/m^3 (172 ppb).

Indoor air exposure estimates following structural fumigation are based on these data as summarized in Table 18. Barnekow and Byrne (2006) monitored chloropicrin concentrations associated with fumigation of sulfuryl fluoride; in that study, chloropicrin was used at the maximum allowed rate of 1 oz per 10,000-ft^3 (equivalent to 0.0107 lbs/1,000 ft^3). One methyl bromide product containing chloropicrin, Methyl Bromide 99.5% (EPA Reg. No. 8536-12-ZA), allows higher rates for chloropicrin, 0.01875 lbs/1,000 ft^3. Exposure estimates associated with use of this product are given in Appendix 5.

Table 18. Estimated Residential Reentry Exposure to Chloropicrin Following Structural Fumigation

Duration	Concentration (µg/m^3)	Concentration (ppb)
1 Hour [b]	3,060	456
8 Hours [c]	1,230	183
24 Hours [d]	1,160	172

[a] Exposure estimates based on the highest indoor air concentrations measured post-aeration following sulfuryl fluoride structural fumigations with chloropicrin as a warning agent (Barnekow and Byrne, 2006). Concentrations were corrected for field spike recovery.
[b] The 1-hour exposure was based on the air concentration during a 1-hour sample following fumigation of a 53,000-ft^3 house in Riverside County, corrected for 81.7% field spike recovery.
[c] The 8-hour exposure was based on the air concentration during an 8-hour sample following fumigation of a 25,000-ft^3 house in Fresno County, corrected for 100% field spike recovery.
[d] The 24-hour exposure is based on the average of consecutive concentrations following fumigation of a 25,000-ft^3 house in Fresno County, corrected for 100% field spike recovery.

Ambient Air

Air monitoring done at the request of DPR (ARB, 1987; 2003a; 2003b) suggests that airborne chloropicrin exposures not associated with particular applications can occur. Ambient air monitoring was done in three counties with relatively high use (Kern, Monterey, and Santa Cruz), during times when peak use was anticipated. Exposures to chloropicrin in ambient air are anticipated to be equal to or less than bystander exposures to chloropicrin, as the highest pesticide concentrations in air occur adjacent to an application (Siebers *et al.*, 2003; Garron *et al.*, 2009). Bystander exposure estimates are thus health-protective estimates for airborne chloropicrin exposures both adjacent to and away from applications.

Occupational Exposure: Soil Fumigation

Occupational exposure scenarios in this section are calculated separately for each application method. Scenarios are further grouped into three categories: exposure to chloropicrin as an active ingredient, involving products containing chloropicrin concentrations above 2%; exposure to chloropicrin as a warning agent, involving products containing chloropicrin concentrations up to 2.0%; and exposure to chloropicrin resulting from use of Methyl Bromide 89.5% (EPA Reg. No. 11220-17-ZA), a product which contains 10.5% chloropicrin. This product is considered separately because it was registered with chloropicrin as a warning agent rather than an active ingredient; however, due to the higher percentage of chloropicrin exposure is anticipated to be greater than from use of other products containing chloropicrin as a warning agent.

Occupational exposure monitoring was conducted of concentrations in the breathing zone of handlers and reentry workers during and following soil fumigation with chloropicrin (Beard *et al*., 1996; Rotondaro, 2004). These studies were reviewed in detail and exposure estimates determined for each scenario (Beauvais, 2010b). Briefly, breathing zone air concentrations of chloropicrin were monitored with air sampling tubes containing 600 mg (400 mg in front section, 200 mg in back section) of XAD-4 sorbent connected to air pumps calibrated at 50 ml per minute. One or two air samplers were attached to each worker collar. Beard *et al.* (1996) used two air samplers, connected with a splitter to a single pump worn at the belt; the mean of the two was considered as a single replicate value in exposure calculations. Rotondaro (2004) monitored individuals with a single sample pump and tube, although some had a second pump and tube that were used to estimate exposure occurring during specific activities for a portion of the workday, including disconnecting the chloropicrin cylinder or equipment repair. Reentry workers monitored by Rotondaro (2004) also had a second pump attached to monitor the concentration during the first hour of their activity. The first hour was monitored separately under the assumption that the highest concentration would occur then; however, that was not always the case.

Results were corrected for field fortification recoveries below 90%. For short-term exposures, results were also adjusted for maximum application rate. Additionally, in many cases product labels and California regulation allow aeration and reentry earlier than when monitoring was conducted. As chloropicrin dissipates with time, exposures could be underestimated for workers entering on days earlier than when monitoring was conducted. Appendix 6 identifies affected scenarios, and describes the adjustment made to aeration and reentry exposures using ratios of flux on the days of interest. Adjustments assume that the flux (expressed as percent chloropicrin lost during equivalent intervals on days being compared) is proportional to the amount of chloropicrin available. For convenience, adjustments to exposures associated with soil fumigation with 100% chloropicrin are summarized in Table 19.

For short-term exposures, DPR estimates the highest exposure an individual may realistically experience during or following legal chloropicrin uses. In order to estimate this "upper bound," for occupational exposures associated with soil fumigation DPR used the estimated population 95th percentile as described by Frank (2009). A sample calculation is shown in Appendix 7. DPR uses a population estimate instead of a sample statistic because sample maxima and upper-end percentiles, in samples of the sizes in the available studies, are both statistically unstable and known to underestimate the population values. The population estimate, on the other hand, is more stable because it is based on all the observations rather than a single value; moreover, it is adjusted, in effect, for sample size, correcting some of the underestimation bias due to small samples. A high percentile is estimated, rather than the maximum itself, because in theory, the maximum value of a lognormal population is infinitely large. In practice, exposures must be bounded because a finite amount of AI is applied. The use of a high percentile acknowledges that the assumed lognormal distribution is probably not a perfect description of the population of exposures, especially at the upper extremes. The population 95th percentile is estimated, rather than a higher percentile, because the higher the percentile the less reliably it can be estimated and the more it tends to overestimate the population value (Chaisson *et al.*, 1999).

Table 19. Adjustment to Short-Term Exposure Estimates for Earliest Allowed Reentry

Scenario	Pre-Adjustment (ppb) [a]		Adjustment [b]	Post-Adjustment (ppb)	
	1-Hour	8-Hour		1-Hour	8-Hour
Broadcast Tarped Shank					
• Tarp Splitter	259	259	4.7 (5, 6)	1,220	1,220
• Tarp Remover	513	513	4.5 (5, 7)	2,310	2,310
• Soil Shaper	41.4	41.4	1 [c] (10, 11)	41.4	41.4
Broadcast Non-Tarped Shank					
• Soil Shaper	6.55	4.29	1 (10, 10)	6.55	4.29
Bedded Tarped Shank					
• Tarp Puncher	6.42	1.69	4.8 (5, 7)	31.0	8.17
Bedded Non-Tarped Shank					
• Pipe Layer	5.19	1.22	1 [cd] (5, 7)	5.19	1.22
Tarped Drip					
• Tarp Puncher	7.79	7.27	1 [c] (5, 10)	7.79	7.27

[a] Short-term exposures are upper-bound concentrations estimates that cover intervals from 1 hour to 1 week. For occupational exposures, 1-hour and 8-hour intervals represent the shortest duration for which toxicity endpoints and concentrations can reasonably be estimated, and a typical workday, respectively. The two intervals have identical estimates unless first-hour monitoring was done and yielded higher concentrations than full-shift monitoring.

[b] Adjustments are ratios of flux (reported as percent loss of applied mass) on earliest post-application day when activity is allowed to post-application day when activity was monitored (days are in parentheses after each value). See Appendix 6 for explanation of adjustment. Products containing methyl bromide and 1,3-dichloropropene allow reentry on different days than chloropicrin-only products, with different adjustments.

[c] Flux ratio is less than or equal to one, and adjustment was set to one.

[d] The daytime 12-hour mass loss was zero on both Day 5 and Day 7; these values were adjusted to 0.01% (lowest reported percent loss in study) for ratio calculation.

To estimate seasonal and annual exposures, the average daily exposure is of interest because over these periods of time, a worker is expected to encounter a range of daily exposures (i.e., DPR assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely). To estimate the average, DPR uses the arithmetic mean of daily exposure (Powell, 2003). Although acknowledging that environmental concentration and exposure monitoring data are likely to be lognormally distributed (Ott, 1990), DPR believes that the arithmetic mean is the appropriate statistic to use in exposure estimates (Powell, 2003). DPR uses the arithmetic mean exposure for intermediate- or long-term exposures because the parameter of interest for exposure assessment is the overall exposure that a person is expected to have during the averaging period. For environmental samples, the arithmetic mean concentration is the best estimate of the average mass of residue per unit of environmental medium; it is equivalent to compositing all of the samples and measuring the concentration of the mixture (Parkhurst, 1998). This is true regardless of the shape of the underlying distribution. The arithmetic mean is used rather than the geometric mean or the median because, although it can be argued that the latter statistics better indicate the location of the center of a skewed distribution, it is not the center that is of interest in exposure assessment, but the expected magnitude of the exposure. While extremely high daily exposures are low-probability events, they do occur, and the arithmetic mean appropriately gives them weight in proportion to their probability. (In contrast, the geometric mean gives decreasing weight as the value of the exposure increases, and the median gives no weight whatsoever to extreme exposures.) In most instances, the mean daily exposure of individuals over time is not known. However, the mean daily exposure of a group of persons observed in a short-term study is believed to be the best available estimate of the mean for an individual over a longer period.

For long-term exposure estimates, rather than adjust application rates to the maximum allowed on current product labels, application rates that are considered typical were used. Investigation of pounds chloropicrin applied and acres treated in chloropicrin applications reported in the PUR suggest that annual median application rates for soil fumigation with chloropicrin do not exceed 190 lbs AI/acre, the rate assumed to be typical (See Appendix 4).

Shank Broadcast Tarped Soil Fumigation

Shank broadcast applications are done as pre-plant soil fumigation, primarily for fruit and vegetable crops including strawberries, carrots, potatoes, and tomatoes. Bed formation, if desired, follows aeration. Table 20 summarizes concentration estimates for activities associated with broadcast tarped shank applications. Shallow shank applications were monitored, but it is assumed that handler exposure during deep shank applications will be equal to or less than during shallow shank. Estimates for handlers (driver, co-pilot, shoveler, tarp splitter, and tarp remover) in Table 20 are based on data from Beard *et al*. (1996); estimates for soil shapers are based on data from both Beard *et al*. (1996) and Rotondaro (2004). Unlike Rotondaro (2004), Beard *et al*. (1996) did not separately monitor concentrations while chloropicrin cylinders were being disconnected, and no concentrations during cylinder disconnect are available for broadcast tarped shank applications.

Beard *et al.* (1996) monitored handler exposures during broadcast tarped applications in Arizona, Washington, and Florida. Treated fields in these applications ranged 5.3 – 13.16 acres, but they were each divided into two or three plots that took 1.4 – 3.1 hours to treat. All plots in a field were treated in the same day. Tarps were split 6 days post-application and were removed the next day, with the exception of one field in Washington where tarps were removed 5 days after splitting. Rotondaro (2004) monitored exposures of soil shapers during reentry. Three fields in California ranging 3.5 – 5.1 acres were treated. Tarps were split 5 days post-application and removed the next day, and soil shapers worked 4 days following tarp removal.

Rotondaro (2004) monitored soil shapers for the first hour they worked, using a second air sampling pump, as well as for the full 4 hours, to determine whether their exposures were higher as the soil was first disturbed. Although mean exposures (adjusted for the maximum application rate of 350 lbs AI/acre) of the five soil shapers monitored were slightly higher during the first hour, at 12.6 ppb (84.4 μg/m^3), than the 4-hour mean of 10.6 ppb (71.4 μg/m^3), the 95th percentile concentration of 27.5 ppb (185 μg/m^3) was lower than the 4-hour 95th percentile of 41.4 ppb (279 μg/m^3). The soil shaper with the highest measured exposure also had a higher full-shift (4-hour) than first-hour concentration, suggesting that the first-hour concentration did not capture the highest 1-hour concentration. The first-hour 95th percentile was lower as a result, and the 4-hour 95th percentile value was used to estimate exposure for soil shapers for both 1-hour and 8-hour intervals.

Table 20. Chloropicrin Time-Weighted Average Concentrations Measured for Handlers and Reentry Workers with Broadcast Tarped Applications

Scenario [a]	N [b]	Minutes (mean)	Chloropicrin (μg/m^3) [c]			Chloropicrin (ppb) [c]		
			Mean	SD	95th	Mean	SD	95th
Driver	16	153	507	320	1,320	75.4	47.5	196
Co-pilot	16	163	653	369	1,380	94.4	54.9	205
Shoveler	32	150	222	189	545	33.0	28.1	81.0
Tarp Splitter	14	31.1	613	1,070	1,740	91.2	158	259
Tarp Remover	29	107	620	755	3,450	92.1	112	513
Soil Shaper (first-hour)	5	60.2	84.4	51.1	185 [d]	12.6	7.60	27.5 [d]
Soil Shaper (4-hour)	5	245	71.4	69.4	279	10.6	10.3	41.4

[a] Data from Beard *et al.* (1996) and Rotondaro (2004).
[b] Number of replicates with data in scenario.
[c] Concentration arithmetic means (Mean), standard deviations (SD), and 95th percentile (95th). The 95th percentile was calculated assuming a lognormal distribution. Concentrations were adjusted for field spike recoveries and for an allowed maximum application rate of 350 lbs AI/acre.
[d] The soil shaper with the highest measured exposures had a lower first-hour than 4-hour concentration, which caused the first-hour 95th percentile to be lower. For this reason, the 4-hour 95th percentile was used to estimate 1-hour as well as 8-hour exposures.

Chloropicrin 15 – 100% (Active Ingredient)

Handler and reentry exposures associated with broadcast tarped soil fumigations using chloropicrin as an AI are summarized in Table 21. To fit estimates for all exposure durations, concentrations are reported only as ppb in Table 21 and other tables summarizing exposure estimates. Multiply these estimates by 6.725 (equivalent to dividing by 0.1487) to express concentrations in μg/m^3. Short-term exposure estimates summarized in Table 21 as 1-hour and 8-hour exposures are based on the full-shift (4-hour) 95th percentile concentration reported in Table 20. The first-hour monitoring did not capture the highest 1-hour exposure for the soil shaper with the highest exposure, and as a result the first-hour 95th percentile estimate was lower than the 4-hour.

For seasonal, annual, and lifetime exposure estimates, an application rate of 190 lbs AI/acre was assumed, based on the median of applications recently reported in California as summarized in Appendix 4. Thus, seasonal exposures are equivalent to means reported in Table 20, multiplied by 190/350 = 0.54 (rounding differences may cause some reported estimates to differ slightly). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Tarp splitting and tarp removal are allowed 5 days post-application on labels of all chloropicrin-containing products. Tarp splitters and removers were monitored on post-application days 6 and 7, respectively. Short-term exposures for tarp splitters were adjusted 4.7-fold, and short-term exposures for tarp removers were adjusted 4.5-fold (see Table 19 and Appendix 6).

Table 21. Occupational Exposure to Chloropicrin During and Following Broadcast Tarped Soil Fumigations with Chloropicrin as an Active Ingredient

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	196	196	40.9	17.1	9.12
• Copilot	205	205	51.2	21.3	11.3
• Shoveler	81.0	81.0	17.9	7.46	3.99
Aeration					
• Tarp Splitter	1,220	1,220	49.5	20.7	11.0
• Tarp Remover	2,310	2,310	50.0	20.8	11.1
Reentry					
• Soil Shaper, 100% chloropicrin	41.4	41.4	5.76	2.41	1.28
• Soil Shaper, Tri-Form 40/60 [e]	106	106	3.46	1.44	0.768
• Soil Shaper, Tri-Con 33/67 [f]	77.3	77.3	3.84	1.60	0.852

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term estimates (1- and 8-hour) for aeration and reentry were adjusted upward because monitoring did not occur on the earliest post-application day that the activities are allowed, 5 days for tarp splitters and tarp removers (monitored on post-application days 6 and 7 days, respectively), and 10 days for soil shaping following application of 100% chloropicrin products (monitored on day 11). Unless otherwise specified, short-term exposures assume the maximum allowed application rate on product labels (350 lbs AI/acre), and seasonal, annual, and lifetime exposures assume a 50th percentile rate of 190 lbs AI/acre. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in µg/m^3.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month high-use season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Tri-Form 40/60 contains 60% chloropicrin, and allows soil to be disturbed at 7 days post-application; monitoring occurred on post-application day 11, and concentrations were adjusted upward 2.6-fold. Short-term exposures assume the maximum rate of 350 lbs chloropicrin/acre, and seasonal, annual, and lifetime exposures assume 60% of the 50th percentile rate of 190 lbs chloropicrin/acre (114 lbs chloropicrin/acre).

[f] Tri-Con 33/67 contains 66.6% chloropicrin, and allows soil to be disturbed at 6 days post-application; monitoring occurred on post-application day 11, and concentrations were adjusted upward 2.5-fold (flux was lower on the 6th day than the 7th). Short-term exposures assume the maximum rate of 266 lbs chloropicrin/acre, and seasonal, annual, and lifetime exposures assume 66.6% of the 50th percentile rate of 190 lbs chloropicrin/acre (127 lbs chloropicrin/acre).

Labels on all products containing 100% chloropicrin contain the following instructions: "After application, leave the soil undisturbed for 10 to 14 days" (some products say "14 days" instead). For this reason, soil shaping – an activity that disturbs soil – is assumed to occur no earlier than 10 days post-application. Labels on 1,3-dichloropropene products specify that soil is to be left "undisturbed and unplanted for at least 7 days," and soil shaping is assumed to occur 7 days following application of those products. In contrast, methyl bromide product labels say, "Wait a minimum of two weeks after fumigation before planting or transplanting," with no instruction not to disturb soil; soil shaping is assumed to occur 5 days post-application (reentry is allowed at 5 days on all product labels). The shorter intervals before soil shaping result in higher short-term exposure estimates, as summarized in Table 21.

Occupational exposure estimates associated with soil fumigation using 100% chloropicrin products are generally higher than estimates associated with mixtures of methyl bromide and 1,3-dichloropropene; that is the case for broadcast tarped soil fumigation. Exposures associated with broadcast tarped fumigation using products in which chloropicrin is 10.5% and 2% are summarized in the following sections.

Chloropicrin 10.5% (Methyl Bromide 89.5%)

For soil fumigation, the maximum application rate on the Methyl Bromide 89.5% product label is 445 lbs product/acre, which would correspond to a rate of 46.72 pounds chloropicrin per acre. Additionally, application rates for several types of soil fumigation are limited by California regulation (3 CCR 6447.3), as summarized in Table 22.

Table 22. Maximum Application Rates for Methyl Bromide Field Fumigation Allowed by California Regulation

Method Number [a]	Method Name	Maximum Application Rate (Pounds per Acre)		
		Methyl Bromide	Chloropicrin 2% [b]	Chloropicrin 10.5% [b]
1	Bedded Non-Tarped Shallow [c]	200	4.08	23.5
2	Broadcast Non-Tarped Deep	400	8.16	46.9
3	Broadcast Tarped Shallow	400	8.16	46.9
4	Bedded Tarped Shallow	250	5.10	29.3
5	Broadcast Tarped Deep	400	8.16	46.9
6	Drip, Hot Gas	225	4.59	26.4

[a] The California Code of Regulation Title 3, Section 6447.3 specifies six methods for field fumigation with methyl bromide and the maximum amount of methyl bromide to be applied, along with other method-specific restrictions. Certain types of fumigation, including tree replant, are excluded from the definition of "field fumigation."

[b] The equivalent rate for chloropicrin was calculated by first dividing the rate of methyl bromide allowed per acre by the percent methyl bromide in each product (98% and 89.5%, respectively) to obtain the rate at which the product can be used, then multiplying the result by the percent chloropicrin in the product.

[c] Current methyl bromide product labels require tarps on practically all applications (fourteen products allow deep non-tarped broadcast for orchard replant in California). No methyl bromide labels allow bedded non-tarped applications, with the exception of one product, Methyl Bromide 99.5%, which is in the process of becoming inactive.

Shallow broadcast tarped shank is the third of the six allowed methyl bromide field fumigation methods in California; injection depths of 10 – 15 inches (25 – 38 cm) are required. Deep broadcast tarped shank is the fifth of the six allowed methyl bromide field fumigation methods; injections must be deeper than 20 inches (50 cm). As shown in Table 22, the maximum rate for deep broadcast tarped application is 400 pounds methyl bromide per acre. For Methyl Bromide 89.5%, which contains 10.5% chloropicrin, the rate of chloropicrin applied would be 46.9 lbs/acre. This is calculated by first dividing the maximum rate of methyl bromide allowed per acre by the percent methyl bromide in the product (89.5%) to obtain the rate at which the product can be used (400/0.895 = 447 lbs/acre), then multiplying the result by the percent chloropicrin in the product (447 x 0.105 = 46.9 lbs/acre). As this amount is higher than the maximum rate allowed on the product label, the rate of 445 lbs product on the product label was assumed in estimating exposure.

Occupational exposures associated with broadcast tarped soil fumigations are shown in Table 23, and are based on data summarized in Table 20. Aeration activities are allowed in methyl bromide-treated fields earlier than when exposure monitoring was conducted, but the chloropicrin flux did not differ substantially between the days and no adjustment was needed for the earliest day when aeration is allowed. Reentry is allowed 5 days post-application if tarps are removed, and soil shaping was assumed to occur at 5 days.

Table 23. Occupational Handler Exposure to Chloropicrin During and Following Broadcast Tarped Soil Fumigations with Chloropicrin 10.5% (Methyl Bromide 89.5%)

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	26.2	26.2	4.29	1.79	0.954
• Copilot	27.4	27.4	5.38	2.24	1.19
• Shoveler	10.8	10.8	1.88	0.783	0.418
Aeration					
• Tarp Splitter	162	162	5.20	2.17	1.16
• Tarp Remover	307	307	5.25	2.19	1.17
Reentry					
• Soil Shaper	9.02	9.02	0.605	0.252	0.134

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 445 pounds product per acre, which corresponds to 46.7 lbs/acre. Seasonal, annual, and lifetime exposures assume a rate of 20 lbs chloropicrin/acre (10.5% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in μg/m^3.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month high-use season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

Seasonal, annual, and lifetime exposures for each scenario were calculated from exposure estimates in Table 21, adjusted for a lower rate of 20 lbs chloropicrin/acre (10.5% of the 50th percentile rate of 190 lbs/acre). For example, driver seasonal exposure is estimated at 40.9 ppb in Table 21, and 40.9 x 0.105 = 4.29 ppb in Table 23. Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Chloropicrin 0.5 – 2% (Warning Agent)

For soil fumigation, the maximum application rate listed on labels of methyl bromide products with chloropicrin as a warning agent is 400 lbs product/acre, which corresponds to 8.16 pounds chloropicrin/acre. Exposures were calculated using the same approach as for products containing chloropicrin 10.5%. Short-term (i.e., 1- and 8-hour) exposures were calculated by adjusting exposures summarized in Table 21 by a ratio of the maximum rate of chloropicrin of 8.16 lbs/acre to the maximum rate allowed in 100% chloropicrin products of 350 lbs/acre. Seasonal, annual, and lifetime exposures were calculated assuming a rate of 3.8 lbs chloropicrin/acre (2% of the 50th percentile rate of 190 lbs/acre). Occupational exposures associated with broadcast tarped soil fumigations are summarized in Table 24.

Table 24. Occupational Exposure to Chloropicrin During and Following Broadcast Tarped Soil Fumigations with Chloropicrin as a Warning Agent

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
<u>Application</u>					
• Driver	4.57	4.57	0.818	0.341	0.182
• Copilot	4.78	4.78	1.02	0.427	0.228
• Shoveler	1.89	1.89	0.358	0.149	0.0796
<u>Aeration</u>					
• Tarp Splitter	28.3	28.3	0.990	0.414	0.221
• Tarp Remover	53.8	53.8	1.00	0.417	0.222
<u>Reentry</u>					
• Soil Shaper	1.57	1.57	0.115	0.0480	0.0256

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 400 pounds methyl bromide per acre under California Code of Regulation Title 3, Section 6447.3; for a product containing 2% chloropicrin, the amount of chloropicrin applied would be 8.16 lbs/acre. Seasonal, annual, and lifetime exposures assume a rate of 3.8 lbs chloropicrin/acre (2% of the 50^{th} percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95^{th} percentiles, calculated with lognormal methods.

[c] Assumes a 5-month high-use season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

Aeration activities are allowed in methyl bromide-treated fields earlier than when exposure monitoring was conducted, but the chloropicrin flux did not differ substantially between the days and no adjustment was needed for the earliest day when aeration is allowed. Reentry is allowed 5 days post-application if tarps are removed, and soil shaping was assumed to occur at 5 days. Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Shank Broadcast Non-Tarped Soil Fumigation

Table 25 summarizes concentration estimates for activities associated with broadcast non-tarped shank applications, both shallow (4 – 13" below soil surface, 10 – 33 cm) and deep (18 – 24" or 46 – 61 cm). Only reentry workers shaping soil were monitored following deep shank applications; no handler activities were monitored during deep shank applications. Statistics reported in Table 25 suggest that concentrations were somewhat lower following deep than they were following shallow applications, suggesting that exposure estimates based on these data may be health-protective for handlers during deep shank applications. Monitored reentry activities occurred at the same post-application interval (10 days post-application) following both shallow and deep applications.

Table 25. Chloropicrin Time-Weighted Average Concentrations Measured for Handlers and Reentry Workers with Broadcast Shank Non-Tarped Applications

Scenario [a]	N [b]	Minutes (mean)	Chloropicrin (µg/m^3) [c]			Chloropicrin (ppb) [c]		
			Mean	SD	95th	Mean	SD	95th
Shallow								
Driver	6	248	244	93.7	446	36.2	13.9	66.3
Driver Disconnect [d]	4	16.5	1,090	630	2,110	162	93.7	314
Soil Sealer	6	224	107	56.5	254	15.9	8.40	37.7
Soil Shaper (first-hour)	5	61.2	35.1	5.53	44.0	5.22	0.823	6.55
Soil Shaper (4-hour)	5	249	16.3	6.09	28.8	2.42	0.905	4.29
Deep								
Soil Shaper (first-hour)	5	59.8	63.7	4.88	72.2	9.47	0.726	10.7
Soil Shaper (4-hour)	5	244	20.3	5.69	30.9	3.02	0.846	4.59

[a] Data from Beard *et al.* (1996) and Rotondaro (2004).
[b] Number of replicates with data in scenario.
[c] Concentration arithmetic means (Mean), standard deviations (SD), and 95th percentile (95th). The 95th percentile was calculated assuming a lognormal distribution. Concentrations were adjusted for field spike recoveries and for an allowed maximum application rate of 175 lbs AI/acre for shallow applications and 350 lbs AI/acre for deep applications.
[d] A second sampling pump was used to monitor drivers while they disconnected cylinders. This operation is part of the overall activity for a driver, and it was not considered as a separate scenario for exposure assessment purposes.

Beard *et al.* (1996) monitored drivers and soil sealer exposures during treatment of two plots in a field in Arizona; together the plots totaled 8.1 acres. The first plot took 3.0 hours and the second 1.8 hours to treat. Rotondaro (2004) monitored driver and soil sealer exposures during treatment of three fields in California. Field sizes ranged 3.7 – 9.7 acres, and applications took between 2.6 hours and 3.6 hours to complete.

One scenario in Table 25, drivers disconnecting chloropicrin cylinders at the end of each application, has an estimated exposure to a mean concentration of 162 ppb (1,090 $\mu g/m^3$) and a 95^{th} percentile concentration of 314 ppb (2,110 $\mu g/m^3$). Rotondaro (2004) used a second sampling pump to monitor drivers while they disconnected cylinders. This operation is part of the overall activity for a driver, lasting on average 16.5 minutes of the 248 minutes drivers were monitored, and it was not considered as a separate scenario for exposure assessment purposes. Concentrations associated with disconnecting the cylinder are also included in the full-application monitoring, and are thus incorporated into exposure estimates for the driver scenario.

Chloropicrin 15 – 100% (Active Ingredient)

Occupational exposures associated with broadcast non-tarped soil fumigations with chloropicrin as an AI are summarized in Table 26. One reentry scenario is associated with this scenario, soil shapers. Exposure monitoring of soil shapers occurred 10 days post-application, which is also the earliest that 100% chloropicrin product labels allow reentry activities that disturb the soil. In contrast, soil shaping is allowed at 7 days post-application for 1,3-dichloropropene products, and at 5 days for methyl bromide products (see Appendix 6). As with broadcast tarped applications, the earlier allowed reentry results in higher short-term exposure estimates for methyl bromide and 1,3-dichloropropene products containing 66.6% and 60% chloropicrin, respectively, and exposure estimates for those products are included in Table 26.

The PUR does not distinguish between tarped and non-tarped applications, and no information is available to determine whether use patterns differ among the types of applications. Annual and lifetime exposures to chloropicrin during non-tarped broadcast applications were assumed to occur during the 5 high-use months shown in Figure 6, and at the median application rate of 190 lbs AI/acre.

Table 26. Occupational Exposure to Chloropicrin During and Following Broadcast Non-Tarped Soil Fumigations with Chloropicrin as an Active Ingredient

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	66.3	66.3	19.7	8.19	4.37
• Soil Sealer	37.7	37.7	8.65	3.60	1.92
Reentry (Shallow Applications)					
• Soil Shaper, 100% chloropicrin	6.55	4.29	2.62	1.09	0.583
• Soil Shaper, Tri-Form 40/60 [e]	39.3	25.7	1.57	0.655	0.349
Reentry (Deep Applications)					
• Soil Shaper, 100% chloropicrin	10.7	4.59	1.64	0.683	0.364
• Soil Shaper, Tri-Form 40/60 [e]	56.3	24.2	0.984	0.410	0.219
• Soil Shaper, Tri-Con 33/67 [f]	356	152	1.09	0.455	0.243

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Unless otherwise stated, short-term exposures assume the maximum allowed application rate on product labels (175 lbs AI/acre for shallow applications and 350 lbs AI/acre for deep); seasonal, annual, and lifetime exposures assume a 50th percentile rate of 190 lbs AI/acre. Soil shaping following application of 100% chloropicrin products was assumed to occur 10 days post-application, as allowed by product labels. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month high-use season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Tri-Form 40/60 contains 60% chloropicrin. Short-term exposures assume the maximum allowed application rate of 350 pounds chloropicrin per acre. Product labels allow reentry at 7 days post-application, and soil shapers were monitored at 10 days post-application; short-term exposure estimates include a 6.0-fold adjustment for higher chloropicrin concentrations at 7 days than at 10 days post-application. Seasonal, annual, and lifetime exposures assume 60% of the 50th percentile rate of 190 lbs chloropicrin/acre (114 lbs chloropicrin/acre).

[f] Tri-Con 33/67 contains 66.6% chloropicrin, and allows soil to be disturbed at 5 days post-application; monitoring occurred on post-application day 10, and concentrations were adjusted upward 44-fold because the flux was 44-fold higher on post-application day 5 than post-application day 10. Short-term exposures assume the maximum rate of 266 lbs chloropicrin/acre, and seasonal, annual, and lifetime exposures assume 66.6% of the 50th percentile rate of 190 lbs chloropicrin/acre (127 lbs chloropicrin/acre).

Chloropicrin 10.5% (Methyl Bromide 89.5%)

Occupational exposures associated with broadcast deep non-tarped soil fumigations are summarized in Table 27, based on data summarized in Table 25.

Non-tarped shallow shank broadcast applications with methyl bromide are prohibited by 3 CCR 6447.3; non-tarped shank broadcast applications (Method 2 in Table 22) are required to be at least 20 inches (50 cm) deep. California regulation (3 CCR 6447.3) restricts broadcast non-tarped application rates to 400 pounds methyl bromide per acre. For a product containing 10.5% chloropicrin, the amount of chloropicrin applied would be 46.9 lbs/acre. However, the maximum application rate allowed on the current product label is 445 pounds product/acre, which corresponds to 46.7 lbs chloropicrin/acre. This lower rate was used to estimate exposure.

Table 27. Occupational Exposure to Chloropicrin During and Following Broadcast Deep Non-Tarped Soil Fumigations with Chloropicrin 10.5% (Methyl Bromide 89.5%)

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	11.1	11.1	2.07	0.860	0.459
• Soil Sealer	6.34	6.34	0.908	0.378	0.202
Reentry (Deep) [e]					
• Soil Shaper	39.1	16.7	0.172	0.0718	0.0383

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 445 pounds product per acre, which corresponds to 46.7 lbs/acre. Seasonal, annual, and lifetime exposures assume a rate of 20 lbs chloropicrin/acre (10.5% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes 5 high-use months. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] The product label allows reentry at 5 days post-application, and soil shapers were monitored at 10 days post-application; short-term exposure estimates include a 44-fold adjustment for higher chloropicrin concentrations at 5 days than at 10 days post-application.

Post-fumigation, soil shaper 1-hour and 8-hour exposure estimates include a 44-fold adjustment for the fact that the product label allows reentry at 5 days following deep broadcast tarped applications, and soil shapers were monitored at 10 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Chloropicrin 0.5 – 2% (Warning Agent)

Occupational exposures associated with broadcast deep non-tarped soil fumigations using chloropicrin as a warning agent are summarized in Table 28, based on data summarized in Table 25.

California regulation (3 CCR 6447.3) restricts broadcast non-tarped application rates to 400 pounds methyl bromide per acre. For a product containing 2% chloropicrin, the amount of chloropicrin applied would be 8.16 lbs/acre. Post-fumigation, soil shaper 1-hour and 8-hour exposure estimates include a 44-fold adjustment for the fact that California regulation and product labels both allow reentry at 5 days following deep broadcast tarped applications, and soil shapers were monitored at 10 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Table 28. Occupational Exposure to Chloropicrin During and Following Broadcast Deep Non-Tarped Soil Fumigations with Chloropicrin as a Warning Agent

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	1.93	1.93	0.394	0.164	0.0874
• Soil Sealer	1.10	1.10	0.173	0.0720	0.0384
Reentry (Deep) [e]					
• Soil Shaper	6.80	2.92	0.0328	0.0137	0.00729

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 400 pounds methyl bromide per acre under California Code of Regulation Title 3, Section 6447.3; for a product containing 2% chloropicrin, the amount of chloropicrin applied would be 8.16 lbs/acre. Seasonal, annual, and lifetime exposures assume a rate of 3.8 lbs chloropicrin/acre (2% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in μg/m^3.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes 5 high-use months. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Product labels allow reentry at 5 days post-application, and soil shapers were monitored at 10 days post-application; short-term exposure estimates include a 44-fold adjustment for higher chloropicrin concentrations at 5 days than at 10 days post-application.

Shank Bedded Tarped Soil Fumigation

Table 29 summarizes concentration estimates for activities associated with shallow tarped bedded shank applications. Beard *et al*. (1996) monitored handler exposures during treatment of two plots in a field in Arizona; together the plots totaled 5.92 acres. The first plot took 7.1 hours and the second 5.0 hours to treat. Rotondaro (2004) monitored handler exposures during treatment of three fields in California. Field sizes ranged 1.11 – 1.93 acres, and applications took between 2.4 hours and 8.0 hours to complete (DPR recognizes that 8 hours is longer than would be expected for a commercially successful application, but these data are the best available).

Rotondaro (2004) used a second sampling pump to monitor the drivers while they disconnected chloropicrin cylinders at the end of the application. This operation is part of the overall activity for a driver, lasting on average 19.2 minutes of the 331 minutes drivers were monitored, and it was not considered as a separate scenario for exposure assessment purposes. Concentrations associated with disconnecting the cylinder are also included in the full-application monitoring, and are thus incorporated into exposure estimates for the driver scenario.

Tarps were punched 6 days following the applications monitored by Beard *et al.* (1996), and 7 days following applications monitored by Rotondaro (2004). Tarps were punched using hand-held propane burners in the field monitored by Beard *et al.* (1996) and in one of the fields monitored by Rotondaro (2004). In the other two fields monitored by Rotondaro

(2004), tarps were punched using a spiked wheel towed behind a tractor. Tarp punchers were monitored for both 1-hour and 4-hour durations by Rotondaro (2004), but only for 4 hours by Beard *et al.* (1996).

Table 29. Chloropicrin Time-Weighted Average Concentrations Measured for Handlers During Shallow Tarped Shank Bedded Soil Fumigation

Scenario [a]	N [b]	Minutes (mean)	Chloropicrin (μg/m³) [c]			Chloropicrin (ppb) [c]		
			Mean	SD	95th	Mean	SD	95th
Driver	8	331	60.9	52.6	160	9.06	7.82	23.7
Driver Disconnect [d]	4	19.2	721	483	2,280	107	71.8	339
Co-pilot	5	326	77.0	81.2	267	11.4	12.1	39.7
Shoveler	7	337	44.0	30.7	104	6.54	4.57	15.5
Tarp Puncher (first-hour)	4	61.2	29.9	6.17	43.1	4.45	0.917	6.42
Tarp Puncher (4-hour)	8	212	6.13	3.05	11.4	0.912	0.454	1.69

[a] Data from Beard *et al.* (1996) and Rotondaro (2004).
[b] Number of replicates with data in scenario.
[c] Concentration arithmetic means (Mean), standard deviations (SD), and 95th percentile (95th). The 95th percentile was calculated assuming a lognormal distribution. Concentrations were adjusted for field spike recoveries and for an allowed maximum application rate of 350 lbs AI/acre.
[d] A second sampling pump was used to monitor drivers while they disconnected cylinders. This operation is part of the overall activity for a driver, and it was not considered as a separate scenario for exposure assessment purposes.

Chloropicrin 15 – 100% (Active Ingredient)

Table 30 summarizes occupational exposures associated with shallow tarped bedded shank applications with chloropicrin as an AI. For all scenarios in Table 30, the highest occupational exposures result from use of 100% chloropicrin at the maximum allowed rate, and separate exposure estimates were omitted for use of mixtures with methyl bromide and 1,3-dichloropropene as they are equal to or less than the estimates shown. Short-term exposure estimates for tarp punchers include a 4.8-fold adjustment for the fact the chloropicrin product labels allow tarp punching 5 days post-application, and tarp punchers were monitored at 6 – 7 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Table 30. Handler Exposure to Chloropicrin During Shallow Tarped Bedded Soil Fumigations with Chloropicrin as an Active Ingredient

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	23.7	23.7	4.92	2.05	1.09
• Copilot	39.7	39.7	6.22	2.59	1.38
• Shoveler	15.5	15.5	3.55	1.48	0.788
Aeration [e]					
• Tarp Puncher	31.0 [e]	8.17 [e]	0.495	0.207	0.110

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate on product labels (350 lbs AI/acre), and seasonal, annual, and lifetime exposures assume a 50th percentile rate of 190 lbs AI/acre. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month high-use season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Chloropicrin product labels allow aeration at 5 days post-application, and tarp punchers were monitored at 6 – 7 days post-application; short-term exposure estimates include a 4.8-fold adjustment for higher chloropicrin concentrations at 5 days than at 7 days post-application.

Chloropicrin 10.5% (Methyl Bromide 89.5%)

This is the fourth of the six allowed methyl bromide field fumigation methods in California; injection depths of 6 – 15 inches (15 – 38 cm) are required. Occupational exposures associated with bedded tarped soil fumigations using the product Methyl Bromide 89.5% are summarized in Table 31, based on data summarized in Table 29. Product labels allow a maximum rate of 445 pounds product per acre for all tarped applications, which is equivalent to 46.7 pounds chloropicrin per acre. However, California regulations (3 CCR 6447.3) restrict broadcast tarped application rates to 250 pounds methyl bromide per acre. For a product containing 10.5% chloropicrin, the amount of chloropicrin applied would be 29.3 lbs/acre, and short-term exposure estimates assume this rate. Tarp puncher 1-hour exposure includes a 4.8-fold adjustment for the fact the California regulation allows tarp punching 5 days post-application, and tarp punchers were monitored at 6 – 7 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Table 31. Occupational Exposure to Chloropicrin During Bedded Tarped Soil Fumigations with Chloropicrin 10.5% (Methyl Bromide 89.5%)

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
<u>Application</u>					
• Driver	1.98	1.98	0.517	0.215	0.115
• Copilot	3.32	3.32	0.653	0.272	0.145
• Shoveler	1.30	1.30	0.373	0.155	0.0829
<u>Aeration</u> [e]					
• Tarp Puncher	2.60	0.682	0.0520	0.0217	0.0116

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 250 pounds methyl bromide per acre under California Code of Regulation Title 3, Section 6447.3; for a product containing 10.5% chloropicrin, the amount of chloropicrin applied would be 29.3 lbs/acre. Seasonal, annual, and lifetime exposures assume a rate of 20 lbs chloropicrin/acre (10.5% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in µg/m3 and parts per billion (ppb). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] California regulation allows aeration at 5 days post-application, and tarp punchers were monitored at 6 – 7 days post-application; short-term exposure estimates include a 4.8-fold adjustment for higher chloropicrin concentrations at 5 days than at 7 days post-application.

Chloropicrin 0.5 – 2% (Warning Agent)

Product labels allow a maximum rate of 400 pounds product per acre for all tarped applications, which is equivalent to 8.16 pounds chloropicrin per acre. However, California regulation (3 CCR 6447.3) restricts bedded tarped application rates to 250 pounds methyl bromide per acre. For a product containing 2% chloropicrin applied at that rate, the amount of chloropicrin applied would be 5.10 lbs/acre, and short-term exposure estimates assume this rate. Occupational exposures associated with bedded tarped soil fumigations using chloropicrin as a warning agent are summarized in Table 32, based on data summarized in Table 29. Tarp puncher 1-hour exposure includes a 4.8-fold adjustment for the fact the California regulation allows tarp punching 5 days post-application, and tarp punchers were monitored at 6 – 7 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Table 32. Occupational Exposure to Chloropicrin During Bedded Tarped Soil Fumigations with Chloropicrin as a Warning Agent

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	0.345	0.345	0.0984	0.0410	0.0219
• Copilot	0.578	0.578	0.124	0.0518	0.0276
• Shoveler	0.226	0.226	0.0710	0.0296	0.0158
Aeration [e]					
• Tarp Puncher	0.452	0.119	0.0198	0.00824	0.00439

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 250 pounds methyl bromide per acre under California Code of Regulation Title 3, Section 6447.3; for a product containing 2% chloropicrin, the amount of chloropicrin applied would be 5.10 lbs/acre. Seasonal, annual, and lifetime exposures assume a rate of 3.8 lbs chloropicrin/acre (2% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] California regulation allows aeration at 5 days post-application, and tarp punchers were monitored at 6 – 7 days post-application; short-term exposure estimates include a 4.8-fold adjustment for higher chloropicrin concentrations at 5 days than at 7 days post-application.

Shank Bedded Non-Tarped Soil Fumigation

Table 33 summarizes concentration estimates for activities associated with non-tarped shallow shank applications. Beard *et al*. (1996) monitored handler exposures during treatment of two plots in a field in Arizona; together the plots totaled 8.46 acres. The first plot took 1.3 hours and the second 1.7 hours to treat. Rotondaro (2004) monitored handler exposures during treatment of three fields in California. Field sizes ranged 1.7 – 8.4 acres, and applications took between 3.0 hours and 3.7 hours to complete. In all applications, soil was sealed using a flat weight, a bed shaper or a ring roller towed behind the application tractor.

Rotondaro (2004) used a second sampling pump to monitor the drivers while they disconnected chloropicrin cylinders at the end of the application. This operation is part of the overall activity for a driver, lasting on average 16.7 minutes of the 229 minutes drivers were monitored, and it was not considered as a separate scenario for exposure assessment purposes. Concentrations associated with disconnecting the cylinder are also included in the full-application monitoring, and are thus incorporated into exposure estimates for the driver scenario.

Reentry workers laying irrigation lines (pipe layers) 6 – 7 days following applications were monitored by Rotondaro for both 1-hour and 4-hour durations. Higher concentrations were measured in first-hour than in full-shift (4-hour) monitoring intervals, and first-hour concentrations were used to estimate 1-hour exposures and 4-hour concentrations were used to estimate 8-hour exposures.

Table 33. Chloropicrin Time-Weighted Average Concentrations Measured for Handlers and Reentry Workers with Shallow Non-Tarped Shank Bedded Soil Fumigation

Scenario [a]	N [b]	Minutes (mean)	Chloropicrin (µg/m^3) [c]			Chloropicrin (ppb) [c]		
			Mean	SD	95th	Mean	SD	95th
Driver	5	229	154	81.6	379	23.0	12.1	56.4
Driver Disconnect [d]	3	16.7	1,640	1,040	3,590	244	155	534
Pipe Layer (first-hour)	6	60.7	30.4	2.54	34.9	4.52	0.377	5.19
Pipe Layer (4-hour)	6	234	7.88	0.197	8.20	1.17	0.0293	1.22

[a] Data from Beard *et al.* (1996) and Rotondaro (2004).
[b] Number of replicates with data in scenario.
[c] Concentration arithmetic means (Mean), standard deviations (SD), and 95th percentile (95th). The 95th percentile was calculated assuming a lognormal distribution. Concentrations were adjusted for field spike recoveries and for an allowed maximum application rate of 175 lbs AI/acre.
[d] A second sampling pump was used to monitor drivers while they disconnected cylinders. This operation is part of the overall activity for a driver, and it was not considered as a separate scenario for exposure assessment purposes.

Chloropicrin 15 – 100% (Active Ingredient)

Table 34 summarizes handler and reentry exposures associated with shallow non-tarped bedded shank applications using chloropicrin as an AI, and assuming a maximum application rate of 175 lbs AI/acre as allowed on labels of 100% chloropicrin products. California regulations allow non-tarped bedded soil fumigation with methyl bromide at a maximum rate of 200 pounds per acre (3 CCR 6447.3); for a product containing 66.6% chloropicrin, the amount of chloropicrin applied would be 244 lbs/acre. However, a methyl bromide product containing 66.6% chloropicrin, Tri-Con 33/67, has a maximum application rate of 400 pounds per acre for deep non-tarped applications, which corresponds to 266 pounds chloropicrin per acre, and exposure estimates assumed this rate.

Exposure monitoring of pipe layers occurred 6 – 7 days post-application. All current product labels allow reentry at 5 days (120 hours) post-application for activities that do not disturb the soil. Assuming that pipe laying does not disturb the soil, pipe layers were assumed to work as early as 5 days post-application. However, flux was equivalent on days 5 and 7 post-application, and the adjustment equals one. Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 6).

Current methyl bromide product labels require tarps on all applications (fourteen products allow deep non-tarped broadcast for orchard replant in California). No methyl bromide labels allow bedded non-tarped applications.

Table 34. Occupational Exposure to Chloropicrin During and Following Bedded Non-Tarped Soil Fumigations with Chloropicrin as an Active Ingredient

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Driver	56.4	56.4	23.0	9.58	5.11
Reentry 100% chloropicrin					
• Pipe Layer	5.19	1.22	1.17	0.488	0.260
Reentry 66.6% chloropicrin [e]					
• Pipe Layer	7.89	1.85	0.850	0.354	0.189

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Unless otherwise stated, exposures assume the maximum allowed application rate on product labels (175 lbs AI/acre). Pipe laying following application of 100% chloropicrin products was assumed to occur 5 days post-application, as allowed by product labels. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95^{th} percentiles, calculated with lognormal methods.

[c] Assumes a 5-month high-use season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Short-term exposures assume the maximum allowed application rate of 400 lbs/acre of Tri-Con 33/67, which corresponds to 266 lbs chloropicrin/acre. Seasonal, annual, and lifetime exposures assume a 50^{th} percentile rate of 190 lbs AI/acre (127 lbs chloropicrin/acre).

Chemigation

Table 35 summarizes concentration estimates for activities associated with tarped surface or non-tarped buried drip irrigation applications. Rotondaro (2004) monitored exposures associated with tarped surface applications to three fields in California, ranging 4.5 – 9.6 acres; applications took 3.6 – 8.6 hours to complete. Exposures of tarp punchers driving tractors and towing spiked wheels were monitored 5 days post-application at one field, and 10 days post-application at the other two fields; higher concentrations were measured in 1-hour than in 4-hour monitoring intervals. As a result, 1-hour concentrations were used to estimate 1-hour exposures and 4-hour concentrations were used to estimate 8-hour exposures. Rotondaro (2004) monitored exposures associated with non-tarped buried applications to three fields in California, ranging 0.7 – 7.9 acres; applications took 3.1 – 11.2 hours to complete. Applicators remained at the site during all monitored tarped and non-tarped drip applications, observing the irrigation system and the field.

Monitored applicators took at an average of 12 minutes to disconnect cylinders, out of an average total monitoring interval of 587 minutes, and concentrations from this activity are included in concentrations for the total monitoring.

Table 35. Chloropicrin Time-Weighted Average Concentrations Measured for Handlers During Drip Irrigation

Scenario [a]	N [b]	Minutes (mean)	Chloropicrin (μg/m^3) [c]			Chloropicrin (ppb) [c]		
			Mean	SD	95th	Mean	SD	95th
Tarped Surface								
Applicator	6	520	65.8	29.1	141	9.79	4.32	20.9
Applicator Disconnect [d]	2	19.0	118	38.2	194	17.6	5.69	28.9
Tarp Puncher (first-hour)	5	61.2	37.5	9.54	52.4	5.58	1.42	7.79
Tarp Puncher (4-hour)	5	252	19.7	23.0	48.9	2.93	3.41	7.27
Non-Tarped Buried								
Applicator	6	587	88.0	93.8	305	13.1	13.9	45.4
Applicator Disconnect [d]	2	12.0	613	351	1,470	91.1	52.2	218

[a] Data from Rotondaro (2004).
[b] Number of replicates with data in scenario.
[c] Concentration arithmetic means (Mean), standard deviations (SD), and 95th percentile (95th). The 95th percentile was calculated assuming a lognormal distribution. Concentrations were adjusted for field spike recoveries and for an allowed maximum application rate of 300 lbs AI/acre.
[d] A second sampling pump was used to monitor applicators while they disconnected cylinders. This operation is part of the overall activity for an applicator, and it was not considered as a separate scenario for exposure assessment purposes.

Chloropicrin 15 – 100% (Active Ingredient)

Table 36 summarizes occupational exposures associated with drip applications. Exposure estimates summarized in Table 36 are based on monitoring conducted during field drip applications, but drip applications are also used in soil fumigations done in greenhouses. Assuming that applications are made from outside the greenhouse (and that self-contained breathing apparatus is required for anyone entering a greenhouse before aeration is completed), these data also represent occupational exposures associated with greenhouse drip applications.

Short-term tarp puncher exposure estimates include an adjustment, equal to unity, for the fact that product labels allow tarp punching 5 days post-application, and tarp punchers were monitored at 5 – 10 days post-application; chloropicrin flux was not higher at 5 days than 10 days post-application (see Appendix 6).

Table 36. Estimates for Occupational Handler Exposure to Chloropicrin During Chemigation with Chloropicrin as an Active Ingredient

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Tarped Surface					
• Applicator	20.9	20.9	6.20	2.59	1.38
• Tarp Puncher	7.79	7.27	1.86	0.773	0.412
Non-Tarped Buried					
• Applicator	45.4	45.4	8.29	3.45	1.84

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate on product labels (300 lbs AI/acre), and seasonal, annual, and lifetime exposures assume a 50th percentile rate of 190 lbs AI/acre. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in μg/m^3.

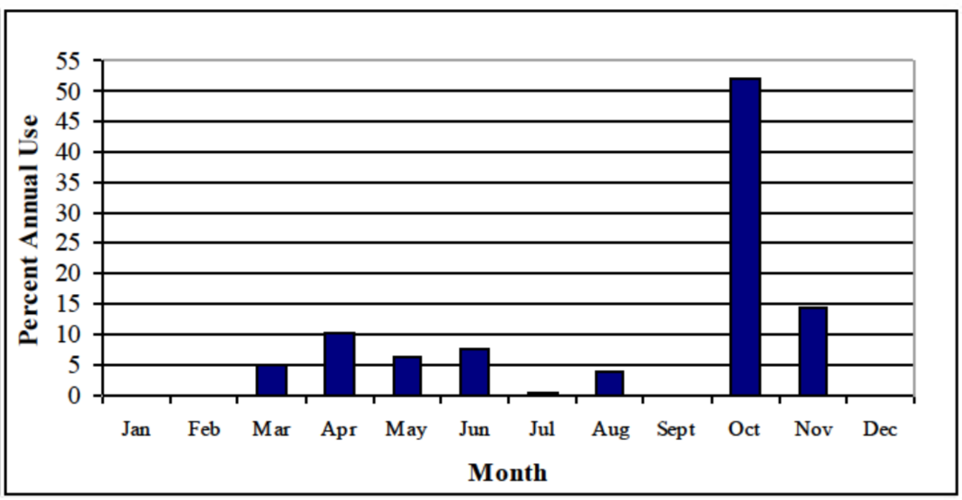
[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes 5 high-use months. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

Figure 7 summarizes monthly applications of chloropicrin in pre-plant nursery soil fumigations in Monterey County during a recent 5 year interval. Examination of Figure 7 shows that between April and June, and between October and November, chloropicrin use was at least 5% each month; these 5 months are considered to be when exposure related to greenhouse drip irrigation applications is most likely to occur. Annual and lifetime exposure estimates assumed annual exposure durations of 5 months.

Figure 7. Greenhouse Soil Fumigation with Chloropicrin in Monterey County, 2004-2008[a]



[a] Percent calculations based on pounds applied to nursery crops (DPR, 2010a; queried October 28, 2010).

Chloropicrin 10.5% (Methyl Bromide 89.5%)

Methyl Bromide 89.5% does not have label directions for drip irrigation; however, it does have directions for hot gas fumigation. California regulation (3 CCR 6447.3) defines hot gas as follows: "A hot gas application through a subsurface drip irrigation system to tarpaulin-covered beds." Hot gas drip soil fumigation is the last of the six methods allowed in California for soil fumigation using methyl bromide, as listed in Table 22. The regulation restricts hot gas application rates to 225 pounds methyl bromide per acre; the amount of chloropicrin applied would be 26.4 lbs/acre.

No monitoring data are available for occupational exposures associated with hot gas fumigation. In the absence of such data, exposures are estimated based on chloropicrin exposure monitoring conducted during surface tarped drip irrigation, as summarized in Table 35. Table 37 summarizes occupational exposures estimated for handlers involved in hot gas drip applications. Applicator and tarp puncher 1-hour exposures are estimated to be 1.84 ppb (12.4 μg/m^3) and 0.684 ppb (4.60 μg/m^3), respectively. Short-term tarp puncher exposure estimates include an adjustment, equal to unity, for the fact the California regulation allows tarp punching 5 days post-application, and tarp punchers were monitored at 5 – 10 days post-application; chloropicrin flux was not higher at 5 days than 10 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 7).

Table 37. Estimates for Occupational Handler Exposure to Chloropicrin During Chemigation with Chloropicrin 10.5% (Methyl Bromide 89.5%)

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Tarped Surface					
• Applicator	1.84	1.84	0.651	0.272	0.145
• Tarp Puncher	0.684	0.639	0.195	0.0812	0.0433

[a] See Appendix 1 for detail about activities. Methyl bromide products with chloropicrin as a warning agent only have chemigation directions for hot gas fumigation, in which gas is heated and applied via a subsurface drip irrigation system to tarpaulin-covered beds. Estimates are based on drip irrigation exposure monitoring data from Rotondaro (2004), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 225 pounds methyl bromide per acre under California Code of Regulation Title 3, Section 6447.3; for a product containing 10.5% chloropicrin, the amount of chloropicrin applied would be 26.4 lbs/acre. Seasonal, annual, and lifetime exposures assume a lower rate of 20 lbs chloropicrin/acre (10.5% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in μg/m^3.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

Chloropicrin 0.5 – 2% (Warning Agent)

No methyl bromide products containing chloropicrin as a warning agent have label directions for drip irrigation; however, methyl bromide products containing 2% chloropicrin have directions for hot gas fumigation. California regulation (3 CCR 6447.3) restricts hot gas application rates to 225 pounds methyl bromide per acre. For a product containing 2% chloropicrin, the amount of chloropicrin applied would be 4.59 lbs/acre.

Estimates for occupational exposures associated with hot gas fumigation are based on chloropicrin exposure monitoring conducted during drip irrigation (see Table 35). Table 38 summarizes occupational exposures associated with drip applications. Applicator 1-hour exposures are estimated to be 0.320 ppb (2.16 $\mu g/m^3$), and tarp puncher 1-hour exposures are estimated at 0.119 ppb (0.803 $\mu g/m^3$). Short-term tarp puncher exposure estimates include an adjustment, equal to unity, for the fact the California regulation allows tarp punching 5 days post-application, and tarp punchers were monitored at 5 – 10 days post-application; chloropicrin flux was not higher at 5 days than 10 days post-application (see Appendix 6). Annual and lifetime exposure estimates assumed annual exposure durations of 5 months (Figure 7).

Table 38. Estimates for Occupational Handler Exposure to Chloropicrin During Chemigation with Chloropicrin as a Warning Agent

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Tarped Surface					
• Applicator	0.320	0.320	0.124	0.0518	0.0276
• Tarp Puncher	0.119	0.111	0.0372	0.0155	0.00825

[a] See Appendix 1 for detail about activities. Methyl bromide products with chloropicrin as a warning agent only have chemigation directions for hot gas fumigation, in which gas is heated and applied via a subsurface drip irrigation system to tarpaulin-covered beds. Estimates are based on drip irrigation exposure monitoring data from Rotondaro (2004), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate of 225 pounds methyl bromide per acre under California Code of Regulation Title 3, Section 6447.3; for a product containing 2% chloropicrin, the amount of chloropicrin applied would be 4.59 lbs/acre. Seasonal, annual, and lifetime exposures assume a lower rate of 3.8 lbs chloropicrin/acre (2% of the 50th percentile rate of 190 lbs/acre). Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 5-month season. Annual average concentrations calculated as follows: Seasonal concentration x (5 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

<u>Tree Replant Handwand</u>

Rotondaro (2004) monitored applicator exposure during tree replant soil fumigations using a hand-held wand in three California orchards, ranging from 0.11 – 0.22 acres. Orchards were divided into 10-ft by 10-ft squares, with one injection site per square; 48 to 96 squares were treated in each orchard. Applications took 2.0 – 3.1 hours to complete. Two handlers were monitored during each application. In two orchards, the handlers each did about half of the injections using a handheld wand while their partners operated a series of valves to the chloropicrin cylinders. In the third orchard, injections used a tractor-mounted wand; one applicator drove the tractor and operated the wand, while the other applicator stood beside the tractor, measuring chloropicrin usage by changes in cylinder weight and covering the injection holes with soil.

Applicator exposure monitoring during tree replant fumigations consisted of air sampling tubes containing XAD-4 connected to air pumps calibrated at 50 ml per minute. One or two air samplers were attached to each worker collar; additionally, workers injecting chloropicrin with handwands for tree replanting had an air sampler attached to the lower leg to allow estimation of dermal exposure to chloropicrin (concentrations near the leg were anticipated to be higher during this application method). Table 39 summarizes concentration estimates for activities associated with replant handwand applications.

Table 39. Chloropicrin Concentrations Measured for Handlers During Tree Replant Handwand Applications

Scenario [a]	N [b]	Minutes (mean)	Chloropicrin (μg/m³) [c]			Chloropicrin (ppb) [c]		
			Mean	SD	95th	Mean	SD	95th
Applicator	6	253	148	181	647	22.0	26.9	96.3
Applicator Disconnect [d]	1	12	132	NA	NA	24.8	NA	NA
Applicator - Leg	6	253	190	205	873	28.3	30.5	130

[a] Data from Rotondaro (2004).
[b] Number of replicates with data in scenario.
[c] Concentration arithmetic means (Mean), standard deviations (SD), and 95th percentile (95th). The 95th percentile was calculated assuming a lognormal distribution. Concentrations were adjusted for field spike recoveries and for an allowed maximum application rate of 431 lbs AI/acre. NA: not applicable (single value).
[d] A second sampling pump was used to monitor applicators while they disconnected cylinders. This operation is part of the overall activity for an applicator, and it was not considered as a separate scenario for exposure assessment purposes.

Chloropicrin 15 – 100% (Active Ingredient)

Table 40 summarizes occupational exposures associated with replant handwand soil fumigations. Maximum application rates are expressed as pounds per 100 square feet; to estimate exposure, these rates were converted to pounds per acre (there are 43,560 ft^2/acre). One chloropicrin-only product allows handwand application, at a maximum rate of 1 lb/100 ft^2 (Chloropicrin 100 Fumigant, EPA Registration Number 8536-2-ZA). This is equivalent to 431 lbs/acre. Based on breathing-zone air monitoring, the handwand applicator 1-hour exposure for fumigation with 100% chloropicrin is estimated to be 96.3 ppb (647 μg/m³).

Current product labels for some mixtures of chloropicrin and methyl bromide (Pic-Brom 25, containing 25% chloropicrin, EPA Registration Number 8536-11-ZA) and 1,3-dichloropropene (Telone C-35, containing 34.7% chloropicrin, EPA Registration Number 62719-302-AA) also allow handwand applications for tree hole fumigation. Estimates for applicators using these products are included in Table 40.

Table 40. Estimates for Occupational Handler Exposure to Chloropicrin During Tree Replant Handwand Soil Fumigation

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Handwand Replant					
• Applicator, 100% chloropicrin	96.3	96.3	9.72	2.42	1.29
• Applicator, Telone C-35 [e]	97.4	97.4	3.37	0.840	0.448
• Applicator, Pic-Brom 25 [f]	36.4	36.4	2.43	0.605	0.322
• Applicator, 10.5% chloropicrin [g]	15.3	15.3	1.02	0.254	0.136
• Applicator, 2% chloropicrin [h]	2.93	2.93	0.194	0.0484	0.0258

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Short-term exposures assume the maximum allowed application rate on product labels (431 lbs AI/acre for handwand replant with 100% chloropicrin), and seasonal, annual, and lifetime exposures assume a 50th percentile rate of 190 lbs AI/acre. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in μg/m^3.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95th percentiles, calculated with lognormal methods.

[c] Assumes a 3-month season. Annual average concentrations calculated as follows: Seasonal concentration x (3 months/12 months).

[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Telone C-35 contains 34.7% chloropicrin. Short-term exposures assume the maximum rate of 436 lbs chloropicrin/acre (112 gallons of product per acre, and 3.89 pounds chloropicrin per gallon). Seasonal, annual, and lifetime exposures assume 34.7% of the 50th percentile rate of 190 lbs chloropicrin/acre (65.9 lbs chloropicrin/acre).

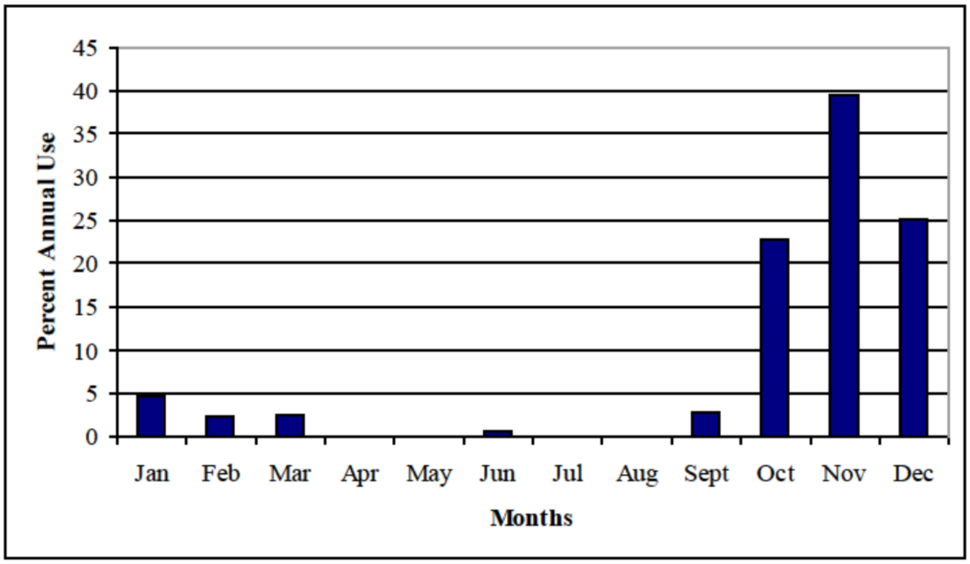
[f] Pic-Brom 25 contains 25% chloropicrin. Short-term exposures assume the maximum rate of 163 lbs chloropicrin/acre (1.5 lbs product per 100 ft^2, multiplied by 25% chloropicrin (i.e., 0.25) and 43,560 ft^2/acre), and seasonal, annual, and lifetime exposures assume 25% of the 50th percentile rate of 190 lbs chloropicrin/acre (47.5 lbs chloropicrin/acre).

[g] Methyl Bromide 89.5% contains 10.5% chloropicrin. Short-term exposures assume the maximum rate of 68.6 lbs chloropicrin/acre (1.5 lbs product per 100 ft^2, multiplied by 10.5% chloropicrin (i.e., 0.105) and 43,560 ft^2/acre). Seasonal, annual, and lifetime exposures assume 10.5% of the 50th percentile rate of 190 lbs chloropicrin/acre (20 lbs chloropicrin/acre).

[h] Short-term exposures assume the maximum rate of 13.1 lbs chloropicrin/acre (1.5 lbs product per 100 ft^2, multiplied by 2% chloropicrin (i.e., 0.02) and 43,560 ft^2/acre). Seasonal, annual, and lifetime exposures assume 2% of the 50th percentile rate of 190 lbs chloropicrin/acre (3.8 lbs chloropicrin/acre).

Figure 8 summarizes monthly applications of chloropicrin to soil before planting tree crops in Tulare County during the most recent 5 years available. Examination of Figure 8 shows that between October and December, chloropicrin use was at least 5% each month; these 3 months are considered to be when exposure related to tree replant applications is most likely to occur. Annual and lifetime exposure estimates assumed annual exposure durations of 3 months.

Figure 8. Tree Replant Chloropicrin Use in Tulare County, 2004 – 2008 [a]



[a] Percent calculations based on pounds applied to tree crops (DPR, 2010a; queried October 28, 2010).

Chloropicrin 10.5% (Methyl Bromide 89.5%)

Table 40 summarizes occupational exposures to chloropicrin associated with handwand replant soil fumigation. This application method is exempt from requirements for field fumigation with methyl bromide at 3 CCR 6447.3, and exposure estimates assume the maximum application rate allowed on product labels. Methyl Bromide 89.5% allows handwand replant soil fumigation at a maximum rate of 1.5 lbs product/100 ft^2, which is equivalent to 68.6 lbs chloropicrin/acre. Annual and lifetime exposure estimates assumed annual exposure durations of 3 months (Figure 8).

Chloropicrin 0.5 – 2% (Warning Agent)

Table 40 summarizes occupational exposures to chloropicrin associated with handwand replant soil fumigation. This application method is exempt from requirements for field fumigation with methyl bromide at 3 CCR 6447.3, and exposure estimates assume the maximum application rate allowed on product labels. The maximum application rate for this use on methyl bromide products containing chloropicrin as a warning agent is 1.5 lbs/100 ft^2, which is equivalent to 13.1 lbs chloropicrin/acre. Annual and lifetime exposure estimates assumed annual exposure durations of 3 months (Figure 8).

Potting Soil

No exposure monitoring data are available for potting soil fumigation with products containing chloropicrin; data from broadcast tarped fumigations were used as surrogates, adjusted for application rate. Potting soil fumigation is only allowed for Methyl Bromide 89.5% and for products in which chloropicrin is a warning agent. Labels on products containing more than 10.5% chloropicrin do not contain use directions for potting soil.

Product labels contain directions for fumigating potting soil mixes in tarp-covered mounds with several fumigant injection points. Exposures of tarp removers are intended to cover all handling activities associated with potting soil fumigation in covered mounds.

Potting soil fumigation involves covering a soil mound with a tarp, then injecting fumigant beneath the tarp (DPR, 2010c). Tarps used for this activity have a thickness of 4.0 mils or greater, thicker than those used for broadcast and bedded soil fumigation (Cohen and Martin, 2008). The thickness of the tarps would be expected to result in substantial retention of applied chloropicrin, and as with tarped broadcast soil applications, the highest exposures associated with potting soil fumigation would be anticipated to occur at tarp removal.

Chloropicrin 10.5% (Methyl Bromide 89.5%)

The Methyl Bromide 89.5% product label contains instructions for potting soil fumigation, in which tarped mounds of soil on an impermeable surface are injected with fumigant. The maximum rate on the Methyl Bromide 89.5% product label is 1 lb methyl bromide/100 ft^2 (1.117 lb product/100 ft^2); this corresponds to a rate of 51.1 lbs chloropicrin/acre. Table 41 summarizes exposure estimates for handlers involved in potting soil fumigation.

Table 41. Estimated Occupational Handler Exposures to Chloropicrin During Potting Soil Fumigation with Methyl Bromide Products Containing Chloropicrin

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Chloropicrin 10.5% [e]					
• Tarp Remover	74.9	74.9	5.25	1.75	0.993
Chloropicrin 2% [f]					
• Tarp Remover	94.5	94.5	1.00	0.333	0.178

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Rotondaro (2004) and Beard *et al.* (1996), adjusted for differences in application rate used in studies and assumed application rate. Concentrations reported in parts per billion (ppb). Multiply by 6.725 to express concentrations in $\mu g/m^3$.

[b] Short-term concentrations are upper-bound estimates that cover intervals from 1 hour to 1 week. Values are 95^{th} percentiles, calculated with lognormal methods.

[c] Assumes a 4-month season. Annual average concentrations calculated as follows: Seasonal concentration x (4 months/12 months).

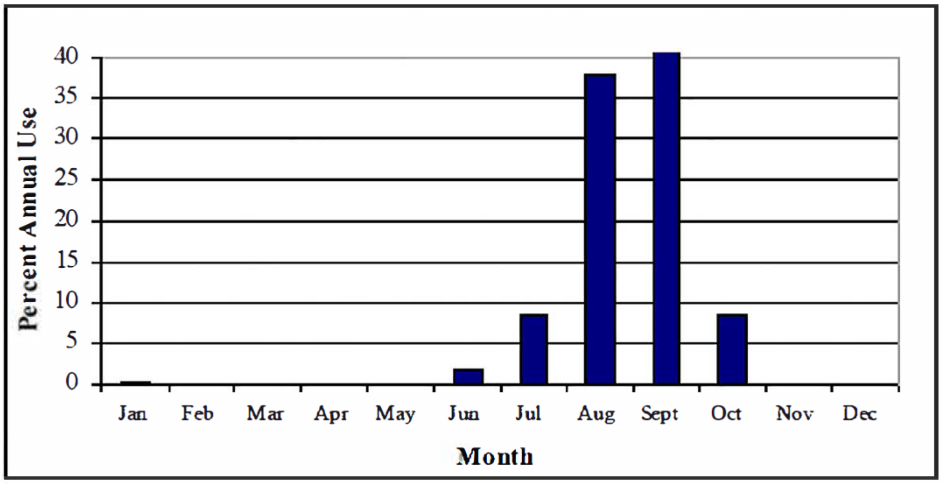
[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[e] Methyl Bromide 89.5% allows a maximum application rate of 1 lb methyl bromide/100 ft^2; this corresponds to a rate of 51.1 lbs chloropicrin/acre. Short-term exposures assume the maximum allowed application rate on product labels, and seasonal, annual, and lifetime exposures assume a rate of 20 lbs chloropicrin/acre (10.5% of the 50^{th} percentile rate of 190 lbs/acre).

[f] Product labels allow a maximum application rate of 1 lb product/yd^3; this corresponds to a rate of 64.5 lbs chloropicrin/acre (see text for assumptions and calculations). Short-term exposures assume the maximum allowed application rate on product labels, and seasonal, annual, and lifetime exposures assume a rate of 3.8 lbs chloropicrin/acre (2% of the 50^{th} percentile rate of 190 lbs/acre).

Figure 9 summarizes monthly applications of chloropicrin for container-grown plants in Kern County during the most recent 5 years available. Examination of Figure 9 shows that between July and October, chloropicrin use was at least 5% each month; these 4 months are considered to be when exposure related to potting soil fumigation is most likely to occur. Annual and lifetime exposure estimates assumed annual exposure durations of 4 months.

Figure 9. Potting Soil Fumigations with Chloropicrin in Kern County, 2004 – 2008[a]



[a] Percent calculations based on pounds applied to container-grown plants (DPR, 2010a; queried October 28, 2010).

Chloropicrin 0.5 -2% (Warning Agent)

Labels on methyl bromide products containing chloropicrin as a warning agent have label directions for potting soil fumigation, with maximum allowed application rates expressed in two different ways. Methyl Bromide 98% (EPA Registration Number 8536-19-ZA) allows a maximum rate of 1 lb product/100 ft2, which corresponds to a rate of 8.71 lbs chloropicrin/acre. Other product labels allow a maximum rate of 1 lb product/yd3 . This corresponds to a rate of 0.02 lbs chloropicrin/yd3 . Methyl bromide fumigation of potting soil mix is regulated and only 400 yd3 (10,800 ft3) is allowed to be fumigated at a time; mound height is limited to 2 ft (DPR, 2010c). Assuming an approximately rectangular pile of that height, it would cover an area of 5,400 ft2: (10,800 ft3)/(2 ft) = 5,400 ft2 Using a conversion of 43,560 ft2/acre, this corresponds to 0.124 acres, and the equivalent chloropicrin rate would be (400 yd3 x 0.02 lbs/yd3)/0.124 acres = 64.5 lbs chloropicrin/acre. This rate was used to estimate exposures, which are summarized in Table 41.

Annual and lifetime exposure estimates assumed annual exposure durations of 4 months (Figure 9).

Occupational Exposure: Structural Fumigation

DPR and outside investigators have monitored on-site air concentrations of chloropicrin during several structural fumigations with either methyl bromide or sulfuryl fluoride, in which chloropicrin was a warning agent (chloropicrin is only registered for warning agent use in structural fumigation). Occupational exposure estimates are based on the most appropriate of these data. Available studies are summarized in Table 42 and briefly described below.

DPR monitored structural fumigations with methyl bromide in which chloropicrin was used as a warning agent (Maddy *et al.*, 1986). This study was initiated in response to reports of fatalities of persons entering buildings during fumigation; there was a suspicion that chloropicrin concentrations were not sufficient to provide warning throughout the entire fumigation period. Monitoring was done of seven structural fumigations in Los Angeles and Sacramento counties. Volumes of structures fumigated ranged from 14,000 to 40,000 ft^3 (400 – 1,100 m^3).

In the fumigations monitored by Maddy *et al.* (1986), target chloropicrin concentrations were below 30 ppm (200,000 $\mu g/m^3$), while target methyl bromide concentrations were in the range of 6,000 to 12,000 ppm (40,000,000 – 80,000,000 $\mu g/m^3$). Two MIRAN 1A infrared gas analyzers were used, one tuned to a peak found only in the methyl bromide spectrum, and the other tuned to a peak found only in the spectrum for chloropicrin. Chloropicrin results were corrected for interference from methyl bromide. Concentrations of both compounds were monitored from air samples pumped at a rate of 25 liters per minute from a tube at a height of 6 ft (1.8 m) in the center of a room in the tarped structure. Monitoring began 15 – 30 minutes before fumigant introduction (fumigant introduction itself took about 5 – 10 min), and continued during the daytime until tarps were removed 40 hours later. In addition to chloropicrin air concentrations inside structures during fumigation, personal air samplers were attached to workers during tarp removal. Sampler pumps operating at 0.1 liter per minute drew air through two tubes; methyl bromide was collected in 600 mg charcoal in one tube, and chloropicrin was collected on 150 mg XAD resin in the other tube.

Peak chloropicrin concentrations in the structures monitored by Maddy *et al.* (1986) ranged 5,000 to 24,000 ppb (34,000 – 160,000 $\mu g/m^3$). As no personal breathing zone air concentrations were measured during fumigant introduction, the highest concentration during the first 2 hours was used to estimate occupational exposure associated with fumigant introduction. After 22 to 42 hours of fumigation, chloropicrin concentrations were between 500 and 11,000 ppb. Individuals who entered structures following fumigation to monitor methyl bromide concentrations had chloropicrin concentrations in their breathing zone ranging from 12 to 1,000 ppb (80 – 6,700 $\mu g/m^3$); these data were used to estimate exposure during clearance activities. Chloropicrin concentrations in the breathing zone of workers removing the tarps were all less than 40 ppb, and five workers experienced concentrations below detection limits (10 ppb) during tarp removal.

Following the DPR study, a study was commissioned by the Structural Pest Control Board to obtain additional data on chloropicrin warning agent concentrations inside houses and under tarps during fumigation (Lee and Liscombe, 1993). Ten applications were monitored, five with methyl bromide and five with sulfuryl fluoride. Chloropicrin concentrations were monitored from air samples pumped at a rate of 90 ml/min from sample inlets 4 ft (1.2 m) high; two sample lines were inside the tarped structure, and three lines sampled between the house and tarp. Samplers consisted of Tygon tubing (0.25" outer diameter) extending from the sampling inlets to SKC personal sampling pumps with XAD-4 resin sampling tubes.

Fifteen-minute samples were collected at 1 hour, 2 hours, 4 hours, 8 hours, 12 hours, and 24 hours after introduction of the fumigant.

Table 42. On-Site Monitoring for Chloropicrin Associated with Structural Fumigations

Monitoring Location	Dates	No. Samples	Application Rate [a]	LOQ [b] ($\mu g/m^3$)	Samples $\geq$ LOQ	Maximum ($\mu g/m^3$) [c]
Breathing zone [d]	6/29/84 – 10/24/84	15	0.01 – 0.0188	0.067	11	6,700
Inside house [e]	6/29/84 – 10/24/84	67	0.01 – 0.0107	0.067	67	160,000
Inside house [f]	5/11/93 – 5/24/93	290	0.0075 – 0.0107	134	276	118,200
Inside house [g]	10/28/02 – 11/3/02	4	0.0075	0.0026	4	2.0
Inside house [h]	7/18/04 – 7/24/04	4	0.0075	0.0026	4	83
Inside house [i]	11/8/04 – 2/20/05	256	0.0107	6.38 – 25.5	231	3,060

[a] Application rate used in the study (lbs chloropicrin per 1,000 ft^3). Multiply by 0.01605 to calculate rate in kg/m^3.
[b] Limit of Quantification. In some study reports, this is called the "estimated quantitation limit," or EQL.
[c] Multiply value by 0.1487 to get result in parts per billion (ppb).
[d] Maddy *et al*. (1986). Sampling occurred during tarp removal (10 samples) and house clearance (4 samples) operations following fumigation of six structures.
[e] Maddy *et al*. (1986). At the seven fumigation sites, 52 samples were collected during fumigation and 15 samples were collected following tarp removal. An inlet tube leading to an outdoor sampler was placed in the center of one of the rooms in each house to allow concentrations to be monitored during fumigation.
[f] Lee and Liscombe (1993). Study was intended to determine concentrations during fumigation. Samples were collected for 24 hours following fumigant introduction in ten houses. Fifteen-minute samples were collected at 1- to 12-hour intervals at two indoor sampling lines in each house and three samplers between the house and tarp. The LOQ was not reported, but the lowest reported non-zero concentration was 20 ppb (134 $\mu g/m^3$).
[g] ARB (2003d). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of a 22,000-ft^3 house; total amount chloropicrin 1.5 ounces for a nominal indoor concentration of 68 $\mu g/m^3$. Two indoor sampling intervals of 24 hours each (total 48 hours) followed 48-hour fumigation followed by a 45-minute mechanical venting interval and 22-hour aeration.
[h] ARB (2005a). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of an 81,000-ft^3 house; total amount chloropicrin 6 ounces for a nominal indoor concentration of 74 $\mu g/m^3$. Two indoor sampling intervals of 24 hours each (total 48 hours) followed 71-hour fumigation followed by 83-minute mechanical venting interval and 72-hour aeration.
[i] Barnekow and Byrne (2006). Following eight applications (two at each of four houses), 8 post-clearance samples were collected at 4 indoor samplers following tarp removal. Indoor sampling intervals of 1 – 8 hours followed 20-hour fumigation and 12- to 24-hour aeration. LOQ was 0.153 µg/tube.

Lee and Liscombe (1993) corrected all sample results for the mean laboratory spike desorption efficiency for each analytical batch, which were in the range of 69% – 78.5%. During methods development, recoveries ranged 89% - 100%, with mean $\pm$ SD of 93 $\pm$ 6.2%. No breakthrough testing was conducted, which Lee and Liscombe (1993) justified by noting that sample intervals were short (15 minutes), and that sampling pump flow rates were below the range where breakthrough would be expected. In other chloropicrin studies, breakthrough did not occur at sampling flow rates at or below 100 ml/min (ARB, 2003c; Barnekow and Byrne, 2006; Ashworth *et al*., 2008; CRLA, 2008). Samplers inside the house measured concentrations ranging from below 20 ppb (134 $\mu g/m^3$) to 17,580 ppb (118,200 $\mu g/m^3$). Samplers between the house and the tarp measured concentrations ranging from below 20 ppb

(134 μg/m^3) to 17,030 ppb (114,500 μg/m^3). However, as monitoring occurred during a time when structures are not occupied, these data were not used to estimate occupational exposure.

ARB sampled indoor air during and following two structural fumigations with sulfuryl fluoride, with chloropicrin used as a warning agent (ARB, 2003d; 2005a). In each house, two sets of 24-hour samples were collected at two indoor samplers, for a total of four samples per study, as summarized in Table 42. Barnekow and Byrne (2006) sampled indoor air during and following eight structural fumigations with sulfuryl fluoride, with chloropicrin used as a warning agent. Indoor air samples collected for up to 36 hours following aeration are summarized in Table 42. In each house, eight post-clearance samples were collected at four indoor samplers. Indoor sampling intervals of 1 – 8 hours followed 20-hour fumigation and 12- to 24-hour aeration. Post-clearance chloropicrin concentrations measured by Barnekow and Byrne (2006) were significantly higher than those measured by ARB (2003d; 2005a), and were used to estimate occupational reentry exposure.

Table 43 summarizes concentrations and assumptions used to calculate occupational exposures associated with structural fumigation. Activity descriptions used in Table 43 are based in part on a description of three main phases of a structural fumigation that involve workers (Andrews, 1995; Cochran and DiPaolo, 2006):

1. Closing or application phase: beginning with structural preparation and tarpaulin placement and ending when the fumigant release is completed;

2. Opening or commencement of aeration phase: the time ventilation is commenced is the period of time beginning when the seal is broken and ending when all seals/tarpaulin are removed (also defined in 16 CCR 1970.5); and

3. Certification phase: when the structure is certified safe for reentry by the licensee or field representative from the fumigation company (licensee).

Cochran and DiPaolo (2006) reported the amount of time each day that certified/licensed fumigators (responsible for overseeing fumigation, introducing fumigant, initiating aeration and verifying fumigant concentrations) and tent crew workers (who set up tents around structures to be fumigated, repaired tears in tarps during fumigation, and removed tarps at the end of the fumigation period) spent in certain activities. Activity times were estimated based on a study summarizing one work week (5 days) of daily observation and timing of 3 crews of structural fumigation workers during their routine activities in Santa Ana and El Monte, California submitted by the registrant (Contardi and Lambesis, 1996).

During the application phase in fumigations with sulfuryl fluoride, the applicator can be exposed to chloropicrin while pouring the required amount into a pan, followed by turning on a fan (or multiple fans) before leaving the structure. This activity takes approximately 10 minutes (Contardi and Lambesis, 1996; Barnekow and Byrne, 2006), and the applicator is assumed to engage in activities outside the structure, such as tarp inspection, for an additional

50 minutes. Once the fumigant introduction is completed, the fumigator typically leaves and travels to another structure, where another fumigation may be initiated or terminated.

Table 43. Chloropicrin Concentrations and Assumptions Used for Occupational Exposure Estimates Associated with Structural Fumigations

Scenario and Activity	Hours Per Day [a]	Application Rate [b]	Measured Concentration [c]		Adjusted Concentration [d]	
			μg/m³	ppb	μg/m³	ppb
Applicator [e]						
• Fumigant Introduction [f]	0.17	0.0107	188,000	28,000	188,000	28,000
• Tarp Inspection [g]	0.83	0.0107	31.4	4.67	31.4	4.67
• 1-Hour TWA [h]					32,000	4,760
Tarp Removal [i]	4	0.0075	94.8	14.1	294	43.7
Aerator [j]						
• Testing for Clearance [k]	0.16	0.0188	53,700	7,990	30,600	4,550
• Outside Structure [l]	0.84	0.0107	243	36.2	243	36.2
• 1-Hour TWA					5,100	758
Reentry [m]	4	0.0107	827	123	827	123

[a] Fumigant introduction, tarp removal, and testing for clearance activity durations are based on a survey of activities by certified fumigators and tent crews doing structural fumigation for one week, conducted by Contardi and Lambesis (1996) and summarized by Cochran and DiPaolo (2006). Durations for other activities are assumed.

[b] Application rate used in the study (lbs chloropicrin per 1,000 ft³). Multiply by 0.01605 to calculate rate in kg/m³.

[c] Unless otherwise indicated, this is the mean concentration; rounded to 3 significant figures.

[d] Concentration adjusted for maximum application rate of 1 ounce per 10,000 ft³ (0.0107 lbs/ 1,000 ft³ or 0.000172 kg/m³).

[e] Applicator introduces fumigant and warning agent, then spends remainder of hour outside of tarped house, inspecting tarps.

[f] Data from Maddy *et al*. (1986), highest concentration reported inside a house during first 2-hour interval after chloropicrin poured into pan and fans turned on; no breathing-zone concentrations were measured.

[g] Data from Barnekow and Byrne (2006), highest concentration reported outside a house during first 2-hour interval after start of fumigation.

[h] 1-hour time-weighted average (TWA) calculated for applicator as follows:

$$\text{1-Hour TWA} = [(0.17 \text{ hour} \times 188{,}000\ \mu g/m^3) + (0.83 \text{ hour} \times 31.4\ \mu g/m^3)]/(1 \text{ hour}) = 32{,}037\ \mu g/m^3.$$

[i] Data from Maddy *et al*. (1986), breathing zone of eleven tarp removers was monitored. The adjusted concentration, used for short-term exposure estimates, is a 95th percentile calculated by lognormal methods. The mean concentration, used for seasonal and longer exposures, is 15.8 ppb (106 μg/m³). Both the 95th percentile and mean concentrations were adjusted for an application rate of 0.0107 lbs/ 1,000 ft³.

[j] Aerator enters home after tarps are removed and verifies that fumigant concentrations are below required concentrations to allow reentry without respiratory protection. Clearance testing takes approximately 10 minutes per day before worker moves on to other activities.

[k] Data from Maddy *et al*. (1986).

[l] Data from Barnekow and Byrne (2006), highest concentration reported outside a house during aeration.

[m] Data from Barnekow and Byrne (2006), 95th percentile of indoor air concentrations measured in first 24 hours following clearance.

Tarp removal occurs during the second phase. Cochran and DiPaolo (2006) report that tent crews remove tarps for approximately 4 hours, based on data from Contardi and Lambesis (1996). Tarp removal was one of the activities monitored by Maddy *et al.* (1986). Following certification, reentry activities can occur. Fumigation workers are no longer present and occupants of treated structures reenter those structures.

Table 44 summarizes occupational exposures to chloropicrin used as a warning agent in structural fumigation. Exposure estimates for tarp removers were based on data from Maddy *et al.* (1986). As summarized in Table 43, applicator, aerator, and fumigator estimates were based on data from both Maddy *et al.* (1986) and Barnekow and Byrne (2006). Reentry exposure estimates were based on data from Barnekow and Byrne (2006). Estimates were adjusted for differences in application rate used in studies and maximum allowed rate for chloropicrin as a warning agent.

Table 44. Estimated Occupational Exposure to Chloropicrin During and Following Structural Fumigation with Chloropicrin as a Warning Agent

Scenario [a]	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal [c] (ppb)	Annual [d] (ppb)	Lifetime [e] (ppb)
Application					
• Applicator [f]	4,760	NA [g]	NA	NA	NA
Aeration					
• Tarp Remover	43.7	43.7	15.8	7.79	4.16
• Aerator [h]	758	NA	NA	NA	NA
Overall					
• Fumigator [i]	4,760	723	62.2	33.4	17.8
Reentry					
• Reentry [j]	123	123	35.9	17.7	9.44

[a] See Appendix 1 for detail about activities. Exposure estimates for tarp removers were based on data from Maddy *et al.* (1986). Applicator, aerator, and fumigator estimates were based on data from both Maddy *et al.* (1986) and Barnekow and Byrne (2006). Reentry exposure estimates were based on data from Barnekow and Byrne (2006). Estimates were adjusted for differences in application rate used in studies and maximum allowed rate for chloropicrin as a warning agent.
[b] Short-term concentrations are the highest realistic exposure estimates and cover intervals from 1 hour to 1 week.
[c] Seasonal exposures are average estimates that cover intervals from 1 week up to 1 year.
[d] Assumes 180 days/year for tarp removers and reentry workers, and 196 days/year for fumigators. Annual average concentrations are as follows: Seasonal concentration x (number of days per year/365 days).
[e] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).
[f] Applicator pours chloropicrin into pan and turns on fan (10 minutes) at the start of an application, then inspects tarps for remainder of hour before moving on to other activities at another fumigation site. This activity is combined with tarp removal and aeration for overall fumigator exposure.
[g] NA = not applicable. Activity is done for less than a full workday before worker moves on to other activities; see fumigator for exposure estimates longer than 1 hour.
[h] Aerator enters home after tarps are removed and verifies that sulfuryl fluoride or methyl bromide concentrations are below required concentrations to allow reentry without respiratory protection. This clearance testing takes approximately 10 minutes per day before worker moves on to other activities. This activity is combined with application and tarp removal for overall fumigator exposure.
[i] Fumigators are licensed and certified to apply pesticides and to monitor aeration. They may perform tarp removal and other activities in addition to their certified/licensed activities. Time-weighted average exposures assume that in each 8-hour workday the fumigator spends 1 hour as an applicator, 1 hour as an aerator and 6 hours as a tarp remover (highest 1-hour exposure is the same as for an applicator).
[j] Reentry includes clean up and other activities that occur post-clearance.

Cochran and DiPaolo (2006) estimated the number of days per year that workers would do structural fumigation with sulfuryl fluoride. Numbers of days per week specific fumigation-related activities occurred were estimated based on data from one work week (5 days) of daily observation and timing of 3 crews of structural fumigation workers during their routine activities in Santa Ana and El Monte, California (November 1993 and May 1994) submitted by the registrant (Contardi and Lambesis, 1996). The average number of days/week was in turn multiplied by 49 weeks/year to estimate days/year for annual exposure estimates; the number of weeks worked per year was based on national averages of paid holidays and vacations collected by the U.S. Department of Labor (2004). Cochran and DiPaolo (2006) estimated that applicators work 196 days/year, tarp removers work 180 days/year and aerators (doing clearance activities) work 196 days/year. No information was available about number of days reentry workers (conducting activities post-clearance), and seasonal and annual exposure assumed 180 days.

EXPOSURE APPRAISAL

Bystanders to Soil Fumigation

Exposure estimates for bystanders to soil fumigation were based on concentrations modeled from flux data. DPR used the ISCST3 air dispersion model, in screening mode, to develop deterministic estimates of off-site concentrations associated with soil fumigation (Barry, 2008a). This model uses the emission rate or flux, along with parameters including emission height, distance from the emission source, wind direction and speed, atmospheric stability (vertical mixing of heated air), the profile of temperature vs. height above ground, and urban or rural air dispersion patterns to estimate the downwind air concentrations (U.S. EPA, 1995). Flux data were available for multiple application methods, with most studies spanning several days. Monitoring included nighttime as well as daytime conditions, an important consideration as off-site concentrations are often highest during calm nighttime periods when peak fumigant emissions combine with atmospheric inversions (Segawa, 1997). Studies monitored flux during applications conducted in accordance with typical soil fumigation practices.

However, with the limited number of studies available, there is insufficient information available to determine how representative the chloropicrin flux measured in association with each application method might be. With the exception of broadcast tarped applications, none of the application methods have replicated data, which precludes estimating variability in the flux. Broadcast tarped applications were replicated three times, in Arizona, Washington, and Florida. The flux CVs of the three applications for different intervals (6-hour day, 6-hour night, and 24-hour) ranged from 48.8% - 116% (Appendix 2). The sources of variability are not known, but could include differences between applications in parameters that affect flux, including field size and shape, soil moisture, size and organic content of soil particles, and temperature. If the estimated flux is significantly greater or less than the true flux of chloropicrin, then concentrations calculated from the flux will be over- or underestimated from actual concentrations encountered by bystanders (Barry *et al.*, 2004). For broadcast tarped applications, estimates relied on data from the Arizona application, which had the highest flux of the three applications.

Although off-site concentrations were measured simultaneously with flux, bystander exposure estimates were not based on the off-site data. Not only might bystanders under different conditions of weather and atmospheric stability potentially be exposed to higher concentrations than were captured in the relatively few studies conducted, but bystanders might also be closer to an application than were samplers in these studies. DPR uses air-dispersion modeling to address limitations in the data and provide health-protective bystander exposure estimates.

Modeling to determine off-site concentrations associated with soil fumigations incorporated various assumptions, each of which is associated with uncertainty. For example, one assumption was that the treated area is a square field, although DPR recognizes that treated areas can be rectangular or otherwise shaped. As explained by Barry *et al.* (2004), use of square fields provides a more consistent estimate "because the same centerline air concentrations will be obtained regardless of which side of the field the wind is blowing perpendicular over. This would not be the case if rectangular fields were used." It was further assumed that the treated area is 40 acres, as available information suggests that 40 acres is likely the maximum amount that can be treated in a single day by a single crew. A query of pesticide use in Monterey County suggests that in a recent 5-year period, between 1.5% and 5.5% of applications each year reported treating more than 40 acres (DPR, 2010a; data not shown). However, PUR reports can collapse multiple-day applications into a single day, and it is likely that not all of these applications actually treated more than 40 acres in one day (e.g., one application reported treating more than 500 acres). If a larger area is treated by using more than one crew, then the off-site concentration would be anticipated to be higher than estimated.

Short-term off-site concentrations associated with soil fumigations were adjusted to account for differences between the application rates monitored in flux studies and the maximum allowed application rate for chloropicrin. DPR believes upper-bound estimates are appropriate for short-term exposures because high-end exposures are possible, and DPR has an obligation to protect all individuals exposed to pesticides as a result of legal uses. Protecting at the level of "average or typical" exposure would, by definition, suggest that many individuals (anyone with above-average exposure) could be exposed to acutely toxic concentrations. In contrast, for seasonal and annual exposures, DPR believes that assumption of more typical exposure conditions is appropriate. Thus, seasonal and annual bystander exposure estimates assume that application rates on average are 190 lbs AI/acre, based on the rates used in a recent 5-year interval as reported in the PUR. Examination of applications made during that interval (2004 – 2008) in the ten counties with the highest chloropicrin use suggest that applications at rates higher than 350 lbs AI/acre are relatively rare, less than 0.2% of all applications (DPR, 2010a; data not shown).

There is evidence that the rate of 190 lbs AI/acre assumed in estimates of seasonal and annual exposure is health-protective. As summarized in Table A4-2 in Appendix 4, the 95th

percentile application rate for chloropicrin-only product uses in a recent 5-year period ranged 200 – 235 lbs AI/acre, which is not much higher than 190 lbs AI/acre. Chloropicrin-only product applications represented 7 to 10% of all applications in which chloropicrin was an AI; when all AI chloropicrin use is included, the 95th percentile ranged 181 – 197 lbs AI/acre. Overall, then, the median assumption of 190 lbs AI/acre is not much below the 95th percentile, suggesting it is a health-protective estimate for intermediate and long-term exposures. Nevertheless, as mentioned in Appendix 4, applications reported in the PUR do not include information about whether they are broadcast or bedded, or whether they are tarped or non-tarped. Because of this, it is not possible to estimate application rates at a particular (e.g., 50th) percentile for individual application methods. If particular uses, such as with a specific application method, are associated with higher application rates, then it is possible that some bystanders might experience higher-than-average exposures over longer periods of time. This possibility supports use of 190 lbs AI/acre as the assumed application rate, even though in some years the median application rate was much lower (e.g., the median in 2005 was 111 lbs AI/acre).

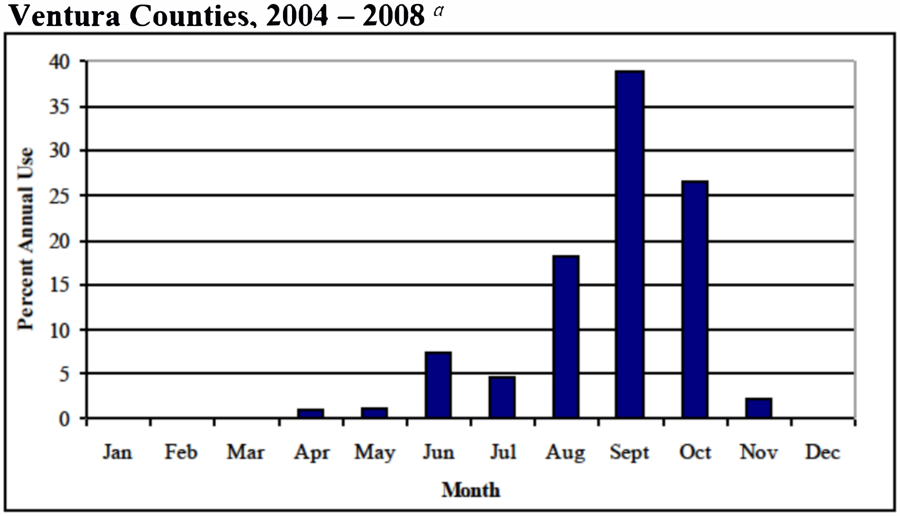
Concentration adjustments for various application rates assume that flux is a constant proportion of the application rate, and that concentrations are directly proportional to flux. Some uncertainty is associated with these adjustments, particularly as the estimates involve higher application rates than were used in the flux studies. With respect to such adjustments, Barry *et al.* (2004) noted that, “It is likely that due to the same or greater soil adsorption and degradation, the flux proportion is the same or less for application rates lower than those monitored. It is not known whether the flux increases proportionally with application rate for rates beyond those monitored.”

Sampling intervals during soil fumigations generally ranged 6-24 hours. Over shorter intervals, higher concentrations can occur as the plume meanders (Csanady, 1973; Pasquill, 1974). As available information suggests that shorter exposures to chloropicrin can result in adverse effects, 1-hour concentrations were estimated by using peak-to-mean ratio techniques to adjust 6-hour concentrations (Barry, 2000). Peak-to-mean calculations are based on the premise that the mean concentration during a longer interval averages a series of peaks, and that shorter intervals will tend to have higher peaks; thus the concentration measured during the longer interval can be adjusted by a factor that incorporates the square root of the ratio of durations of the longer and shorter intervals (O’Malley *et al.*, 2004b).

Seasonal, annual, and lifetime exposure estimates associated with soil fumigations are based on a 2-week concentration for a bystander adjacent to a single application. The 5-month interval for seasonal and annual exposure assumes a bystander is exposed to airborne chloropicrin from multiple applications during the high-use season, occurring 2 weeks apart. Soil fumigation is done before crops are planted. Generally, a single application is made prior to planting; however, a second fumigation is possible. For example, two fumigations 2 weeks apart are recommended to control nematodes in walnut orchard areas (McKenry and Westerdahl, 2007). The PUR data do not report if a field is treated only once or more than once. The likelihood of multiple soil fumigations near a bystander is supported by the frequency of applications in some sections of Monterey County. For example, in one section chloropicrin applications to strawberries were reported 22 – 38 days each year, over 5-month intervals, in the years 2002 – 2006 (DPR, 2010a; data not shown). The 1-mi^2 (259-hectare) sections are the smallest increment in which PUR data are reported (Wilhoit *et al*., 2001). Not all of these applications would be adjacent to a single location, but a single location could be in the same section as all of the applications.

In the absence of information with greater spatial resolution, 5 months duration for seasonal and annual exposures is considered a reasonable yet health-protective assumption. According to DPR practice, this exposure duration was based on chloropicrin use reported in a single county. However, strawberry pickers can move between counties, often living in worker camps near fields where they work. Thus they could be both residential and occupational bystanders to chloropicrin applications. Figure 10 summarizes monthly applications of chloropicrin to strawberry fields in Monterey, Santa Barbara, Santa Cruz, and Ventura Counties during a recent 5-year interval. These counties were selected because they include the highest chloropicrin use in the state and because in these counties strawberry harvest overlaps soil fumigation with chloropicrin. Examination of Figure 10 shows that during each month between June and October, chloropicrin use was at least 5% of the annual total use, and that 95% of annual use occurred during these 5 months. This duration supports the 5-month interval based on use in Ventura County (Figure 6). High-use periods reported in the PUR support exposure estimates for a population of bystanders, and probably overestimate the number of days any single individual is exposed. For bystanders to be exposed at the level estimated for annual and lifetime exposures would require them to be adjacent, or practically adjacent, to applications for 5 months. The extent to which this assumption overestimates individual exposures is not known. In the absence of data on individual activity patterns, the PUR provides the best available data for estimating long-term exposure estimates.

Figure 10. Applications of Chloropicrin in Monterey, Santa Barbara, Santa Cruz, and Ventura Counties, 2004 – 2008 [a]



[a] Percent calculations based on pounds applied (DPR, 2010a; queried November 1, 2010).

Concentrations estimated from modeling can be compared to concentrations found in off-site monitoring. For short-term durations, Table 10 summarizes measured off-site concentrations adjusted for maximum application rate. These concentrations can be compared to concentrations obtained through modeling and summarized in Table 12. For example, the highest concentration following a broadcast non-tarped application, adjusted for the maximum application rate, was 5,322 $\mu g/m^3$ occurring during a 6-hour sample and reported in Table 10. In Table 12, the comparable concentrations are 7,500 $\mu g/m^3$ and 44,000 $\mu g/m^3$, for 6-hour day and night intervals, respectively. It is unlikely that the highest possible concentrations for an application method would be measured in any given study, and it's not surprising that concentrations in Table 12 are higher than those in Table 10. Yet, the modeling-based estimates are within an order of magnitude of measured concentrations, which does not represent an extreme difference given the variability of concentrations measured within each study and given that off-site samplers were further from the edge of the field than the distance assumed by the modeling-based estimates. At least two other factors are anticipated to substantially contribute to differences between modeled and measured concentrations: weather conditions were likely different during study sampling intervals than the conditions assumed during modeling to obtain reasonable worst-case estimates, and modeled concentrations assumed a 40-acre field, while monitored fields receiving applications ranged 5.92 – 8.67 acres, or 4.6- to 6.8-fold smaller. For two fields treated at the same application rate, a greater amount of material is emitted from the larger field, increasing downwind concentrations (Barry, 2005b; Reaves and Smith, 2008).

Bystanders to Structural Fumigation and Indoor Air Exposures

Off-site chloropicrin concentrations and exposure estimates were lower for bystanders to structural fumigations than for bystanders to soil fumigations. Smaller amounts of chloropicrin are used with structural fumigations, both because of the smaller unit being treated and because chloropicrin is only used as a warning agent for structural fumigations. The largest application monitored involved a 81,000-ft^3 (2,300-m^3) structure (ARB, 2005a), yet the highest concentration measured in association with any of the monitored structural fumigations occurred adjacent to a smaller home with an approximate volume of 32,000 ft^3 (900 m^3). No data are available to estimate exposures of bystanders to fumigation of apartment buildings, which could potentially involve substantially larger amounts of chloropicrin than were used in the study houses.

Unlike bystander exposure estimates associated with soil fumigation, which were calculated using air dispersion modeling for the reasons previously stated, bystander exposures associated with structural fumigation were based on measured off-site concentrations. These concentrations are anticipated to be health-protective, although little information is available to assess how representative the applications monitored by ARB and Barnekow and Byrne are of upper-bound exposures to bystanders.

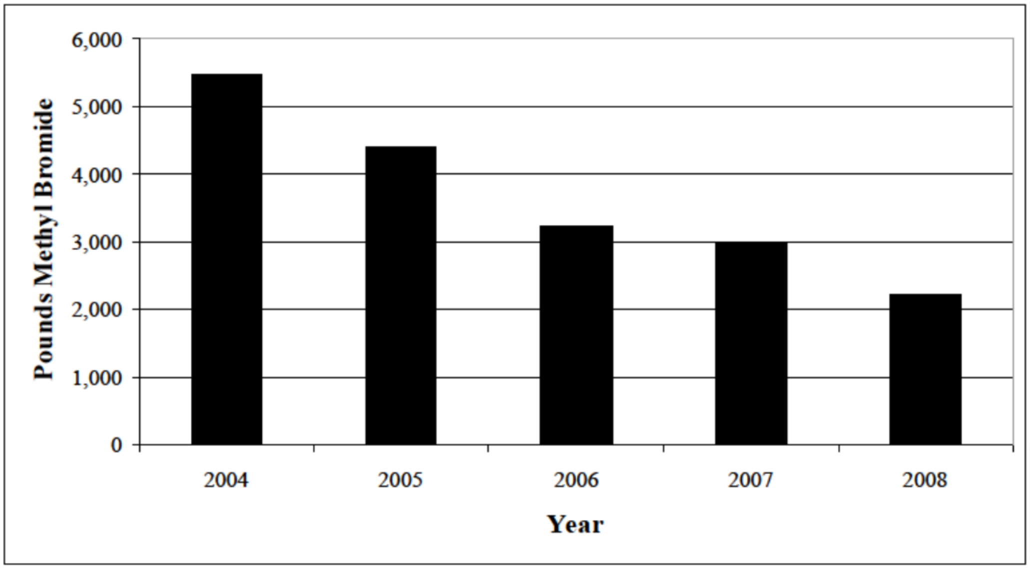
To decrease the likelihood of underestimating exposures, results were corrected for field spike recoveries. This practice is recommended by U.S. EPA for data used to estimate exposure (U.S. EPA, 1992); DPR is in accordance with U.S. EPA policy to correct only for field spike recoveries below 90% (U.S. EPA, 1998). Corrections for field spike recoveries are intended to compensate for loss of analyte during the sampling period and subsequent transportation and storage, as well as incomplete recovery in the analysis; the correction assumes that both sample and spiked tubes are subjected to the same factors at similar intensities. Rather than correct for field spike recoveries, Barnekow and Byrne (2006) corrected results for pooled laboratory and field spike recoveries. Laboratory spikes are intended to account for differences between analytical batches in factors such as extraction, reagents, and equipment calibration, and do not account for conditions in the field during sample collection and processing. As sampling intervals were quite long in some cases (as long as 8 hours), and as conditions differed substantially between some sites, DPR believes that correction for field spike recoveries is appropriate for these samples.

Nominally, the highest rate for chloropicrin was used in all eight replicates, suggesting that results do not need adjustment for application rates. Although the amount of chloropicrin used during each fumigation was reported (to two significant figures), the fumigation volume was not reported. Insufficient information was provided to verify application rates were the same between the four houses; however, different amounts of chloropicrin were reported between replicates in the third and fourth houses. It is possible that the houses were tarped differently, or that there was another factor causing a difference in fumigation volume between the first and second fumigations of these houses. Alternately, perhaps the chloropicrin was not measured with the same precision in those houses as in the first two houses. Regardless of the reason for the difference in chloropicrin amounts used, as all fumigations were conducted by commercial fumigators they are considered to reflect realistic conditions.

Exposure estimates assume a chloropicrin use rate of 0.0107 lbs/1,000 ft^3, the maximum rate for chloropicrin used as a warning agent with sulfuryl fluoride. This rate was assumed because sulfuryl fluoride is presently the dominant structural fumigant. Additionally, the only methyl bromide product which allows structural fumigation, Methyl Bromide 99.5%, is in the process of becoming inactive. Examination of PUR data from the 5-year interval 2004 – 2008 suggests that relatively few applications use Methyl Bromide 99.5%. These applications are summarized in Figure 11, which shows that during the 5-year interval use of Methyl Bromide 99.5% did not exceed 6,600 lbs per year. Assuming the maximum product application rate of 3 lbs/1,000 ft^3, the amounts shown in Figure 11 suggest that less than 2,200 ft^3 are treated annually in structural fumigations (the volume treated in a structural application are not reported in the PUR). Appendix 5 reports occupational exposure estimates associated with structural fumigation using Methyl Bromide 99.5%.

Off-site concentrations associated with structural fumigation were corrected for field spike recoveries and adjusted for maximum allowed application rate, but not for application size. The largest structure for which data are available was the two-story house described by ARB (2005a) as having an estimated volume of 81,000-ft^3 (2,300-m^3). Assuming each story is 10 feet (2.5 m) high, the house size is 4,050 ft^2 (376 m^2). This is on the larger end of houses in California; the national median house size was estimated at 1,769 ft^2 (164 m^2) in 2007 (U.S. Census Bureau, 2008). Although larger homes could be fumigated, they are likely to be located on larger properties, suggesting that bystanders might be expected to be farther from the application than with smaller homes in more closely-packed neighborhoods. Furthermore, available data do not suggest that fumigation of larger structures necessarily correlates with higher bystander exposures.

Figure 11. Annual Use of Methyl Bromide 99.5% in Structural Fumigation in California, 2004 – 2008 [a]



[a] Pounds product applied for structural pest control (DPR, 2010a; queried November 1, 2010).

Outdoor concentrations were measured only during fumigation and aeration. Once the aeration was considered complete (and sulfuryl concentrations were below 5 ppm), only indoor samples were collected. However, the indoor samples suggest that substantial chloropicrin was present indoors, particularly in Replicates 3, 4, and 5. Bystanders could potentially continue to be exposed to chloropicrin following clearance.

Chloropicrin Degradation to Phosgene

No phosgene monitoring has been done in conjunction with any chloropicrin application. Under laboratory conditions with simulated sunlight, chloropicrin vapor undergoes photodegradation, producing phosgene in addition to several nitrogen-containing products, with an estimated half-life in the range of 3 – 18 hours under constant illumination (Allston *et al.*, 1978; Carter *et al.*, 1997; Hatakeyama *et al.*, 1999; Wade *et al.*, 2007; Vera *et al.*, 2010). As part of its data call-in for chloropicrin, DPR requested information on whether the photodegradation product phosgene should be monitored as part of the air monitoring studies (Jones, 2002). In response, Gills *et al.* (2002) reviewed the literature on chloropicrin photolysis and estimated air concentrations of phosgene based on computer modeling. Gills *et al.* (2002) concluded that under field conditions chloropicrin degradation products, including phosgene, would remain below levels of concern. DPR staff in the Environmental Monitoring Branch reviewed the submission by Gills *et al.* (2002), and agreed with its general conclusions (Barry and Segawa, 2002). Limited data are available about phosgene generation and breakdown in the environment, as well as the potential significance of phosgene exposure to bystanders. Phosgene is a photodegradation product of many chlorinated hydrocarbon compounds, and was found in ambient air samples collected at several sites in California in 1975 and 1976 (Singh *et al*., 1977). Additional data are needed to determine whether bystanders to chloropicrin applications are exposed to phosgene at concentrations higher than background. In its evaluation of chloropicrin, the European Food Safety Authority also identified phosgene concentrations associated with chloropicrin applications as a data gap that must be addressed (EFSA, 2011).

Residential Reentry Exposure Estimates

Indoor air exposures to chloropicrin were estimated for individuals entering structures following fumigation and aeration, based on post-clearance concentrations reported by Barnekow and Byrne (2006). Monitoring of indoor air was conducted for 36 hours post-clearance. Elevated chloropicrin concentrations, exceeding 140 $\mu g/m^3$ (20.8 ppb), occurred in the last 8-hour interval (spanning 24 to 36 hours post-clearance) in Replicates 2, 3, 5, and 6 monitored by Barnekow and Byrne (2006). Quantifiable concentrations, ranging 13.9 – 565 µg/m3 (2.06 – 84.1 ppb), occurred during the last monitoring interval in all eight replicates. Additionally, in the studies monitored by ARB (2003d; 2005a) chloropicrin concentrations at two indoor-air samplers were monitored for two 24-hour intervals post-clearance; in both cases, chloropicrin was above the LOQ, ranging 0.95 – 53 µg/m3 (0.14 – 7.9 ppb), in the second 24-hour sample (spanning 24 to 48 hours post-clearance). These results suggest that some individuals reentering fumigated houses chloropicrin exposures could potentially continue to be exposed to chloropicrin for two days or longer following clearance.

Occupational Exposure: Soil Fumigation

Occupational exposure estimates associated with soil fumigation are based on exposure monitoring conducted by Beard *et al.* (1996) and Rotondaro (2004). Various soil sealing equipment was used in non-tarped applications. All chloropicrin product labels require soil sealing immediately following application, including ring rollers, drag sleds, etc., for non-tarped applications (some labels require use of tarps). Thus, the use of cultipackers and other equipment in non-tarped applications was appropriate. No information is available on relative effectiveness of various equipment, and equipment types were not replicated in either broadcast or bedded applications, precluding conclusions about potential effects on exposures.

Chloropicrin concentrations reported by Beard *et al.* (1996) and Rotondaro (2004) were corrected for field spike recoveries, according to DPR policy. Rather than correct for field spike recoveries, Rotondaro (2004) corrected results for laboratory spike recoveries, which focuses on differences between analytical batches in the laboratory rather than between conditions in the field during sample collection and processing. As sampling intervals were quite long in some cases (as long as 13 hours), and as conditions differed substantially between some sites, DPR believes that correction for field spike recoveries is appropriate for these samples.

Chloropicrin concentrations were also adjusted based on application rates. For short-term exposure estimates, chloropicrin concentrations were adjusted to reflect the maximum application rates allowed in California. Seasonal, annual, and lifetime estimates were adjusted to the application rate considered typical in California, based on use reported in the Pesticide Use Report for a recent 5-year interval. Concentration adjustments for various application rates assume that the concentration that individuals involved in an application or reentering an area post-application is proportional to the application rate. No adjustment was made for size of applications monitored. In some cases, applications to small plots might result in exposures being underestimated. For example, shank bedded tarped fumigation monitored by Beard et al. (1996) and Rotondaro (2004) involved field sizes ranging 1.11 – 1.93 acres; these applications took 2.4 – 8.0 hours to complete. Commercial applicators would be anticipated to fumigate small fields in a much shorter time than it took in the monitoring study, and exposure estimates based on these data could potentially underestimate exposure of commercial applicators handling more chloropicrin while treating larger areas.

Occupational Exposure: Structural Fumigation

Occupational scenarios associated with structural fumigation were based on information summarized by Andrews (1995) and Cochran and DiPaolo (2006), as well as data presented in three studies (Maddy *et al*., 1986; Contardi and Lambesis, 1996; Barnekow and Byrne, 2006). Exposure estimates for applicators during fumigant introduction are based on the best data that are presently available, which are concentrations measured inside a fumigated structure (Maddy *et al*., 1986). These data may overestimate applicator exposure, as more chloropicrin would be expected to volatilize during the 2-hour interval that concentrations inside the structure were monitored, than during the much shorter time needed to introduce chloropicrin. Ideally, breathing-zone chloropicrin concentrations would be measured while an applicator pours chloropicrin at the start of a fumigation, particularly for applications involving multiple chloropicrin pans.

Structural fumigations are not reported individually in the Pesticide Use Report, and the PUR does not give information about application rates or sizes. Instead, structural fumigators report amounts of pesticide used during particular intervals. From applications reported in various studies (Maddy *et al*., 1986; Lee and Liscombe, 1993; ARB, 2003d; ARB, 2005a), it is apparent that chloropicrin is not always used at the maximum allowed rate. However, there is no way to determine typical use rates. For short-term exposure estimates (1-hour and 8-hour durations), concentrations were adjusted to the maximum chloropicrin use rate of 1 ounce per 10,000 ft^3 (0.0107 lbs/1,000 ft^3). In the absence of information about typical use rates, concentrations were also adjusted to the maximum rate for seasonal, annual, and lifetime exposures.

For seasonal and annual exposures, handlers were assumed to work 180 days/year for tarp removers and reentry workers, and 196 days/year for fumigators. These estimates were based on average frequencies of these activities of 3.67 and 4 days per week, respectively, during a week of monitoring structural fumigations by Contardi and Lambesis (1996). These average frequencies are the same as those used by Cochran and DiPaolo (2006), and imply a precision that is supported by Contardi and Lambesis (1996), but that may not actually be warranted by the data. However, the impact on exposure estimates of the differences in days is minimal.

Respiratory Protection

Product labels require handlers to wear respiratory protection when sensory irritation occurs. DPR assumes a default protection factor for half-face respirator of 90% when an air-purifying respirator is required; that is, inhaled concentrations might reasonably be anticipated to decrease at least 10-fold when the appropriate respirator is properly used (OSHA, 2006). The level of respiratory protection conveyed by respirators can be a source of uncertainty, with some authors suggesting that the default protection factor should be set to a lower level, and others arguing that 10-fold is sufficiently protective. For example, Nicas and Neuhaus (2004) suggest that air-purifying respirators reduce exposure by 5-fold instead of 10-fold; i.e., that data support a protection factor of 80% rather than 90%. In contrast, Myers and Zhuang (1998) and Crump (2007) cite evidence indicating that a 90% protection factor is sufficiently protective. The uncertainty may be attributed to improper testing, maintenance, or improper use of these devices. There is no consensus on how to determine the degree of efficacy of respiratory protection for the multitude of industrial and agricultural uses (Nelson, 1996; Myers and Zhaung, 1998; Caretti and Gardner, 1999; Nelson *et al.*, 2000; Cohen *et al.*, 2001; Janssen *et al.*, 2002; Nicas and Neuhaus, 2004; Zhaung et al., 2005; Crump, 2007; Greskevith *et al.*, 2007).

Key Differences Between Exposure Assessments by DPR and U.S. EPA

U.S. EPA estimated exposure and risk for the purpose of reregistering chloropicrin products under FIFRA requirements. Uses are eligible for reregistration following one of two determinations by U.S. EPA: 1) the use is associated with acceptable risks, or 2) uses may have unacceptable risks yet have favorable risk-benefit results that prompt U.S. EPA to allow reregistration. In its exposure estimates, U.S. EPA incorporated proposed mitigation measures, such as assuming application rates lower than those on existing product labels. DPR estimated exposure and risk to determine whether there are unacceptable risks requiring mitigation, based on current product labels. Thus, DPR calculated exposure estimates assuming the maximum application rate allowed on current product labels, and that no mitigation measures are employed other than ones stated on the label or required by state or federal regulation. When the risk assessment process is completed, DPR may address risks determined to need mitigation by requiring changes in how affected products are used, or DPR may cancel certain uses.

U.S. EPA used the same data as DPR to estimate exposures of bystanders to soil and structural fumigation, as well as indoor-air exposures (reentry into fumigated residences). U.S. EPA used additional soil fumigation studies, conducted more recently and incorporating mitigation measures such as high-barrier tarps and specially designed application equipment. Such measures are not required on current product labels, and DPR's estimates do not assume their use. U.S. EPA based exposure estimates related to structural fumigation on ARB studies. Although DPR considered the ARB studies, structural exposure estimates were instead based on a recent study submitted by registrants (Barnekow and Byrne, 2006). DPR used the newer study because it reported higher concentrations than the ARB studies. It is not clear if the study was available to U.S. EPA (2009).

Even when relying on the same studies, U.S. EPA approached the data somewhat differently. One key difference is in exposure durations used: U.S. EPA focused on acute exposures, "because chloropicrin produces peak off-gassing concentrations in the first 24 or 48 hours after application." U.S. EPA did not estimate seasonal, annual, or lifetime bystander exposures. DPR calculated long-term estimates for bystanders to soil fumigation (DPR calculated exposures only for durations of 1 day or less for bystanders to structural fumigation and for individuals exposed to chloropicrin in indoor air following structural fumigation).

U.S. EPA estimated acute exposure over 4-hour intervals for bystanders to soil fumigation. In contrast, DPR calculated 1-hour bystander exposure estimates, using ISCST3 to calculate deterministic estimates for use in determining risk. U.S. EPA reported ISCST3-based exposure estimates in an appendix to its risk assessment, but based risk decisions in part on probabilistic exposure estimates and in part by assuming that certain mitigation measures would reduce exposure to an acceptable level (U.S. EPA, 2009).

For occupational scenarios associated with soil fumigation, U.S. EPA estimated exposures for acute (defined as less than 24 hours), short-term (1 – 30 days), and intermediate-term (1 month to 6 months) durations (Smith and Reaves, 2009). U.S. EPA used the same studies as DPR for occupational exposures associated with soil fumigation, Beard *et al.* (1996) and Rotondaro (2004). For acute exposures, U.S. EPA used the highest concentration reported for each scenario, and U.S. EPA used geometric mean air concentrations. For most occupational scenarios, DPR calculated upper-bound (usually 95th percentile) concentrations for 1-hour and 8-hour durations, and used arithmetic mean concentrations for seasonal, annual, and lifetime occupational exposures. U.S. EPA did not estimate occupational exposures associated with structural fumigation; for fumigator, tarp remover, and reentry into treated structures, DPR estimated 1-hour, 8-hour, seasonal, annual, and lifetime occupational exposures.

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APPENDIX 1. OCCUPATIONAL SCENARIOS FOR CHLOROPICRIN USES IN CALIFORNIA

Every combination of application method and work activity is a scenario potentially requiring exposure data. Some scenarios may be used as surrogates for others if the registrant presents compelling arguments for it. This appendix lists all application methods and associated occupational handler and reentry activities that might occur with chloropicrin use in California.

Soil Fumigation

All chloropicrin-containing products registered in California have product label directions for soil fumigation. Some products are limited to use on specific crops or have limitations such as requiring use of tarps. Ranges of application rates are specified for various crops.

Table A1-1 lists all soil fumigation application methods allowed with products containing chloropicrin, along with handler activities. Most of these activities are defined in DPR (2004):

Copilots - Employees assisting in the overall operation, ensuring proper tarpaulin placement and condition, and changing cylinders.

Drivers - Operating fumigation equipment.

Shovelers - Employees involved in assisting with covering the tarpaulin with soil at the end of the rows (Note: Shovelers can work ONLY at the ends of the rows in methyl bromide applications, according to California regulation (3 CCR 3784).

Supervisors – Employees (handlers) who oversees the fumigation operation, and may assist the applicator by monitoring the smoothness of the mechanics of the fumigation operation, and loading and unloading methyl bromide canisters from supply truck, to and from tractor (note: this scenario will be covered in the exposure assessment by the copilot scenario).

Tarpaulin Cutters (Splitters) and Tarpaulin Removers – Employees who assists with the fumigation process by cutting tarpaulins using an ATV or a tractor with a cutting wheel to facilitate the aeration portion of the fumigation; or, by punching holes in the tarpaulin prior to planting transplant crops; or, removes the tarpaulin from the fumigation site.

Table A1-2 lists soil fumigation application methods allowed in greenhouses and pre-aeration handler activities associated with each method. Table A1-3 summarizes pre-aeration handler activities associated with structural fumigations. Tables A1-4 through A1-6 summarize aeration and reentry activities associated with field fumigations, greenhouse soil fumigations, and structural fumigations, respectively.

Table A1-1. Handler Scenarios (Pre-Aeration) for Soil Fumigation with Chloropicrin-Containing Products in Field and Other Outdoor Soil Fumigation [a]

	Application Method	Handler Activities	Comments
Shallow Shank	Broadcast/Tarped	Tractor Driver, Copilot, Supervisor, Shoveler	Data available for all listed activities except supervisor (Beard *et al.*, 1996); this activity covered by copilot.
	Broadcast/Non-tarped	Tractor Driver, Soil Sealer [b]	Data available for all listed activities (Beard *et al.*, 1996; Rotondaro, 2004).
	Bedded/Tarped	Tractor Driver, Copilot, Shoveler	Data available for all listed activities (Beard *et al.*, 1996; Rotondaro, 2004).
	Bedded/Non-tarped	Tractor Driver, Soil Sealer	Data available (Beard *et al.*, 1996; Rotondaro, 2004).
Deep Shank	Broadcast/Tarped	Tractor Driver, Copilot, Soil Sealer, Supervisor, Shoveler	Use surrogate data from shallow shank/broadcast/tarped applications [c].
	Broadcast/Non-tarped	Tractor Driver, Soil Sealer [b]	Use surrogate data from shallow shank/broadcast/non-tarped applications [c].
	Bedded/Tarped	Tractor Driver, Copilot, Shoveler	Use surrogate data from shallow shank/bedded/tarped applications [c].
	Bedded/Non-tarped	Tractor Driver, Soil Sealer	Data available (Beard *et al.*, 1996).
Surface Drip	Tarped	Applicator	Data available (Rotondaro, 2004).
Buried Drip (>5 inches)	Tarped	Applicator	Use surrogate data from surface drip/tarped applications [c].
	Non-tarped	Applicator	Use surrogate data from surface drip/tarped applications with adjustment for lack of tarp.
Hot Gas Drip [e]	Bedded/Tarped	Applicator	Instructions on methyl bromide labels only; regulated under 3 CCR 6450.3(a)(6). Handler exposure data available for methyl bromide only.
Potting soil	Tarped	Applicator	Instructions on methyl bromide labels only; regulated under 3 CCR 6452, which requires tarps. Used data for broadcast tarp remover.
Tree Replant	Hand-Held Wand Injection	Applicator	Data available (Rotondaro, 2004).

[a] Based on product labels registered by the California Department of Pesticide Regulation (DPR), California regulations on field fumigation (Title 3, Code of California Regulations (3 CCR), Section 6784), and descriptions from Beard *et al.* (1996) and Rotondaro (2004). Activities related to aeration following a tarped fumigation are legally considered to be handler activities, but are listed separately in this appendix for convenience.

[b] Copilot activities not needed for non-tarped applications (the copilot's major job is to monitor tarp rolls and sealing). Other tarp-related activities (punching, splitting, removal) are not needed, either.

[c] DPR agreed to use data from exposure monitoring during shallow shank applications to estimate handler exposure during deep shank applications (Jones, 2002).

Table A1-2. Handler Scenarios (Pre-Aeration) for Soil Fumigation with Chloropicrin-Containing Products in Greenhouse Soil Fumigation [a]

	Application Method	Handler Activities	Comments
Surface Drip	Tarped	Applicator	DPR waived the requirement for these handler replicates (Jones, 2002), provided that applications are made from outside the greenhouse, and that self-contained breathing apparatus is required for anyone entering a greenhouse before aeration is completed.
Buried Drip (>5 inches)	Tarped	Applicator	DPR waived the requirement for these handler replicates (Jones, 2002), provided that applications are made from outside the greenhouse, and that self-contained breathing apparatus is required for anyone entering a greenhouse before aeration is completed.
	Non-tarped	Applicator	This application method is not supported by CMTF [b].
Hot Gas Drip [c]	Bedded/Tarped	Applicator	Instructions on methyl bromide labels only; regulated under 3 CCR 6450.3(a)(6). Handler exposure data available for methyl bromide only. This application method is not supported by CMTF [b].
Shank	(Any shank fumigation in a greenhouse)	Applicator	This application method is not supported by CMTF [b]. Shank applications are not anticipated in greenhouses.
Tree Replant	Hand-Held Wand Injection	Applicator	This application method is not supported by CMTF [b], and is not anticipated in greenhouses.

[a] Based on product labels registered by DPR, California regulations on greenhouse fumigation (Title 3, Code of California Regulations (3 CCR), Section 6752), and descriptions from Beard *et al.* (1996) and Rotondaro (2004). Activities related to aeration following a tarped fumigation are considered to be handler activities, but are listed separately in this appendix for convenience.

[b] CMTF = Chloropicrin Manufacturers Task Force. CMTF does not support because it is “not used for chloropicrin as an active ingredient” (Wilhelm, 2001).

[c] Labels on the following products contain directions for hot gas: Methyl Bromide 89.5% (EPA Registration Number 11220-17-ZA); 98-2 Contains 2% Chloropicrin (8622-12-AA); MBC Concentrate Soil Fumigant (8853-2-AA-11220); and Methyl Bromide 98% (8536-19-ZA)

Table A1-3. Handler Scenarios (Pre-Aeration) for Structural Fumigation with Chloropicrin-Containing Products [a]

	Aeration Method	Handler Activities	Comments
Tarp-Covered Structure	Active (e.g., use of exhaust fans)	Applicator	All chloropicrin-containing products with label instructions for this use contain $\leq$ 2% chloropicrin. Data are available for concentrations inside a tarped home being fumigated (Maddy *et al.*, 1986).
	Passive (e.g., simple tarp removal)	Applicator	Ditto.
Taped and Sealed Structure	Active	Applicator	All chloropicrin-containing products with label instructions for this use contain $\leq$ 2% chloropicrin. No data are available for concentrations of taped and sealed structures.
	Passive	Applicator	Ditto.
Other Structures	Active	Applicator	There is no information to suggest that other structure sealing techniques are used with chloropicrin fumigation. If such information becomes available, then these scenarios will be more specifically defined; otherwise, they'll be omitted.
	Passive	Applicator	Ditto.

[a] Based on product labels registered by DPR, California regulations on structural fumigations (Title 3, Code of California Regulations (3 CCR), Section 6454). Activities related to aeration following a tarped fumigation are considered to be handler activities, but are listed separately in this appendix for convenience.

Table A1-4. Aeration Scenarios for Soil Fumigation with Chloropicrin-Containing Products in Field and Other Outdoor Soil Fumigation [a]

	Application Method	Activities [b]	Comments
Shallow Shank	Broadcast/Tarped	Tarp Splitter, Tarp Remover,	Data available for soil shaper, tarp splitter, and tarp remover (Rotondaro, 2004).
	Bedded/Tarped	Tarp Puncher	No data available.
Deep Shank	Broadcast/Tarped	Tarp Splitter, Tarp Remover,	Data available for tarp puncher, tarp splitter, tarp remover (Beard *et al*., 1996; Rotondaro, 2004).
	Bedded/Tarped	Tarp Puncher	This application method is not supported by CMTF [c].
Surface Drip	Tarped	Tarp Puncher	Data available for tarp puncher (Rotondaro, 2004).
Buried Drip (>5 inches)	Tarped	Tarp Puncher	No data available.
Hot Gas Drip	Bedded/Tarped	Tarp Puncher	Instructions on methyl bromide labels only; regulated under 3 CCR 6450.3(a)(6) [d]. Use surrogate data from surface drip/tarped.
Potting soil	Tarped	Tarp Splitter, Tarp Remover	Instructions on methyl bromide labels only; regulated under 3 CCR 6452, which requires tarps. Used data for broadcast tarp remover.

[a] Aeration activities occur following tarped soil and structural fumigations, and those are the only application methods listed in this table. Activities related to aeration following a tarped fumigation are considered to be handler activities, but are listed separately in this appendix for convenience.
[b] Tarp splitting involves slicing a tarp lengthwise with a cutting disk.
[c] CMTF = Chloropicrin Manufacturers Task Force. For application methods and rates not supported by CMTF, data may be requested from individual registrants.
[d] 3 CCR = Title 3 of the Code of California Regulations. Numbers that follow are section numbers in the CCR.

Table A1-5. Aeration Scenarios for Soil Fumigation with Chloropicrin-Containing Products in Greenhouse Soil Fumigation [a]

	Application Method	Activities	Comments
Surface Drip	Tarped	Aerator	DPR waived the requirement for these handler replicates (Jones, 2002), provided that applications are made from outside the greenhouse, and that self-contained breathing apparatus is required for anyone entering a greenhouse before aeration is completed.
Buried Drip (>5 inches)	Tarped	Aerator.	No data available.
Hot Gas Drip	Bedded/Tarped	Tarp Puncher.	Instructions on methyl bromide labels only; regulated under 3 CCR 6450.3(a)(6).

[a] Aeration activities occur following tarped soil and structural fumigations, and those are the only application methods listed in this table. Activities related to aeration following a tarped fumigation are legally considered to be handler activities, but are listed separately in this appendix for convenience.
[b] 3 CCR = Title 3 of the Code of California Regulations. Numbers that follow are section numbers in the CCR.

Table A1-6. Reentry Scenarios for Soil Fumigation with Chloropicrin-Containing Products in Field and Other Outdoor Soil Fumigation [a]

	Application Method	Activities [b]	Comments
Shallow Shank	Broadcast/Tarped	Soil Shaper, Pipe Layer (and other irrigator activities), Planting	Data available for soil shaper (Rotondaro, 2004).
	Broadcast/Non-tarped	Soil Shaper, Pipe Layer, Planting	Data available for soil shaper (Rotondaro, 2004).
	Bedded/Tarped	Tarp Puncher, Pipe Layer, Planting	No data available.
	Bedded/Non-tarped	Pipe Layer, Planting	Data available for pipe layer (Rotondaro, 2004).
Deep Shank	Broadcast/Tarped	Soil Shaper, Pipe Layer, Planting	No data available.
	Broadcast/Non-tarped	Soil Shaper, Pipe Layer, Planting	Data available for soil shaper (Rotondaro, 2004).
	Bedded/Tarped	Pipe Layer, Planting	This application method is not supported by CMTF [c].
	Bedded/Non-tarped	Pipe Layer, Planting	No data available.
Surface Drip	Tarped	Planting	No data available.
Buried Drip (>5 inches)	Tarped	Planting	No data available.
	Non-tarped	Planting	No data available.
Hot Gas Drip	Bedded/Tarped	Planting	Instructions on methyl bromide labels only; regulated under 3 CCR 6450.3(a)(6) [d]. No data available.
Potting soil	Tarped	Potting plants or seeds	Instructions on methyl bromide labels only; regulated under 3 CCR 6452, which requires tarps.
Tree Replant	Hand-Held Wand Injection	Planting	No data available.

[a] Reentry activities include potentially any activity that disturbs treated soil.
[b] Planting covers all soil-disturbing cultivation activities for crops planted following soil fumigation.
[c] CMTF = Chloropicrin Manufacturers Task Force. For application methods and rates not supported by CMTF, data may be requested from individual registrants.
[d] 3 CCR = Title 3 of the Code of California Regulations. Numbers that follow are section numbers in the CCR.

Table A1-8. Reentry Scenarios for Soil Fumigation with Chloropicrin-Containing Products in Greenhouse Soil Fumigation [a]

	Application Method	Activities	Comments
Surface Drip	Tarped	Any worker entering a greenhouse following fumigation, especially those performing activities that disturb the soil.	No data available [b].
Buried Drip (>5 inches)	Tarped	Any worker entering a greenhouse following fumigation, especially those performing activities that disturb the soil.	No data available [b].
Hot Gas Drip	Bedded/Tarped	Any worker entering a greenhouse following fumigation, especially those performing activities that disturb the soil.	Instructions on methyl bromide labels only; regulated under Title 3, Code of California Regulations, Section 6450.3(a)(6). No data available [b].

[a] Reentry activities include potentially any activity that disturbs treated soil. Non-tarped soil applications, shank applications, and tree replant handwand applications are not allowed in greenhouses (Title 3, Code of California Regulations, Section 6452), and are not listed in this table.

[b] DPR waived the requirement for exposure monitoring of greenhouse reentry workers (Jones, 2002), as the product label specifies that reentry cannot occur until air concentrations are within acceptable limits.

Table A1-9. Reentry Scenarios for Structural Fumigation with Chloropicrin-Containing Products [a]

	Aeration Method	Activities	Comments
Tarp-Covered Structure	Active	Any worker entering structure following fumigation (including collector of air samples).	All chloropicrin-containing products with label instructions for structural fumigation contain ≤ 2% chloropicrin. Indoor air concentration data following structural fumigation are available from the California Air Resources Board.
	Passive	Ditto.	Ditto.
Taped and Sealed Structure	Active	Ditto.	Ditto.
	Passive	Ditto.	Ditto.
Other Structures	Active	Ditto.	There presently is no information to suggest that other structure sealing techniques are used with chloropicrin fumigation. If such information becomes available, then these scenarios will be more specifically defined; otherwise, they'll be omitted.
	Passive	Ditto.	Ditto.

[a] Reentry involves entering a treated structure following aeration. Based on product labels registered by DPR and California regulations on structural fumigations (Title 3, Code of California Regulations (3 CCR), Section 6454).

APPENDIX 2. VARIATION IN CHLOROPICRIN FLUX FROM BROADCAST TARPED APPLICATIONS

Table A2-1. Coefficient of Variation for Chloropicrin Flux from Broadcast Tarped Applications [a]

Sampling Interval [b]	Flux (µg/m²/sec) [c]	Study Application Rate (lbs/Acre)	Flux Adjusted to Maximum Application Rate of 500 lbs AI/acre (µg/m²/sec) [d]
6-Hour Day			
Arizona	132	332	199
Washington	70	343	102
Florida	58	346	84
Mean			128
Standard Deviation			61.8
Coefficient of Variation [e]			**48.2 %**
6-Hour Night			
Arizona	142	332	214
Washington	20	343	29.2
Florida	22	346	31.8
Mean			91.6
Standard Deviation			106
Coefficient of Variation			**116 %**
24-Hour			
Arizona	108	332	163
Washington	34	343	49.6
Florida	28	346	40.5
Mean			84.2
Standard Deviation			68.1
Coefficient of Variation			**80.8 %**

[a] From Barry (2008a), based on data from Beard *et al*. (1996). Flux estimates were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model.
[b] The flux values for 1-hour day and night intervals were calculated from the corresponding 6-hour intervals, and would have the same coefficient of variation as the 6-hour flux values.
[c] The reported flux is the highest flux value obtained using the study flux profiles; a rolling average method was used to obtain the highest flux for each 24-hour interval when sampling intervals were less than 24 hours (Barry, 2008a).
[d] This rate is the maximum broadcast tarped application rate allowed on any chloropicrin product label currently registered in California.
[e] Coefficient of variation calculated as follows: 100% x (standard deviation)/(mean)

APPENDIX 3. OFF-SITE CHLOROPICRIN CONCENTRATIONS FOR TWO-DAY ROLLING APPLICATIONS

Table A3-1. Chloropicrin Off-Site Air Concentrations Estimated for Two Sequential Application Days at a Distance of 10 Feet (3.0 Meters) from the Edge of the Field [a]

Application Method	Study Location	Maximum Application Rate (lbs/Acre) [b]	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Day [c]					
Broadcast non-tarped	Arizona	350	5,300	**31,000**	5,400
Bedded non-tarped	Arizona	175	12,000	19,000	3,500
Bedded tarped	Arizona	350	**13,000**	22,000	**5,200**
Broadcast tarped	Arizona	350	12,000	2,600	3,000
Bedded drip tarped	California	300	4,700	840	1,100
Previous Day [d]					
Broadcast non-tarped	Arizona	350	**11,000**	17,000	5,000
Bedded non-tarped	Arizona	175	7,200	12,000	3,600
Bedded tarped	Arizona	350	**11,000**	**23,000**	**5,700**
Broadcast tarped	Arizona	350	7,000	13,000	3,600
Bedded drip tarped	California	300	2,400	4,200	1,200
Total [e]					
Broadcast non-tarped	Arizona	350	16,000	**48,000**	10,000
Bedded non-tarped	Arizona	175	19,000	31,000	7,100
Bedded tarped	Arizona	350	**24,000**	45,000	**11,000**
Broadcast tarped	Arizona	350	19,000	16,000	6,600
Bedded drip tarped	California	300	7,100	5,000	2,300

[a] From Barry (2008c), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. Bolded values represent the highest concentration for each interval.

[b] This application rate is the maximum allowed for that method on any product label currently registered in California. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre treated area, in the first 24 hours of a fumigation.

[d] A second field, also 40 acres and square, and treated the previous day, is assumed to be upwind of the field treated during the current day. Note that in some cases higher concentrations occur on the day after application than on the day of application (i.e., previous day's concentration may be higher than current day's).

[e] Concentrations are assumed to be additive. For example, 7,500 + 14,000 = 21,500 (rounded to 22,000 for total concentration).

APPENDIX 4. APPLICATION SIZES AND RATES FOR CHLOROPICRIN USE REPORTED IN CALIFORNIA

The two tables below summarize chloropicrin applications reported in California over a recent 5-year interval (DPR, 2010a). Only applications of products containing 94 – 100% chloropicrin are included, as screening estimates are based on these products.

Table A4-1. Chloropicrin Application Sizes Using Chloropicrin-Only Formulations [a]

Year	N [b]	Acres Treated (Percentile) [c]						
		10th	25th	50th	75th	90th	95th	100th [d]
2004	237	2.0	6.5	15.9	28.0	70.0	87.2	255
2005	281	2.4	5.0	12.0	23.8	46.0	80.0	155
2006	221	2.5	5.0	13.0	27.0	48.0	73.7	265
2007	220	2.3	7.8	15.5	33.0	77.0	110	263
2008	222	3.6	9.0	19.0	36.8	71.9	89.4	228
CV [e]		23%	26%	18%	17%	23%	16%	20%
5-year mean [f]	5	2.6	6.7	15.1	29.7	62.6	88.1	233
5-year aggregate [g]	1,181	2.4	6.2	14.4	30.0	60.0	89.0	265

[a] Applications in California, reported as acres treated, using products containing 94 – 100% chloropicrin (DPR, 2010a; queried on multiple dates between January 29, 2009 and November 8, 2010).
[b] Number of applications reported in each year, and number of observations used in statistics.
[c] Calculated with PERCENTILE function in Microsoft Excel.
[d] Application sizes above 120 acres or so are likely to have spanned multiple days. Some smaller applications might also have occurred over multiple days.
[e] Coefficient of variation in percentiles across 5 years (i.e., CV on 5-year mean).
[f] Mean of the five percentile values shown above.
[g] Percentiles of all 5 years grouped into a single data set.

Over the 5-year interval, the 50th percentile of application sizes ranged between 12.0 and 19.0 acres. When the data from all five years were considered together, the median application size was 14.4 acres. The 50th percentile estimate for exposure assessment was assumed to be 15 acres, slightly higher than the 5-year median but within the range of the medians for individual years.

Percentile application rates reported in Table A4-2 showed greater variability than application sizes in Table A4-1 at both the 50th and 100th percentiles. The 50th percentile of application rates ranged between 111 and 188 lbs AI/acre. The high end of this range was selected as the 50th percentile, and rounded to 190 lbs AI/acre.

Table A4-2. Chloropicrin Application Rates Using Chloropicrin-Only Formulations [a]

Year	N [b]	Application Rate in Lbs AI/Acre (Percentile) [c]						
		10th	25th	50th	75th	90th	95th	100th
2004	237	49.9	75.2	148	200	205	212	372
2005	281	21.0	59.4	111	188	204	218	398
2006	221	5.4	45.5	113	168	198	200	255
2007	220	51.5	75.2	149	188	199	203	498
2008	222	60.8	103	188	198	200	213	749
CV [d]		62%	31%	22%	7%	2%	4%	41%
5-year mean [e]	5	37.7	71.1	142	188	201	209	454
5-year aggregate [f]	1,181	39.6	69.0	141	197	201	209	749

[a] Applications in California, reported as acres treated, using products containing 94 – 100% chloropicrin (DPR, 2010a; queried on multiple dates between January 29, 2009 and November 8, 2010). Application rates are in pounds chloropicrin per acre.
[b] Number of applications reported in each year, and number of observations used in statistics.
[c] Application rates reported in pounds active ingredient per acre (lbs AI/acre), calculated with PERCENTILE function in Microsoft Excel.
[d] Coefficient of variation in percentiles across 5 years (i.e., CV on 5-year mean).
[e] Mean of the five percentile values shown above.
[f] Percentiles of all 5 years grouped into a single data set.

Applications reported in the PUR do not include information about whether they are broadcast or bedded, or whether they are tarped or non-tarped. Furthermore, sizes of bedded applications might be reported as bedded acres, or as the entire field including beds and furrows; possibly some bedded applications are reported each way. Because of these limitations, it is not possible to estimate application rates at a particular (e.g., 50th) percentile for individual application methods.

In conclusion, the 50th percentile application size is assumed to be 15 acres and the 50th percentile effective broadcast application rate is assumed to be 190 lbs AI/acre. These values were used for seasonal, annual, and lifetime exposure estimates for all soil fumigation scenarios, regardless of application method.

APPENDIX 5. EXPOSURES ASSOCIATED WITH USE OF METHYL BROMIDE 99.5%

Structural Fumigation

Only one methyl bromide product has directions for structural fumigation, Methyl Bromide 99.5%. Estimates of bystander exposure to chloropicrin associated with use of this product is given in table A5-1.

Table A5-1. Estimated Bystander and Reentry Exposure to Chloropicrin from Structural Fumigation with Methyl Bromide 99.5% [a]

Duration	Bystanders		Reentry	
	(µg/m^3)	(ppb)	(µg/m^3)	(ppb)
1 Hour [b]	427	63.5	5,360	796
8 Hours [c]	118	17.6	2,150	320
24 Hours [d]	87.0	12.9	2,030	302

[a] Exposure estimates were based on the highest off-site concentrations measured during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent (Barnekow and Byrne, 2006). Concentrations were measured in Ventura County during the fumigation of a structure with an estimated fumigation volume of about 32,000 ft^3 (900 m^3), and were corrected for 62.7% field spike recovery and adjusted to the maximum application rate for Methyl Bromide 99.5% by multiplying by 0.01875/0.0107 = 1.75.

[b] The 1-hour exposure was based on the air concentration during the 1-hour sample.

[c] The 8-hour exposure was based on the time-weighted average of consecutive concentrations. Calculations shown in Table 18.

[d] The 24-hour exposure is based on the average of consecutive concentrations.

Table A5-2 summarizes estimates for occupational exposures to chloropicrin associated with structural fumigation with Methyl Bromide 99.5%. The maximum application rate for Methyl Bromide 99.5% is 3.75 lbs/1,000 ft^3, which corresponds to a rate of 0.01875 pounds chloropicrin per 1,000 ft^3 (0.000301 kg/m^3).

Table A5-2. Occupational Exposure to Chloropicrin During and Following Structural Fumigation with Methyl Bromide 99.5% [a]

Scenario	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal (ppb)	Annual [c] (ppb)	Lifetime [d] (ppb)
Application					
• Applicator [e]	8.18	NA [g]	NA	NA	NA
Aeration					
• Tarp Remover	76.5	76.5	27.7	13.6	7.28
• Aerator [h]	1,330[f]	NA	NA	NA	NA
Overall					
• Fumigator [i]	1,330[f]	225	25.5	13.7	7.30
Reentry					
• Reentry	215[f]	215[f]	62.8	31.0	16.5

[a] See Appendix 1 for detail about activities. Estimates based on exposure monitoring data from Maddy *et al.* (1986) and Barnekow and Byrne (2006), adjusted for differences in application rate used in studies and maximum application rate for Methyl Bromide 99.5% by multiplying by 0.01875/0.0107 = 1.75.
[b] Short-term concentrations are the highest realistic exposure estimates and cover intervals from 1 hour to 1 week.
[c] Assumes 180 days/year for tarp removers and 196 days/year for fumigators. Annual average concentrations are as follows: Seasonal concentration x (number of days per year/365 days).
[d] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).
[e] Applicator introduces fumigant from outside tarp (chloropicrin is mixed with methyl bromide in this product).
[f] Chloropicrin product labels specify that handlers are required to wear a respirator anytime the air concentration of chloropicrin exceeds 100 ppb (672.5 µg/m^3).
[g] NA = not applicable. Activity is done for less than a full workday before worker moves on to other activities.
[h] Aerator enters home after tarps are removed and verifies that methyl bromide concentrations are below required concentrations to allow reentry without respiratory protection. This clearance testing takes approximately 10 minutes per day before worker moves on to other activities.
[i] Fumigators are licensed and certified to apply pesticides and to monitor aeration. They may perform tarp removal and other activities in addition to their certified/licensed activities.

Enclosed Space Fumigation

One methyl bromide product containing 0.5% chloropicrin (Methyl Bromide 99.5%) has instructions for space fumigation. The maximum application rate for this product is 3.75 pounds per 1,000 cubic feet, corresponding to a chloropicrin application rate of 0.01875 lbs/1,000 ft^3. Using simple units conversions (453,592,370 µg/lb and 35.315 ft^3/m^3), this rate corresponds to a maximum chloropicrin concentration during treatment of 4,325,026 µg/m^3 (643,131 ppb). Table A5-3 summarizes screening exposure estimates for bystanders to enclosed space fumigation. In the absence of data specific to enclosed space fumigation, estimates were based on data from Barnekow and Byrne (2006), adjusted for maximum application rate (0.01875 lbs/1,000 ft^3 and an estimated building size of 300,000 ft^3 (8,500 m^3), based on information from the University of California County Extension (Stoddard *et al.*, 2006; Stoddard, 2009).

Enclosed space fumigation occurs between crops, and annual exposures were estimated assuming exposure of two days per year (assuming two crops per year). No seasonal exposures are anticipated: less than one week is considered a short-term exposure. Lifetime exposures assume average annual exposures occur each year over a lifetime for residential bystanders residing at the same location.

Table A5-3. Estimated Exposure of Bystanders to Chloropicrin from Enclosed Space Fumigation with Methyl Bromide 99.5% [a]

Duration	Concentration (µg/m^3)	Concentration (ppb)
1 Hour [b]	4,410	656
8 Hours [c]	1,220	182
24 Hours [d]	898	134
Annual [e]	4.92	0.732
Lifetime [f]	4.92	0.732

[a] Exposure estimates were based on the highest off-site concentrations measured during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent (Barnekow and Byrne, 2006). Concentrations were corrected for 62.7% field spike recovery and multiplied by 18.025 because the amount of chloropicrin used in monitoring study (1 oz/10,000 ft^3) was below the maximum allowed for fumigating enclosed spaces of 0.01875 pounds per 1,000 ft^3, and the structure monitored by Barnekow and Byrne (2006) was 32,000 ft^3 (900 m^3), vs. size of 330,000 ft^3 (9,300 m^3) for the largest potato warehouses used in California (Stoddard *et al*., 2006; Stoddard, 2009).
[b] The 1-hour exposure was based on the air concentration during the 1-hour sample.
[c] The 8-hour exposure was based on the time-weighted average of the consecutive concentrations. Calculations shown in Table 15.
[d] The 24-hour exposure is based on the average of consecutive concentrations.
[e] Annual average concentrations calculated as follows: 24-hour concentration x (2 days/365 days).
[f] Lifetime concentrations assume average annual exposures occur each year over a lifetime for residential bystanders residing at the same location.

No exposure monitoring data are available for individuals fumigating spaces with chloropicrin. In the absence of data specific to enclosed space fumigation, estimates were based on data from Table 45. Space fumigation is assumed to involve activities similar to structural fumigation with either of these products, and the same scenarios are used. Occupational exposures associated with space fumigation can be estimated based on exposure monitoring data from Maddy *et al.* (1986) and Barnekow and Byrne (2006), adjusting for differences in application rate used in the studies and the maximum application rate for Methyl Bromide 99.5% by multiplying by 0.01875/0.0107 = 1.75. The applicator introduces the Methyl Bromide 99.5% fumigant from outside the tarped space to be fumigated; chloropicrin is mixed with methyl bromide in this product. Applicator exposure was calculated by multiplying 1.75 times 4.67 ppb, highest concentration reported by Barnekow and Byrne (2006) outside a house during first 2-hour interval after start of fumigation. 1.75 x 4.67 ppb = 8.17 ppb.

Occupational exposures associated with space fumigation are summarized in Table A5-4. Enclosed space fumigation occurs between crops, and annual exposures were estimated assuming exposure of two days per year (assuming two crops per year). No seasonal exposures are anticipated: less than one week is considered a short-term exposure. Lifetime exposures assume average annual exposures occur each year over a worker's lifetime, which is assumed to be 40 years.

Table A5-4. Estimates for Occupational Handler Exposure to Chloropicrin During and Following Space Fumigations with Chloropicrin as a Warning Agent [a]

Scenario	1-hour [b] (ppb)	8-hour [b] (ppb)	Seasonal [c] (ppb)	Annual [d] (ppb)	Lifetime [e] (ppb)
Application					
• Applicator [f]	8.17	NA [g]	NA	NA	NA
Aeration					
• Tarp Remover	135	135	NA	0.268	0.143
• Aerator [h]	1,330	NA	NA	NA	NA
Overall					
• Fumigator [i]	1,330	328	NA	0.228	0.122
Reentry					
• Reentry	215	215	NA	0.344	0.184

[a] Tarp remover exposure estimates were based on data from Maddy *et al.* (1986). Aerator and fumigator estimates were based on data from both Maddy *et al.* (1986) and Barnekow and Byrne (2006). Applicator and reentry exposure estimates were based on data from Barnekow and Byrne (2006). Estimates were adjusted for differences in application rate used in studies and maximum application rate for Methyl Bromide 99.5% by multiplying by 0.01875/0.0107 = 1.75.

[b] Short-term concentrations are the highest realistic exposure estimates and cover intervals from 1 hour to 1 week.

[c] Seasonal exposures are average estimates that cover intervals from 1 week up to 1 year. As enclosed space fumigation occurs between crops, and two crops are assumed each year, exposures are estimated to last 2 days per year. Thus, no exposure durations between 1 week and 1 year are anticipated.

[d] Assumes 2 days/year. Annual exposure = average concentration x (2 days per year/365 days).

[e] Lifetime exposure = annual exposure x (40 years of work in a lifetime)/(75 years in a lifetime).

[f] Applicator introduces fumigant from outside tarp (chloropicrin is mixed with methyl bromide).

[g] NA = not applicable. Activity is done for less than a full workday before worker moves on to other activities.

[h] Aerator enters structure after tarps are removed and verifies that methyl bromide concentrations are below required concentrations to allow reentry without respiratory protection. This clearance testing takes approximately 10 minutes per day before worker moves on to other activities.

[i] Fumigators are licensed and certified to apply pesticides and to monitor aeration. They may perform tarp removal and other activities in addition to their certified/licensed activities.

APPENDIX 6. EARLIEST ALLOWED POST-APPLICATION INTERVALS AND DAYS MONITORED

Table A6-1 summarizes post-application intervals when Beard *et al.* (1996) and Rotondaro (2004) monitored aeration and reentry scenarios. For broadcast application, tarp splitters were monitored 5 – 6 days post-application, and tarp removers were monitored 6 – 7 days post-application. Most soil shapers were monitored at 10 days post-application, with the exception of one worker in Washington, who was monitored 11 days post-application.

Table A6-1. Activity Intervals Following Chloropicrin Applications When Occupational Exposure Monitoring Was Conducted

Study [a]	Application Method	Minimum Interval (Days)		
		Tarps Cut (Post-Application)	Tarps Removed (Post-Cut)	Reentry (soil shaping after broadcast, pipe laying after bedded)
B & R	Broadcast Tarped Shallow	5 to 6	1	4 – post-tarp removal [b]
R	Broadcast Non-Tarped Shallow	Not Applicable		10 – post-application
R	Broadcast Non-Tarped Deep	Not Applicable		10 – post-application
B & R	Bedded Tarped Shallow	Tarps punched at 6 to 7 days		No reentry monitoring
R	Bedded Non-Tarped Shallow	Not Applicable		6 to 7 – post-application
R	Chemigation	Tarps punched at 5 to 10 days		No reentry monitoring

[a] Aeration and post-application monitoring conducted by: B = Beard *et al.* (1996) and/or R = Rotondaro (2004). Monitoring of handlers during application is not included here.
[b] Total number of days post-application =10 or 11 days.

Following broadcast non-tarped applications, soil shapers were monitored at 10 days post-application. With tarped bedded applications, tarp punchers were monitored after 6 – 7 days. Following bedded non-tarped applications, pipe layers were monitored at 6 – 7 days post-application. Finally, tarp punchers were monitored 5 – 10 days after chemigation applications.

Current labels on chloropicrin-only products allow several of these activities on earlier post-application days, as shown in Table A6-2. Chloropicrin product labels allow tarps to be split, punched, or removed after a minimum of 120 hours (5 days), and reentry only after 10 to 14 days for activities disturbing treated soil. Soil shaping is an activity that disturbs soil, and was assumed to occur at 10 days post-application. In contrast, pipe laying can be accomplished with minimal disturbance of soil and was assumed to occur 5 days post-application.

Table A6-2. Minimum Activity Intervals Following Chloropicrin Applications Allowed by Chloropicrin Product Labels [a]

EPA Reg. No.	Product Name	Minimum Interval (Days)	
		Tarps Split or Removed (Post-Application) [b]	Leave Soil Undisturbed [c]
8622-43-AA	Metapicrin	5	14
66330-47-ZA	Nutrapic	5	14
8536-2-ZA	Chloropicrin 100 Fumigant	5	10 to 14
58266-2-AA-11220	Tri-Clor	5	10 to 14
58266-2-AA	Tri-Clor	5	10 to 14
58266-5-AA-11220	Tri-Clor EC Fumigant	5	14
58266-5-AA	Tri-Clor EC Fumigant	5	14
58266-6-AA-11220	Pic Plus Fumigant	5	10 to 14

[a] Products containing 94 – 100% chloropicrin. The California Code of Regulation Title 3, Section 6447.3 does not limit activities following soil fumigation with chloropicrin-only formulations.
[b] Chloropicrin product labels do not allow tarp splitting, punching, or removal for 120 hours post-application, other than for an emergency (e.g., high winds that have damaged the tarp, or flooding). Tarp removal is allowed a minimum of 2 hours after splitting.
[c] Reentry activities disturbing the soil, such as soil shaping, are assumed to occur no earlier than 10 days post-application; other activities, such as pipe laying do not necessarily disturb soil and are assumed to occur on or after 5 days post-application.

Exposure estimates for chloropicrin in methyl bromide formulations are affected by California regulation, as summarized in Table A6-3. Tarp punching and splitting are not allowed within 5 days post-application, which is equal to or shorter than the intervals for individuals monitored by Beard *et al.* (1996) and Rotondaro (2004). Also, tarp removal intervals are equal to or shorter than the intervals in the monitoring studies.

Reentry intervals following non-tarped applications monitored in the study (6 – 7 days for bedded and 10 days for broadcast applications) were longer than the 3 and 4 days, respectively, required by regulation. However, current labels approved prohibit reentry for a minimum of 120 hours (5 days) following soil fumigation. Monitoring of reentry following other application methods occurred at or before earliest allowed reentry.

Table A6-3. Minimum Activity Intervals Following Methyl Bromide Field Fumigation Allowed by California Regulation (3 CCR 6447.3) [a]

Method Number	Method Name	Minimum Interval (Days)		
		Tarps Cut (Post-Application)	Tarps Removed (Post-Cut)	REI – Soil Shall Not Be Disturbed Post-Application
1	Bedded Non-Tarped Shallow	Not Applicable		3 [b]
2	Broadcast Non-Tarped Deep	Not Applicable		4 [b]
3	Broadcast Tarped Shallow	5	1	6 [c]
4	Bedded Tarped Shallow	5	1	6 [d]
5	Broadcast Tarped Deep	5	1	6 [c]
6	Drip, Hot Gas	5	1	6 [c]

[a] The California Code of Regulation Title 3, Section 6447.3 specifies six methods for field fumigation with methyl bromide and the maximum amount of methyl bromide to be applied, along with other method-specific restrictions. Certain types of fumigation, including tree replant, are excluded from the definition of "field fumigation."

[b] The restriction for bedded non-tarped shallow applications is stated as follows at 3 CCR 6447.3(a)(1)(F): "The soil shall not be disturbed for at least three days (72 hours) following completion of injection to the application block." The restriction is similarly stated at 3 CCR 6447.3(a)(2)(G) for broadcast non-tarped deep, except that the soil is to be undisturbed for 4 days (96 hours). The restricted entry intervals (REI) for the two application methods are 3 and 4 days, respectively (i.e., equal to the amount of time the soil is to be undisturbed). Product labels, however, prohibit reentry for 5 days post-application.

[c] The restriction for broadcast tarped shallow is stated as follows, "The tarpaulin shall not be cut until a minimum of five days (120 hours) following completion of injection to the application block. The tarpaulin shall be cut pursuant to section 6784(b)(4). (G) Tarpaulin removal shall begin no sooner than 24 hours after tarpaulin cutting has been completed. (H) The application block restricted entry interval shall end at completion of tarpaulin removal, and shall be at least six days."

[d] Bedded tarped applications also contain tarp "cut" intervals, followed by instructions in case tarps are removed before planting: "E) The tarpaulin shall not be cut until at least five days (120 hours) following completion of injection to the application block. (F) If tarpaulins are removed before planting, tarpaulin removal shall begin no sooner than 24 hours after tarpaulin cutting has been completed. The application block restricted-entry interval shall end at completion of tarpaulin removal, and shall be at least six days. (G) If tarpaulins are not to be removed before planting, the application block restricted-entry interval shall either: 1. consist of the five-day period described in subsection (E) plus an additional 48 hours after holes have been cut for planting, or 2. be at least 14 days. If this option is chosen, the methyl bromide air concentration underneath the tarpaulin must test less than five parts per million before planting begins." From this, it appears that the tarp cutting in this regulation also includes tarp punching.

Table A6-4 summarizes when aeration and reentry scenarios were monitored, and when the activities can legally occur in California. For activities that can occur earlier than when exposure monitoring was conducted, exposures are potentially underestimated. These scenarios are marked in bold in Table A6-4.

Table A6-4. Post-Application Days When Aeration and Reentry Scenarios Were Monitored and Earliest Allowed Reentry [a]

Scenario	Monitored [b]	Chloropicrin 100% [c]	Chloropicrin 60% [d]	Chloropicrin 66.6% [e]	Chloropicrin 10.5% [e]	Chloropicrin 2% [e]
Broadcast Tarp						
• Tarp Splitter	5 – 6 [f]	**5**	**5**	**5**	**5**	**5**
• Tarp Remover	7	**5**	**5**	**5**	**5**	**5**
• Soil Shaper	10 – 11	**10**	**7**	**6**	**6**	**6**
Broadcast NT						
• Soil Shaper	10	**10**	**7**	**5**	**5**	**5**
Bedded Tarped						
• Tarp Puncher	6 – 7	**5**	**5**	**5**	**5**	**5**
Bedded NT						
• Pipe Layer	6 – 7	**5**	**5**	**5**	**5**	5
Chemigation						
• Tarp Puncher	5 – 10 [g]	**5**	**5**	**5**	**5**	**5**

[a] Bold: activity can occur earlier than when monitoring by Beard *et al.* (1996) and Rotondaro (2004) was done.
[b] Number of days post-application when activity was monitored.
[c] Number of days post-application when activity can legally occur, based on current chloropicrin-containing product labels approved in California.
[d] Number of days post-application when activity can legally occur, based on current labels for products containing mixtures of 1,3-dichloropropene and chloropicrin; 60% is the most chloropicrin in these mixtures.
[e] Number of days post-application when activity can legally occur, according to current methyl bromide product labels and California regulation of soil fumigation with methyl bromide (California Code of Regulation Title 3, Section 6447.3). Chloropicrin percentages in the three categories of formulations are the highest for chloropicrin use as an active ingredient (66.6%), in the product Methyl Bromide 89.5%, containing an elevated chloropicrin concentration for a warning agent (10.5%), and for chloropicrin as a warning agent (2%).
[f] All tarp splitters monitored at 5 days post-application, except one replicate in Washington who was monitored at 6 days.
[g] One tarp puncher was monitored at 5 days post-application, and two were monitored at 10 days.

To estimate aerator and reentry worker exposures on the earliest allowed days, the ratio of chloropicrin flux on the post-application day monitored to earliest post-application day when activity can legally occur was calculated. Ratios were of flux, expressed as percent lost of application rate, over 12-hour intervals, on days of interest (Personal communication, Dr. Terrell Barry, May 4, 2010). Valid comparisons necessitated using equivalent time intervals. Both Beard et al. (1996) and Rotondaro (2004) monitored flux over 12-hour intervals with the exception of the first few days, when the intervals were 6 hours. For these early intervals, time-weighted averages of consecutive 6-hour results were used to get 12-hour estimate. Calculations are summarized in Beauvais (2010b).

Flux ratios during daytime 12-hour monitoring intervals were determined, based on the assumption that activities are likely done in daytime (though labels do not restrict aeration and reentry to daytime). These ratios are summarized in Table A6-5.

Table A6-5. Adjustment for Short-Term Aeration and Reentry Scenarios for Earliest Allowed Reentry [a]

Scenario	Chloropicrin 100% [b]	Chloropicrin 60% [c]	Chloropicrin 66.6% [d]	Chloropicrin 10.5% [d]	Chloropicrin 2% [d]
Broadcast Tarp					
• Tarp Splitter	4.7 (5, 6)	4.7 (5, 6)	4.7 (5, 6)	4.7 (5, 6)	4.7 (5, 6)
• Tarp Remover	4.5 (5, 7)	4.5 (5, 7)	4.5 (5, 7)	4.5 (5, 7)	4.5 (5, 7)
• Soil Shaper	1 [e] (10,11)	2.6 [f] (7, 11)	2.5 (6, 11)	2.5 (6, 11)	2.5 (6, 11)
Broadcast NT					
• Soil Shaper	1 (10, 10)	6.0 (7, 10)	44 (5, 10)	44 (5, 10)	44 (5, 10)
Bedded Tarped					
• Tarp Puncher	4.8 (5, 7)	4.8 (5, 7)	4.8 (5, 7)	4.8 (5, 7)	4.8 (5, 7)
Bedded NT					
• Pipe Layer	1 [eg] (5, 7)	1 [eg] (5, 7)	1 [eg] (5, 7)	1 [eg] (5, 7)	1 [eg] (5, 7)
Chemigation					
• Tarp Puncher	1 [e] (5, 10)	1 [e] (5, 10)	1 [e] (5, 10)	1 [e] (5, 10)	1 [e] (5, 10)

[a] Adjustments are ratios of flux (reported as percent loss) on earliest post-application day when activity is allowed to post-application day when activity was monitored (days are in parentheses after each value).
[b] Based on current chloropicrin-containing product labels approved in California.
[c] Based on current labels for products containing mixtures of 1,3-dichloropropene and chloropicrin; 60% is the most chloropicrin in these mixtures.
[d] According to current methyl bromide product labels and California regulation of soil fumigation with methyl bromide (California Code of Regulation Title 3, Section 6447.3). Chloropicrin percentages in the three categories of formulations are the highest for chloropicrin use as an active ingredient (66.6%), in the product Methyl Bromide 89.5%, containing an elevated chloropicrin concentration for a warning agent (10.5%), and for chloropicrin as a warning agent (2%).
[e] Flux ratio is less than or equal to one, and adjustment was set to one.
[f] The flux for broadcast non-tarped applications was higher on post-application day 7 than day 6.
[g] The daytime 12-hour mass loss on both Day 5 and Day 7 was zero; these values were adjusted to 0.01% (lowest reported percent loss in study) for ratio calculation.

APPENDIX 7. SAMPLE CALCULATION OF 95TH PERCENTILE CONCENTRATION

For short-term exposures, DPR estimates the highest exposure an individual may realistically experience during or following legal chloropicrin uses. In order to estimate this upper bound of short-term exposure, DPR generally uses the estimated population 95th percentile of daily exposure, assuming daily exposures have a lognormal distribution:

$$95^{th}\text{ percentile} = \exp\left\{\hat{\mu} + 1.645 \cdot \hat{\sigma}_P\right\}$$

where $\hat{\mu}$ and $\hat{\sigma}_p$ stand for the arithmetic mean and arithmetic standard deviation of the natural (base e) logarithms of measured daily exposure, and 1.645 is the value corresponding to the 95th percentile of the standard normal distribution (often called a Z value). The arithmetic standard deviation used in this formula is the "population" standard deviation, calculated by dividing the sum of squared deviations by N. The population standard deviation is calculated as:

$$\hat{\sigma}_P = \sqrt{\frac{\sum_{i=1}^{n}(Y_i - \bar{Y})^2}{n}}$$

where Yi is the natural logarithm of an exposure value. This is obtained in Excel by applying the STDEVP function to the natural logarithms of exposure

The 95th percentile concentration estimates were calculated in Excel. First the natural logarithm (ln) was calculated for each concentration value using the LN function; the arithmetic mean and population standard deviation were then calculated for the natural logarithms. The NORMSINV function, with a probability of 0.95, was used to get the inverse of the standard normal cumulative distribution, which was multiplied by the population standard deviation of lns. This result was added to the arithmetic mean of lns, and the sum taken as the power of e with the EXP function. The entire Excel formula is:

= EXP(AVERAGE(lns) + NORMSINV(0.95)*STDEVP(lns)).

A sample calculation is shown in Table A7-1.

Table A7-1. Sample Calculation of 95th Percentile Concentrations [a]

Table in Memo [b]	Rate Adjustment Factor [c]	Minutes	Concentration (µg/m^3)	Adjusted (µg/m^3) [d]	ln (µg/m^3) [e]	Concentration (ppb)	Adjusted (ppb) [d]	ln (ppb) [e]
Table 6	2.92	215	41.6	122	4.801	6.19	18.1	2.896
Table 6	2.92	137	42.9	125	4.832	6.38	18.7	2.923
Table 19	2.62	260	112	293	5.681	16.7	43.7	3.775
Table 19	2.96	243	13.2	39.0	3.665	1.96	5.80	1.759
Table 19	2.87	245	42.7	123	4.810	6.35	18.2	2.904
Table 19	2.87	245	74.6	214	5.368	11.1	31.9	3.462
Mean		224		153	4.86		22.7	2.95
Standard Deviation		41		80.7	0.628		12.0	0.628
95th Percentile:				**362**			**53.9**	

Assuming lognormal distribution, 95th percentile is calculated in Excel as follows [f]:

EXP(AVERAGE(lns)+NORMSINV(0.95)*STDEVP(lns))

Stepwise calculations (shown to clarify the above equation):

(1)	NORMSINV(0.95) = 1.645	NORMSINV(0.95) = 1.645
(2)	(4.859 + (1.645)(0.6280)) = 5.892	(2.954 + (1.645)(0.6280)) = 3.987
(3)	$e^{5\ 892} = 362$	$e^{3\ 987} = 53.9$

[a] Calculations shown for soil sealer involved in shallow broadcast non-tarped chloropicrin applications. Data from Beard *et al.* (1996) and Rotondaro (2004).

[b] Data for individual replicates are summarized in the indicated tables in Beauvais (2010b).

[c] Ratio of the maximum allowed application rate to rate used in the monitored application.

[d] Concentrations were adjusted by multiplying them by the rate adjustment factor.

[e] This column lists the natural logarithm of the adjusted concentrations, which are used to calculated the 95th percentile concentration.

[f] In this equation, the abbreviation "lns" means the natural logarithms of adjusted concentrations. Four Excel functions are used. EXP gives the constant e raised to the power of the specified number (e equals 2.71828182845904; it is the base of the natural logarithm). AVERAGE gives the arithmetic mean. STDEVP gives the population arithmetic standard deviation. NORMSINV gives the inverse of the cumulative standard normal distribution (which has a mean of zero and a standard deviation of one). Given a value for probability, here 0.95, NORMSINV finds that value z such that NORMSDIST(z) = probability (Microsoft, 2003).