HUMAN EXPOSURE ASSESSMENT FOR ALLYL ISOTHIOCYANATE AS SOIL FUMIGANT

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ACRONYM

1,3-D	1,3-dichloropropene
AADD	Annual average daily dose
AITC	Allyl isothiocyanate
CalPIP	California Pesticide Information Portal
CalPIQ	California Pesticide Illness Query
DPR	California Department of Pesticide Regulation
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
ISAGRO	ISAGRO USA, Inc
Kow	Octanol-water partitioning coefficient
LADD	Life-time average daily dose
NRC	National Research Council
PC code	Pesticide chemical code
PE	Polyethylene
Pic	Chloropicrin
PPE	Personal protective equipment
REI	Restricted entry interval
MITC	Methyl isothiocyanate
MITC-K	Metam-potassium
MITC-Na	Metam-sodium
PISP	Pesticide Illness Surveillance Program
PUR	Pesticide use reporting
SADD	Seasonal average daily dose
STADD	Short-term absorbed daily dose
TIF	Totally impermeable film
US EPA	U.S. Environmental Protection Agency

I. EXECUTIVE SUMMARY

ISAGRO USA, Inc (ISAGRO) submitted one product label to the California Department of Pesticide Regulation (DPR) to register allyl isothiocyanate (AITC) for use as soil fumigant. As fumigant use of AITC has not been permitted in California, there is no use data available or human illness cases recorded. The primary exposure route is through inhalation.

Listed below are ranges of handler, re-entry worker, occupational and residential bystander exposures for short-term, seasonal, annual and life-time exposure scenarios:

- The estimated short-term absorbed daily doses (STADDs) for handlers range from 8 µg/kg/d for applicators in drip application to 1321 µg/kg/d for loaders in broadcast shallow and deep shank applications;
- The estimated seasonal average daily doses (SADDs) for handlers range from 1 µg/kg/d for applicators in bed/strip shallow shank application to 254 µg/kg/d for loaders in broadcast shallow and deep shank applications;
- The annual average daily dose (AADDs) for handlers range from 0.2 µg/kg/d for applicators in bed/strip shallow shank application to 66 µg/kg/d for loaders in broadcast shallow shank application;
- The life-time average daily dose (LADDs) for handlers range from 0.1 µg/kg/d for applicators in bed/strip shallow shank and drip applications to 35 µg/kg/d for loaders in broadcast shallow shank application;
- The STADDs for re-entry workers range from 22 µg/kg/d for bed/strip shallow shank and drip applications to 30 µg/kg/d for broadcast shallow and deep shank applications;
- The SADDs for re-entry workers range from 8 µg/kg/d for bed/strip shallow shank application to 26µg/kg/d for broadcast shallow and deep shank applications;
- The AADDs for re-entry workers range from 1 µg/kg/d for bed/strip shallow shank application to 10 µg/kg/d for broadcast deep shank application;
- The LADDs for re-entry workers range from 1 µg/kg/d for bed/strip shallow shank and drip applications to 5 µg/kg/d for broadcast deep shank application;
- The STADDs for occupational bystanders at the edge of a 40 ac treated field range from 175 µg/kg/d for the field using shallow shank application and tarp-covered to 2391 µg/kg/d for the field using drip application without tarp cover;
- The STADDs for residential adult bystanders at 25 ft away from a 40 ac treated field range from 98 µg/kg/d for the field using shallow shank application and tarp-covered to 1335 µg/kg/d for the field using drip application without tarp cover;
- The STADDs for residential child bystanders at 25 ft away from a 40 ac treated field range from 238 µg/kg/d for the field using shallow shank application and tarp-covered to 3169 µg/kg/d for the field using drip application without tarp cover.

- Due to the lack of both use and ambient air monitoring data, SADDs, AADDs and LADDs of occupational and residential bystander exposures to AITC were not estimated in this assessment.

II. INTRODUCTION

The California Department of Pesticide Regulation (DPR) received an application from ISAGRO USA, Inc (ISAGRO) to allow one product containing allyl isothiocyanate (AITC) for use in California. The product name is Dominus® and the AITC content is 96.3% (EPA Reg. No. 89285-2, December 28, 2015; https://www3.epa.gov/pesticides/chem_search/ppls/089285-00002-20151228.pdf). This section provides background information of AITC and its current regulation status with both the U.S. Environmental Protection Agency (US EPA) and DPR.

A. AITC and the submitted product

The chemical structure of AITC is shown in Figure 1, together with some key physiochemical properties (Jones, 2013). At room temperature, AITC is liquid with very pungent odor.

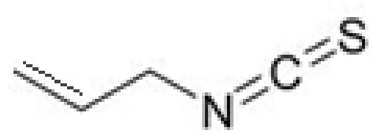


Figure 1. Chemical structure of AITC

- CAS No.: 56-06-7
- Molecular formula: C_4H_5NS
- Molecular weight: 99.2 g/mol
- Relative density: 1.0
- Boiling point: 148-154 °C
- Vapor pressure: 0.493 kPa at 20 °C
- Henry's Law constant: 3.7 x 10^{-5} Pa/m^3/mol
- Solubility (g/L, 20ºC): 2 in distilled water, 545.9 in acetone, 3.0 in toluene

Based on the product label, the proposed use of Dominus® is a pre-plant soil fumigant to control various nematodes, fungi, insects and weeds. In addition, Dominus® may be used in post-plant crop termination application. The product can be applied via broadcast shank or bed/strip shank applications, or through drip irrigation (i.e., chemigation).

III. FACTORS CONSIDERED TO DEVELOP EXPOSURE SCENARIOS

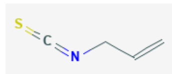
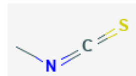
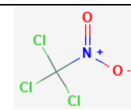
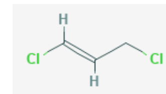
National Research Council (NRC) recommends DPR include a problem formulation/scoping step in the risk assessment process. NRC envisions the problem formulation as a phase to determine "*the major factors to be considered, the decision-making context, and the timeline and depth needed to ensure that the right questions are being asked in the context of the assessment*" (NRC, 2009). NRC suggested DPR that "*risk managers should be consulted in the problem-formulation stage so that a risk assessment can be designed to address the decisions that need to be made by managers and other stakeholders. Consideration should be given to whether a general set of problems and risk-management options could be formulated to use as a starting point in problem formulation*" (NRC, 2015).

DPR accepted this recommendation and during the problem formulation phase, reviewed exposure information and data relevant to AITC, especially the California-specific data (DPR, 2018). This section describes factors considered in the development of the exposure scenarios of AITC. Due to scarcity of AITC-specific data, this assessment used data from various sources including those from other soil fumigants (i.e., surrogates). The rationale for selecting these surrogates is explained below.

A. Physiochemical properties

The chemical structure of AITC is similar to methyl isothiocyanate (MITC), which is a soil fumigant produced from metam-sodium (MITC-Na) or metam-potassium (MITC-K). Table 1 compared some key physiochemical properties of AITC with MITC and two other fumigants commonly used in California: chloropicrin (Pic) and 1,3-dichloropropene (1,3-D). Both MITC and AITC are liquid at room temperature but readily volatize because of their high vapor pressure and low boiling points. AITC has lower water solubility and higher octanol-water partitioning coefficient (K_{ow}) than MITC, implying its higher potential of sorption to soil organic matter and lower transfer from soil surface to water. The water solubility and Kow values of AITC are similar to Pic and 1,3-D, indicating a similar partitioning and transport behavior among these fumigants in soil. AITC has higher boiling point and lower vapor pressure than Pic and 1,3-D, suggesting that at the soil surface, AITC may be less ready to volatize into air.

Table 1. Comparisons of physiochemical properties between allyl isothiocyanate (AITC) and other soil fumigants

Property[a]	AITC	MITC	Pic	1,3-D
Molecular formula				
Density (g/cm^3)	1.0	1.1	1.6	1.2
Molecular weight (g/mol)	99.2	73.3	164.4	111.0
Boiling point (°C)	148-154	119	112	108
Solubility in water (mg/mL)	2 (at 20 °C)	7.6 (at 20 °C)	1.9 (at 20 °C)	2 (at 20 °C)
Vapor pressure (mmHg)	3.7 (at 30°C)	3.54 (at 25°C)	24 (at 25 °C)	34 (trans), 23 (cis) (at 25 °C)
$\log K_{ow}$	2.1	0.94	2.1	2.1

a: data obtained from Jones (2013); NIH (2019);

b: AITC=allyl isothiocyanate, MITC=methyl isothiocyanate, Pic=chloropicrin, 1,3-D=1,3-dichloropropene.

B. Application method

According to the product label submitted to DPR, the application methods of AITC include shank injection and chemigation. Detailed application methods and tarp requirements are summarized in Table 2 below.

Table 2. Application method, injection depth and tarp requirement for Dominus® (EPA Registration No. 89285-2)

Application method	Injection depth (in)	Tarp	Comment
Broadcast shank	4-15	Yes	PE, VIF, TIF[a]
		No[b]	Overhead sprinkler, water cap and/or roller/packer, close chisel traces
	>17	No	Roller/packer
Bed shank or strip	4-15	Yes	PE, VIF, TIF
		No	Overhead sprinkler, water cap and/or roller/packer, close chisel traces
Drip	subsurface[c]	Yes	N/A[d]
		No	>1 in buried drip tape

a: PE=polyethylene, VIF=virtually impermeable film, TIF=totally impermeable film;
b: tarp is not necessary, if alternative methods as described in the comment column are used;
c: drip emitters are placed at shallow subsurface positions;
d: tarp materials are not specified on the product label.

C. Label precaution and PPE requirement

Pesticide labels use three signal words, i.e., Danger, Warning, or Caution, to categorize how dangerous a product may be to humans. Dominus® carries the signal word "DANGER" due to their "*corrosive*" property that "*causes irreversible eye damage and skin burns.*" Other language on product labels also include "*keep out of reach of children*" and "*…causes irreversible eye damage and skin burns. Maybe fatal if swallowed, absorbed through skin, or inhaled. Do not get in eyes, on skin or on clothing. Do not breathe vapor. Prolonged or frequently repeated skin contact may cause allergic reactions in some individuals. Wash thoroughly with soap and water after handling and before eating, drinking, chewing gum, using tobacco or using the toilet. Remove and wash contaminated clothing before use.*"

<u>Handlers.</u> Dominus® label requires personal protective equipment (PPE) for handlers "*when performing activities with the potential for liquid contact.*" The required PPE include "*coveralls*

worn over long-sleeved shirt and long pants, chemical-resistant footwear plus socks, chemical resistant gloves, protective eyewear and respirator." For tarp cutters and removers, both product labels requires "*long-sleeved shirt, long pants and gloves when removing tarps following application prior to plants*" and a minimum 5-day restricted entry interval (REI). Respirators are not required for tarp cutters and removers.

<u>Re-entry workers.</u> Dominus® label requires a minimum 5-day REI.

<u>Occupational and residential bystanders.</u> Dominus® label requires a minimum 25 feet buffer zone from "*any occupied structure, such as a school, daycare, hospital, retirement home, business or residence.*" This statement is different from US EPA's description of buffer zone, which requires "*all non-handlers including field workers, nearby residents, pedestrians, and other bystanders must be excluded from the buffer zone during the buffer zone period, except for people in transit*", and is also different from the language used on the labels of other soil fumigant products (AMVAC, 2009; US EPA, 2009; Dow AgroSciences, 2017). As occupational bystanders are not subject to this 25 ft requirement based on the Dominus® label, this assessment estimated occupational bystander exposures assuming they could be at the edge of a fumigated field. In addition, in the training materials prepared by ISAGRO for the applicators, it is suggested the application should not be within 100 ft of any "*sensitive sites*" which include "*…occupied nursing homes, hospitals, or prisons, and occupied licensed schools, state licensed day care centers (any childcare facility other than a family day care home, including infant centers, preschools, extended day care facilities and school age child care centers) playgrounds, and licensed assisted living facilities (licensed by state or local governments)*" (ISAGRO, 2015).

D. Projected AITC use in California

Use information of AITC as soil fumigant is not available as this use has not been registered in California. Based on the submitted product label, some application methods of AITC are similar to other soil fumigants that are already registered in California, including 1,3-D, Pic, methyl bromide (MeBr), MITC-Na and MITC-K. Accordingly, use data of these fumigants was obtained from DPR's pesticide use reporting (PUR) database, i.e., California Pesticide Information Portal (CalPIP), and analyzed to project potential AITC use regions (DPR, 2019).

This analysis used fumigant use data from 2012-2017[1]. In 2012-2017, the above five fumigants were used in different counties around the entire state. Seventeen counties had fumigant use >1% of total state use in any of the six years (2012-2017). These counties are located in several geological regions of California, including Central Coast (Santa Cruz, Monterey, San Luis Obispo), Central Valley (San Joaquin, Stanislaus, Merced, Fresno, Kings, Tulare, Kern, Madera), Inland Empire (Riverside, Imperial), South Coast (Santa Barbara, Ventura, Los Angeles), and the northern region (Siskiyou). Fields in these counties were fumigated for planting different crops (strawberry in Monterey *vs.* grape in Tulare), which implies the application methods can be different (shank *vs.* drip, deep *vs.* shallow injection).

Some fumigant use information, such as the application method and name of the company that performed the applications, is not available from CalPIP. Among the five soil fumigants above, 1,3-D has the highest annual use for six years (2012-2017). AGRIAN® is a proprietary pesticide-use database that includes some 1,3-D application information not available from CalPIP. Therefore, this analysis used AGRIAN 1,3-D data to collect information that is not available from CalPIP. This database has been previously used in the 1,3-D risk characterization document (DPR, 2015). Table 3 compares annual 1,3-D use recorded by CalPIP or AGRIAN and shows the similarities between their records (<7% difference).

Table 3. 1,3-Dichloropropene (1,3-D) use (lbs) recorded by CalPIP and AGRIAN from 2012 to 2018

Year	CalPIP	AGRIAN
2012	11,928,106	11,153,954
2013	12,930,424	13,188,984
2014	13,584,325	13,957,997
2015	15,689,571	15,893,927
2016	14,128,700	14,366,348
2017	12,581,936	12,584,993
2018	No data[b]	12,828,742

CalPIP records pesticide use in California by licensed applicators. CalPIP is maintained by California Department of Pesticide Regulation (DPR) and available to the public. AGRIAN database only records 1,3-D use in California and the proprietary database is not publicly available; b: pesticide use data in 2018 is not available as of November, 2020.

[1] PUR data in 2018 was not available as of November, 2020. DPR later analyzed 2018 PUR data and determined inclusion of 2018 data would not change the conclusion of this analysis.

Figure 2 shows 1,3-D use from different application methods from 2012-2018. According to AGRIAN, deep shank injection accounted for most of the 1,3-D uses (~80%) in California. However, the 1,3-D use pattern varies greatly among different counties. In central valley counties such as Fresno, Merced and Kern, 1,3-D was almost exclusively applied (>90%) via deep shank injections for deep root-zone crops such as almonds and grapes. However, for coastal counties such as Monterey, Santa Barbara and Ventura, deep shank applications were used much less and only accounted for <20% of the total 1,3-D uses. For instance, in 2018, over 80% of 1,3-D use in Santa Cruz was applied using shallow shank equipment. In San Luis Obispo and Santa Barbara, around half of 1,3-D use was applied via drip irrigation tubes.

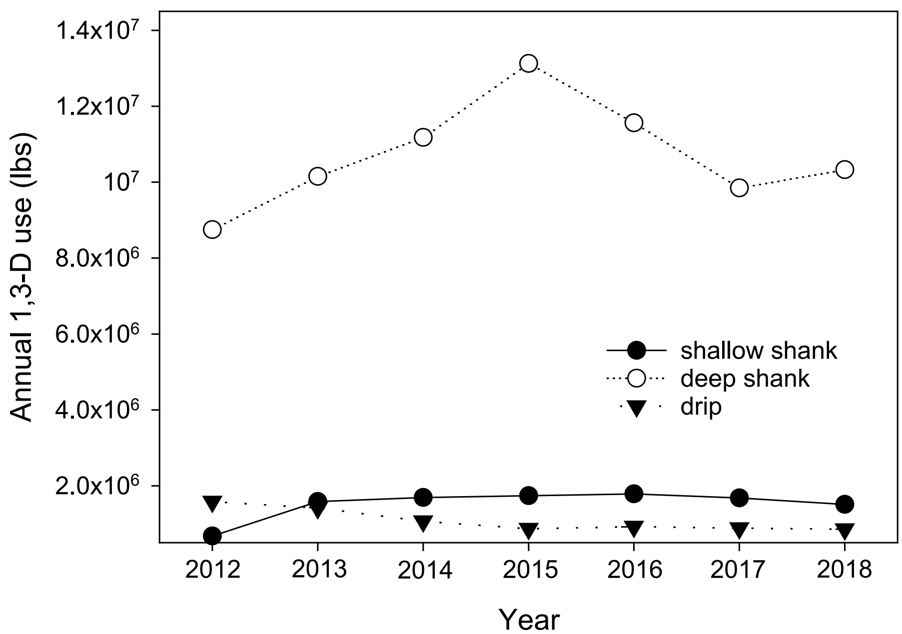


Figure 2. 1,3-Dichloropropene (1,3-D) uses from different application methods in from 2012-2018. Raw data was obtained from AGRIAN 1,3-D use database

Information needed to assess AITC intermediate- (seasonal) and long-term (annual and life-time) exposures, i.e., seasonal application rate and days of exposure per year, is summarized in Table 4. As AITC has no use data available, Table 4 is summarized based on the 1,3-D data from the AGRIAN database, assuming the use patterns (e.g., season, seasonal application rate, number of applications per year) of AITC would be similar to 1,3-D. Information in the column "Seasonal application rate (lbs/ac)", which was used to estimate intermediate-term (seasonal) exposures, was derived from the median of the application rates within the use season. Information in the column "Days of exposure in a year", which was used to estimate long-term (annual) exposures, was derived from the number of application days within a year. For handlers, both types of information were summarized from the highest-use company in the highest-use county and also assumed within one company all the applications within the same county and using the same application method were performed by the same applicator crew. For re-entry workers, information in the columns "Days of exposure in a year" and "Seasonal application rate (lbs/ac)" were summarized from the highest-use county. In contrast to handlers, re-entry workers are not likely to enter all fumigated fields within one county. Accordingly, using the number in the column "Days of exposure in a year" may overestimate the long-term exposures for re-entry workers. However, re-entry workers could enter the same fumigated field(s) multiple times within a year. Currently there is no data that tracks re-entry worker activity pattern. In the lack of activity pattern data, further refinement of the method described in Table 4 cannot be performed. It is noteworthy that 1,3-D and Pic are combined in many fumigant applications. Hence, if applicable, the total application rates of 1,3-D and Pic were combined to estimate AITC application rates because AITC is listed as the sole fumigant active ingredient in Dominus®.

Table 4. Estimated AITC seasonal and annual use information based on 1,3-D use data retrieved from AGRIAN database in 2014-2018

Application method	Bed/Strip or Broadcast	Days of exposure in a year	Seasonal application rate[a] (lbs/ac)
Handler exposure scenarios (including tarp cutter, puncher and remover)			
Shallow shank	Broadcast	95	327[b]
	Bed/Strip	61	97
Deep shank	Broadcast	75	327[b]
Drip	Bed/Strip	49	246[b]
Re-entry worker			
Shallow shank	Broadcast	95	327[b]
	Bed/Strip	61	97
Deep shank	Broadcast	142	327[b]
Drip	Bed/Strip	59	246[b]

a: for applications when chloropicrin was applied together with 1,3-dichloropropene, the application rates of both compounds were combined to represent the total application rate;
b: the estimated application rate is over AITC maximum application rate (327 lb/ac for shank application and 246 lb/ac for drip application) hence the AITC maximum application rate is used instead.

In addition to the label requirements, 1,3-D is a toxic air contaminant and a restricted material that requires a permit from the county agricultural commissioner prior to its application (DPR, 2017). However, similar regulations do not exist for AITC since it is not yet registered for use in California. As shown in Table 4, except shallow bed/strip application which only treats part of a field, the application rates used for AITC seasonal exposure estimations are already equal to the maximum application rates listed on AITC product labels. Also, starting 2017, 1,3-D applications are also prohibited in December. This assessment used 2014-2018 1,3-D use data and selected the year with the highest number of applications or highest application rates. Therefore, the 1,3-D data is expected to provide a theoretical upper bound to both the intermediate and long-term exposure estimates (annual and lifetime).

E. Reported Illnesses

California. There are no AITC soil fumigant products registered in California, therefore the Pesticide Illness Surveillance Program (PISP) managed by DPR, i.e., California Pesticide Illness Query (CalPIQ), does not have any illness records associated with AITC. As of November 2020, CalPIQ did not have any illness records associated with use of oil of mustard, either.

F. Environmental concentrations

AITC degradation and its degradates have been discussed in a few previous publications (Borek *et al.*, 1995; Pechacek *et al.*, 1997; US EPA, 2013). However, DPR did not find any studies that monitored the occurrence of AITC and its degradates in different environmental media (air, surface water, etc.). Although quantitative assessment of human exposures to AITC from ambient air is not included in this document, the exposures are expected to be lower than worker and bystander exposures because AITC and its environmental degradates are expected to dissipate quickly in the environment (US EPA, 2013). Detailed discussions are provided later in the Exposure Appraisal section.

G. Significant exposure scenarios

The assessed exposure scenarios can be grouped into four categories as listed below:

Handler exposure. This group of scenarios includes occupational exposures occurring at the time of AITC application, such as loader and applicator (driver and co-pilot). The product labels require all handlers wear "*coveralls over long-sleeved shirt and long pants, chemical-resistant footwear plus socks, chemical-resistant gloves, protective eyewear and respirator.*" For applications with tarp, this group of scenarios also includes AITC exposures for tarp cutter, remover and puncher who enter the treated field after the REI (5 days) expires. The product labels state that workers performing tarp cutting, punching and removing are required to "*wear long-sleeved shirt, long pants and gloves.*" Protective respirator is not required for tarp cutter, remover, and puncher.

Re-entry worker exposure. This group of scenarios covers post-application occupational exposures for workers preparing the treated field for next planting, such as soil shaper and pipe layer. The product labels do not specify the PPEs required for re-entry workers.

Bystander exposure (occupational). This group of scenarios covers occupational exposures for workers in areas near the AITC treated field. Occupational bystanders are not subject to the 25 feet buffer zone requirement.

Bystander exposure (residential). This group of scenarios covers non-occupational exposures for adults and children that reside near the AITC-treated field. The product labels specify AITC treatment should be a minimum 25 feet from "*any occupied structure, such as a school, daycare, hospital, retirement home, business or residence.*" In addition, as discussed above, an applicator training materials prepared by ISAGRO also suggests the application should not be within 100 ft of any "*sensitive sites*" such as nursing homes and day care centers (ISAGRO, 2015).

The exposure conceptual model is shown in Figure 3.

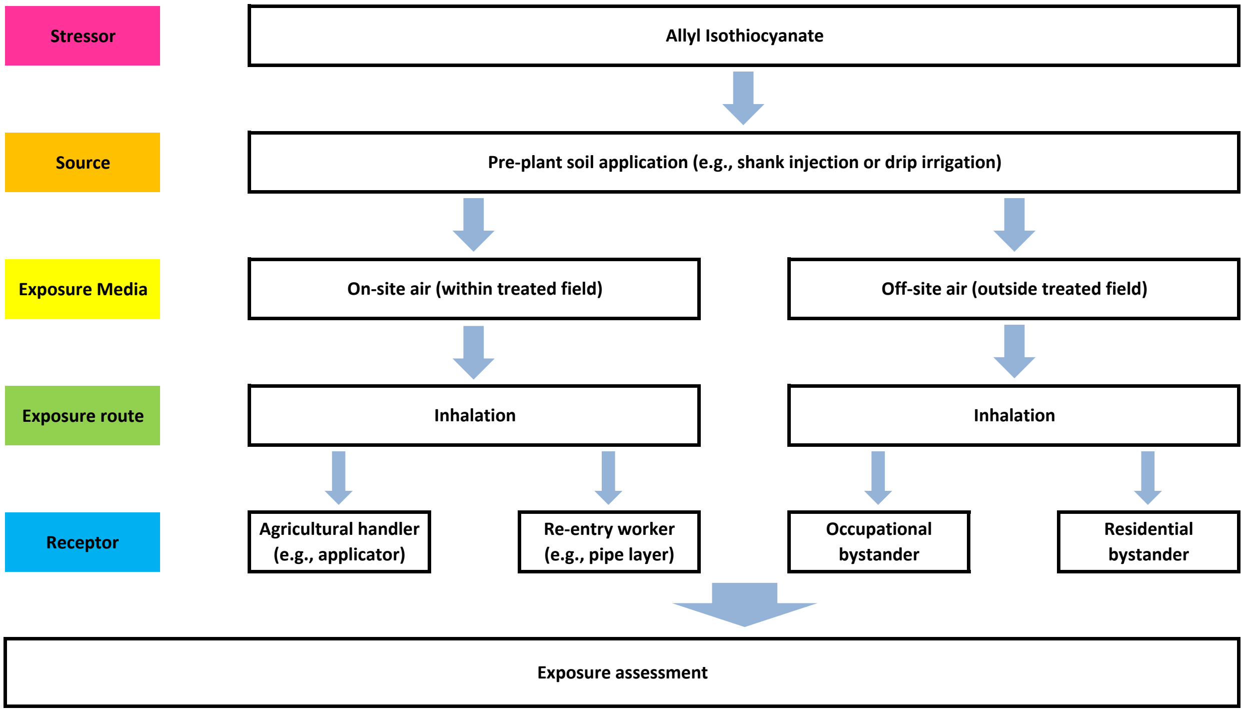


Figure 3. Exposure conceptual model for allyl isothiocyanate

IV. INHALATION ABSORPTION

This analysis only assesses human exposure through inhalation, based on the volatile property of AITC and PPE requirements for handlers on the Dominus® product label submitted to DPR. In the absence of experimental data, the inhalation exposure was characterized using a default inhalation absorption rate of 100% (Frank, 2008). The inhalation absorption rate was used to calculate human internal exposures, and was not incorporated in the calculations of external air concentrations as summarized in Appendix 3: Summary of air concentration tables that was used to calculate margin of exposures.

V. EXPOSURE ASSESSMENT

A. Exposure duration

For occupational handlers and re-entry workers, this analysis assessed the AITC exposures for four periods: short-term, seasonal, annual and lifetime. Short-term exposure represents the highest exposure an individual may realistically experience while performing a label-permitted activity, and is assessed using the "upper-bound" estimate of exposure, i.e., the 95th percentile of daily exposure (Powell, 2002). In addition, to assess short-term exposures for re-entry workers, it was also assumed the workers enter the fumigated areas immediately after the REI (5 days) expired. For assessing seasonal, annual and lifetime exposures, this assessment used the arithmetic mean instead of 95th percentile exposure value, as continuous daily exposure at the upper-bound level is unlikely.

Due to the lack of both air monitoring data and AITC use information in California, this analysis only assessed short-term exposures for both occupational and residential bystanders.

B. Occupational handler exposure

This assessment identified no registrant submitted studies that monitored handler exposure to AITC during soil applications, nor any data from open literature related handler exposure to AITC from soil fumigation. Therefore, studies that monitored handler exposure to other soil fumigants were used as surrogate data. The potential uncertainties associated with using surrogate data for AITC handler exposure assessment will be discussed in the appraisal section.

<u>Applicator, shallow shank with tarp.</u> Applicator exposures for broadcast or bed/strip shallow shank with tarp application were assessed based on two studies which monitored the applicator exposures to Pic during 11 shank applications (Beard *et al.*, 1996; Rotondaro, 2004). Both studies have been reviewed by DPR and determined to be of acceptable study quality for use in exposure assessment (Beauvais, 2005; Beauvais, 2010). These applications were conducted in four different states (CA, WA, AZ and FL). Among these 11 applications, seven used broadcast shank applications and the remainder used bed shank applications. In both studies, Pic exposure of each applicator was monitored by placing a XAD-4 tubes close to the collar area (i.e., breathing zone) and drawing air through the tube using an air pump at the flow rate of 50 mL/min. Monitored workers included 1) tractor drivers who loaded and connected Pic cylinders before application, operated the application tractors, and disconnected and removed cylinders when applications were complete, 2) co-pilots who worked closely with tractor drivers and

assisted Pic application and tarp-laying, and 3) tarpers who drove tarp laying tractor following the Pic application tractor.

Statistics of worker exposures are summarized in Table 5 and used to calculate the air concentration estimates (i.e., average and 95th percentile values) needed for assessing the exposures of different time periods. To assess seasonal, annual, and lifetime exposures, this analysis used 1,3-D use data from 2014-2018 as a surrogate to estimate AITC use patterns (i.e., seasonal application rate and number of applications per year). The estimated AITC exposures for applicators using shallow shank with tarp are summarized in Table 6.

Table 5. Summary statistics of chloropicrin air concentrations (µg/m^3) measured from applicators using broadcast and bed shank applications with tarp

Application[a]	*N*[b]	Average	Std. Dev.[c]	95th %ile[d]
Broadcast	32	533	328	1300
Bed/Strip	13	183	190	719

a: information was summarized from Beard *et al.* (1996); Rotondaro (2004). Chloropicrin was applied through shallow shank and the treated field was covered with polyethylene tarp. Air concentrations were normalized to the same application rates of 327 lbs/ac for broadcast and 246 lbs/ac for bed applications;
b: number of observations;
c: standard deviation;
d: 95th percentile value was calculated based on the method from Frank (2009). Shapiro-Wilk tests were performed and confirmed the exposure data followed log-normal distribution.

Table 6. Estimated applicator exposure to allyl isothiocyanate using shallow shank applications with tarp

Exposure (µg/kg/d)	STADD[a]	SADD[b]	AADD[c]	LADD[d]
Broadcast	23	10	2	1
Bed/Strip	13	1	0.2	0.1

a: short-term absorbed daily dose (STADD) = air concentration (1300 µg/m^3 for broadcast or 719 µg/m^3 for bed/strip) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
b: seasonal average daily dose (SADD) = air concentration (533 µg/m^3, normalized to 327 lbs/ac for broadcast application or 72 µg/m^3, normalized to 97 lbs/ac for bed/strip application) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: annual average daily dose (AADD) = SADD × 95 d/yr for broadcast or 61 d/yr for bed/strip ÷ 365 d/yr. See Table 4 for more details;
d: life-time average daily dose (LADD) = AADD × 40 yrs ÷ 75 yrs.

Applicator, shallow shank without tarp

Applicator exposures for broadcast and bed/strip shallow shank without tarp applications were assessed based on three studies with 11 fumigant applications and a total of 34 applicators monitored (Houtman, 1993; Beard *et al.*, 1996; Rotondaro, 2004). Two of these studies monitored Pic exposures, and the other nine study monitored 1,3-D exposures (Beard *et al.*, 1996; Beauvais, 2005; Beauvais, 2010). Data from this 1,3-D study has been used in the previous 1,3-D risk assessment (DPR, 2015a). This assessment used both 1,3-D and Pic exposure data, and the rationale will be discussed later in the exposure appraisal section. Statistics of these exposure data are summarized in Table 7, and the estimated applicator exposures are summarized in Table 8.

Table 7. Summary statistics of air concentrations (µg/m^3) measured from applicator breathing zones using broadcast and bed shank applications without tarp

Application[a]	*N*[b]	Average	Std. Dev.[c]	95th %ile[d]
Broadcast	22	822	1268	2909
Bed/Strip	10	2604	3920	11492

a: information was summarized from Houtman (1993); Beard *et al.* (1996); Rotondaro (2004). Chloropicrin or 1,3-dichloropropene was applied through shallow shank and the treated field was not covered with tarp. Air concentrations were normalized to the same application rates of 327 lbs/ac for broadcast and 246 lbs/ac for bed applications;
b: number of observations;
c: standard deviation;
d: 95th percentile value was calculated based on the method from Frank (2009). Shapiro-Wilk tests were performed and confirmed the exposure data followed log-normal distribution.

Table 8. Estimated applicator exposure to allyl isothiocyanate using shallow shank applications without tarp

Exposure (µg/kg/d)	STADD[a]	SADD[b]	AADD[c]	LADD[d]
Broadcast	52	15	4	2
Bed/Strip	205	18	3	2

a: short-term absorbed daily dose (STADD) = air concentration (2909 µg/m^3 for broadcast or 11492 µg/m^3 for bed/strip) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
b: seasonal average daily dose (SADD) = air concentration (822 µg/m^3, normalized to 327 lbs/ac for broadcast application or 1027 µg/m^3, normalized to 97 lbs/ac for bed/strip application) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: annual average daily dose (AADD) = SADD × 95 d/yr for broadcast or 61 d/yr for bed/strip ÷ 365 d/yr. See Table 4 for more details;
d: life-time average daily dose (LADD) = AADD × 40 yrs ÷ 75 yrs.

Applicator, deep shank with and without tarp

CalPIP data indicates deep shank applications accounted for the greatest portion of soil fumigant use in California especially in the Central Valley areas (Fig. 2). Because there is no study that monitored applicator exposures during deep shank applications, applicator exposures for deep shank applications with and without tarp were assessed using Pic and 1,3-D data from shallow shank applications as surrogate. To assess seasonal, annual and life-time exposures, these surrogate data were also used together with deep shank-specific use information, i.e., seasonal application rate and number of applications per year, as summarized in Table 4. The estimated applicator exposures for deep shank applications with and without tarp are summarized in Table 9. Applicator exposures for deep shank applications were only assessed for broadcast applications, as bed/strip deep shank is not listed on Dominus® product label.

Table 9. Estimated applicator exposure to allyl isothiocyanate using deep shank applications with and without tarp

Exposure (μg/kg/d)	STADD[a]	SADD[b]	AADD[c]	LADD[d]
with tarp	23	10	2	1
without tarp	52	15	3	2

a: short-term absorbed daily dose (STADD) = air concentration (1300 μg/m^3 for with-tarp or 2909 μg/m^3 without-tarp scenario) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
b: seasonal average daily dose (SADD) = air concentration (533 μg/m^3 for with-tarp or 822 μg/m^3 for without-tarp scenario, normalized to 327 lbs/ac) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: annual average daily dose (AADD) = SADD × 75 d/yr ÷ 365 d/yr. See Table 4 for details;
d: life-time average daily dose (LADD) = AADD × 40 yrs ÷ 75 yrs.

Applicator, drip application with and without tarp

Applicator exposures for drip applications was assessed using a study that monitored drip applicator exposures to Pic in six applications (three with tarp and three without tarp) (Rotondaro, 2004). As shown in Table 10, the applicator exposures were comparable between tarped and non-tarped applications, which was also confirmed by permutation test ($p = 0.44$). The exposure estimates are summarized in Table 11.

Table 10. Statistics of air concentrations (μg/m^3) measured from applicator breathing zones using drip applications

Tarp[a]	*N*[b]	Average	Std. Dev.[c]	95th %ile[d]
PE & no-tarp	12	146	157	438
PE	6	105	48	226
Without tarp	6	188	209	686

Information was summarized from Rotondaro (2004). Air concentrations were normalized to the same application rate of 246 lbs/ac.
a: tarp material, PE=polyethylene;
b: number of observations;
c: standard deviation;
d: 95th percentile value was calculated based on the method described elsewhere (Frank, 2009). Shapiro-wilk test was performed and confirmed the log-normal distribution of the used exposure data.

Table 11. Estimated applicator exposure to allyl isothiocyanate using drip applications

	STADD[a]	SADD[b]	AADD[c]	LADD[d]
Exposure (μg/kg/d)	8	3	0.3	0.2

a: short-term absorbed daily dose (STADD) = air concentration (438 μg/m^3, normalized to 246 lbs/ac application rate) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
b: seasonal average daily dose (SADD) = air concentration (146 μg/m^3, normalized to 246 lbs/ac application rate) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: Annual average daily dose (AADD) = SADD × 49 d/yr ÷ 365 d/yr. See Table 4 for more details;
d: life-time average daily dose (LADD) = ADD × 40 yrs ÷ 75 yrs.

Loader

Loader exposure was assessed based on a monitoring study of 1,3-D during shallow shank applications without tarp (Houtman, 1993). The breathing zone concentrations were monitored during three different application conditions: 1) no mitigation used, 2) using dry disconnects, and 3) using both dry disconnects and vapor recovery. This study described "*dry disconnects*" as a technique utilized "*during detachment of the product loading line from the applicator rig following completion of product loading*". In the same study, "*vapor recovery*" was described as "*a vapor return line was installed between the applicator tank and the nurse truck… to exchange the product leaving the nurse tank with an equal volume of displaced vapor from the applicator tank during the loading process*". This analysis used data from the first condition (no mitigation), as neither dry disconnects nor vapor recovery is required in the submitted product labels. Statistics of loader exposures in this study are summarized in Table 12. Due to the lack of monitoring data, loader exposures for deep shank applications was estimated using the air concentration from shallow shank applications as surrogate combined with deep shank-specific use information (Table 4). The calculated loader exposures for both shallow and deep shank applications are summarized in Table 13.

Table 12. Summary statistics of 1,3-dichloropropene air concentrations (µg/m^3) measured from loaders in shallow shank applications

Application[a]	*N*[b]	Average	Std. Dev.[c]	95th %ile[d]
Broadcast	15	14261	8649	74076
Bed/Strip	15	10728	6507	55727

a: information was summarized from (Houtman, 1993). Air concentrations were normalized to the application rate of 327 lbs/ac for broadcast application or 246 lbs/ac for bed application;
b: number of observations;
c: standard deviation;
d: 95th percentile value was calculated based on the method from Frank (2009). Although Shapiro-Wilk test rejects the data following log-normal distribution ($p<0.05$), the rejection was caused by an outlier value. There is no evidence to exclude that value. 95^{th} percentile was estimated using the same method to be consistent with other exposure scenarios.

Table 13. Estimated loader exposure to allyl isothiocyanate using shallow and deep shank applications

Exposure (µg/kg/d)	STADD[a]	SADD[b]	AADD[c]	LADD[d]
Broadcast shallow shank	1321	254	66	35
Bed shallow shank	993	75	13	7
Broadcast deep shank	1321	254	52	28

a: short-term absorbed daily dose (STADD) = air concentration (74076 (for broadcast shallow shank), 55727 (for bed shallow shank), or 74076 µg/m^3 (for broadcast deep shank)) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
b: seasonal average daily dose (SADD) = air concentration (14261 (for broadcast shallow shank), 4230 (for bed/strip shallow shank), or 14261 µg/m^3 (for broadcast deep shank)) × protection factor (0.1) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: annual average daily dose (AADD) = SADD × 95, 61 or 75 d/yr for broadcast shallow, bed/strip shallow, or broadcast deep shank respectively ÷ 365 d/yr. See Table 4 for more details;
d: life-time average daily dose (LADD) = AADD × 40 yrs ÷ 75 yrs.

<u>Tarp cutter, remover and puncher</u>

This scenario includes AITC handlers that cut and remove tarps (for shank applications) or perforate on tarps (for drip applications). According to the submitted product labels, respiratory protections are not required for tarp cutters, removers and punchers, and the REI is 5 days.

There is no AITC-specific study that monitored tarp cutter/remover/puncher exposures; hence, the exposures for this scenario were assessed based on a Pic exposure monitoring study where Pic was applied via shallow shank applications with polyethylene (PE) tarps (Beard *et al.*, 1996). In this study, the shortest time interval between applications and worker re-entry was 6 days. Therefore, monitoring data from those 6th-day re-entry workers were used to assess AITC exposures for this scenario. Statistics of worker exposures for tarp cutter, remover and puncher are summarized in Table 14. The same data were also used for worker exposures in deep shank and drip applications combined with deep shank- or drip-specific use information as summarized in Table 4. The estimated exposure values for shallow shank, deep shank and drip applications are summarized in Table 15.

Table 14. Statistics of air concentrations (µg/m3) measured from Tarp cutter/remover/puncher breathing zones using shallow shank applications

Application[a]	*N*[b]	Average	Std. Dev.[c]	95th %ile[d]
Broadcast	14	573	996	1625
Bed/Strip	14	431	749	1222

a: information was summarized from (Beard et al., 1996). Air concentrations were normalized to the application rate of 327 lbs/ac for broadcast application or 246 lbs/ac for bed application;
b: number of observations;
c: standard deviation;
d: 95^{th} percentile value was calculated based on the method from Frank (2009). Shapiro-Wilk test was performed and confirmed the log-normal distribution of the used exposure data.

Table 15. Estimated allyl isothiocyanate exposure of tarp cutter, remover and puncher

Exposure (µg/kg/d)	STADD[a]	SADD[b]	AADD[c]	LADD[d]
Broadcast shallow shank	290	102	27	14
Bed/strip shallow shank	218	30	5	3
Broadcast deep shank	290	102	21	11
Drip	218	77	10	6

a: short-term absorbed daily dose (STADD) = air concentration (1625 µg/m^3 (for broadcast shallow shank or broadcast deep shank applications) or 1222 µg/m^3 (for bed/strip shallow shank and drip applications) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
b: seasonal average daily dose (SADD) = air concentration (573 µg/m^3 (for broadcast shallow shank or broadcast deep shank applications), 431 µg/m^3 (for drip application) or 170 µg/m^3 (for bed/strip shallow shank application) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: annual average daily dose (AADD) = SADD × 95 (for broadcast shallow shank), 61 (for bed/strip shallow shank), 75 (for broadcast deep shank) or 49 (for drip) d/yr ÷ 365 d/yr. See Table 4 for more details;
d: life-time average daily dose (LADD) = AADD × 40 yrs ÷ 75 yrs.

C. Occupational re-entry worker

There is no AITC-specific study that monitored re-entry worker exposures. Hence, this assessment used data from 1,3-D as surrogates for estimating the exposure. The selected data is from workers entering the treated field 4 days after fumigation, which represents the available data with the time interval closest to AITC's REI at 5 days (Houtman, 1993). The field was applied with 1,3-D using broadcast shank equipment and the workers were performing winterization activities. Statistics of re-entry worker exposures from the data are summarized in Table 16. As monitoring data is not available for deep shank and drip applications, 1,3-D data from shallow shank applications was used as surrogate. To assess seasonal, annual and life-time exposures, the deep shank- or drip-specific use information, i.e., seasonal application rates and number of applications per year, was also used (Table 4). The estimated AITC exposures for different application types are summarized in Table 17.

Table 16. Statistics of air concentrations (μg/m^3) measured from Tarp cutter/remover/puncher breathing zones using shallow shank applications

Application[a]	*N*[b]	Average	Std. Dev.[c]	95th %ile[d]
Broadcast	5	145	13	167
Bed/Strip	5	109	9	125

a: information was summarized from (Beard et al., 1996; Rotondaro, 2004). Air concentrations were normalized to the application rate of 327 lbs/ac for broadcast application or 246 lbs/ac for bed application;
b: number of observations;
c: standard deviation;
d: 95th percentile value was calculated based on the method from Frank (2009). Shapiro-Wilk test was performed and confirmed the log-normal distribution of the used exposure data.

Table 17. Estimated allyl isothiocyanate exposures for re-entry workers

Exposure (μg/kg/d)	STADD[a]	SADD[b]	AADD[c]	LADD[d]
Broadcast shallow shank	30	26	7	4
Bed/Strip shallow shank	22	8	1	1
Broadcast deep shank	30	26	10	5
Drip	22	19	3	2

a: short-term absorbed daily dose (STADD) = air concentration (167 μg/m^3 (for both broadcast shallow shank and broadcast deep shank applications), or 125 μg/m^3 (for bed/strip shallow shank and drip applications) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);

b: seasonal average daily dose (SADD) = air concentration (145 μg/m^3 (for broadcast shallow shank and broadcast deep shank application), 43 μg/m^3 (for bed/strip shallow shank application), or 109 μg/m^3 (for drip application) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg (Andrews and Patterson, 2000);
c: annual average daily dose (AADD) = SADD × 95 (for broadcast shallow shank), 61 (for bed/strip shallow shank), 142 (for broadcast deep shank) or 59 (for drip) d/yr ÷ 365 d/yr. See Table 4 for more details;
d: life-time average daily dose (LADD) = AADD × 40 yrs ÷ 75 yrs.

D. Occupational and residential bystander

This assessment identified no registrant-submitted study that monitored bystander exposures to AITC. Thus, the exposure assessment for both occupational and residential bystanders used computer software to simulate the air concentrations. The software used in this simulation is AERMOD View™, and the modeling engine integrated in this software is AERMOD developed by American Meteorological Society and US EPA (Lakes Environmental, 2020). In addition to meteorological data, the simulation requires soil emission rates as model inputs. For shallow shank and drip applications with the use of tarp, AITC-specific emission data was used to generate the needed emission rates, and for application scenarios with no-AITC specific emission data, the emission rates were derived from the most appropriate surrogate (1,3-D or Pic). Detailed descriptions on preparing soil emission profiles for different application types and tarp methods, and simulating breathing zone air concentrations using the prepared emission profiles, can be found in two memorandums (Jiang, 2021b; Jiang, 2021a, See appendix). With the simulated air concentrations, STADD values were calculated for both residential (adult and child) and occupational (adult only) bystanders and are summarized in Table 18-20.

Table 18. Model estimated allyl isothiocyanate exposures for occupational bystanders[a]

STADD[b] (μg/kg/d)	1 ac[c]	40 ac	100 ac
Shallow shank with PE[d] tarp	59	175	219
Shallow shank without tarp	568	1690	2115
Deep shank without tarp	370	1103	1380
Drip with PE tarp	319	1022	1274
Deep drip without tarp	746	2391	2982

a: The occupational bystander was assumed to work right next to the treated field during the work day (8 hours);
b: STADD = short-term absorbed daily dose. Exposures were assessed using air concentrations at the treated field edge. 8-hr time-weighted average emission rates were used and normalized to the maximum application rates as described on the submitted product labels; STADD = air concentration (μg/m^3) × inhalation rate (1.6 m^3/hr) × 8 hr/d ÷ 71.8 kg.
c: size of the treated field;
d: PE=polyethylene.

Table 19. Model estimated allyl isothiocyanate exposures for residential adult bystanders

STADD[a] (µg/kg/d)	1 ac[b]	40 ac	100 ac
25ft[c]			
Shallow shank with PE[d] tarp	32	98	123
Shallow shank without tarp	297	959	1189
Deep shank without tarp	255	830	1035
Drip with PE tarp	205	626	791
Deep drip without tarp	423	1335	1654
100ft			
Shallow shank with PE tarp	19	79	103
Shallow shank without tarp	177	712	942
Deep shank without tarp	165	663	857
Drip with PE tarp	114	501	663
Deep drip without tarp	242	1031	1369

a: STADD = short-term absorbed daily dose; Rolling hourly emission rates from the periods with maximum 24-hr emissions were used and normalized to the maximum application rates on the Dominus® label; STADD = air concentration at 5 ft above ground (µg/m^3) × inhalation rate (0.28 m^3/kg/d);

b: size of treated fields;

c: distance from the treated field edge, based on the 25 ft buffer zone as specified on the product labels and 100 ft as described in the ISAGRO applicator training materials (ISAGRO, 2015);

d: PE=polyethylene.

Table 20. Model estimated allyl isothiocyanate exposures for residential child bystanders

STADD[a] (µg/kg/d)	1 ac[b]	40 ac	100 ac
25ft[c]			
Shallow shank with PE[d] tarp	93	238	293
Shallow shank without tarp	822	2234	2722
Deep shank without tarp	760	1968	2414
Drip with PE tarp	592	1529	1879
Deep drip without tarp	1189	3169	3888
100ft			
Shallow shank with PE tarp	44	175	225
Shallow shank without tarp	400	1544	2028
Deep shank without tarp	379	1472	1872
Drip with PE tarp	273	1103	1446
Deep drip without tarp	559	2274	2990

a: STADD = short-term absorbed daily dose; Rolling hourly emission rates from the periods with maximum 24-hr emissions were used and normalized to the maximum application rates on the Dominus® label; STADD = air oncentration at 1.7 ft above ground (µg/m^3) × inhalation rate (0.59 m^3/kg/d);

b: size of treated fields;

c: distance from the treated field edge, based on the 25 ft buffer zone as specified on the product labels and 100 ft as described in the ISAGRO applicator training materials (ISAGRO, 2015);

d: PE=polyethylene.

VI. EXPOSURE APPRAISAL

This section evaluates uncertainties associated with the exposure assessment process. This analysis attempted to use AITC-specific information to assess the exposures, but the needed information in some instances was not be available. Hence, this section discusses the data gaps identified and their impact on the exposure assessment.

A. Occupational handler exposure

Applicator. Applicator exposures to AITC were assessed for three application methods (shallow shank, deep shank and drip) and 2 tarp conditions (tarp and non-tarp), and the assessment used human exposure monitoring data, i.e., data from collecting and analyzing air samples from worker breathing zones. Due to the lack of AITC-specific exposure data, applicator exposures were assessed using surrogate data from 1,3-D and Pic (Houtman, 1993; Beard *et al.*, 1996; Rotondaro, 2004). This is because the physiochemical properties of AITC that determine its movements in the soil environment, such as boiling point, water solubility and lipophilicity, are similar to 1,3-D and Pic (Table 1). Although AITC is structurally similar to MITC, applicator exposure data from MITC was not used because of the following reasons. First, unlike AITC, MITC is not a directly applied pesticide but produced in soils after the applications of other active ingredients such as MITC-Na and MITC-K. Second, the application techniques of MITC-Na and MITC-K, such as using rotary tillers and sprinklers, are different from shank and drip methods for AITC (Meyers, 1992; Meyers, 1993). Between AITC and MITC, only two of the nine MITC application methods (i.e., drip and shank) are allowable for AITC, suggesting that emission profiles and the associated pattern of human exposure to these two fumigants are rather different (DPR, 2015b). There was no MITC exposure monitoring data available for deep shank and drip applications. By contrast, almost all application methods for 1,3-D and Pic are also allowable for AITC. In addition, 1,3-D and chloropicrin exposure monitoring data is available for applicator, loader, tarp remover and re-entry workers. There is one study that monitored applicator exposures to MITC during shank applications without tarp (Meyers, 1992). Using this monitoring study, the estimated STADD is125 µg/kg/d, which is comparable to STADD values (52 or 205 µg/kg/d) determined in this analysis using 1,3-D and Pic data. No MITC use data are currently available for estimating the intermediate- and long-term exposures. Therefore, to ensure an internal consistency in data quality and coverage, 1,3-D and Pic data (instead of MITC data) was used for all application scenarios in this assessment.

The approach of using surrogate data to fill in data gaps has been employed in the DPR 1,3-D Exposure Assessment Document (DPR, 2015a). In that assessment, 1,3-D exposure data were only available for the applicator scenario using shallow shank without tarp. To estimate exposures for other scenarios, such as applicators using shallow shank with tarp, Pic exposure data were used as the surrogate data. To account for the differences in the physiochemical properties between 1,3-D and Pic, an exposure adjustment ratio was calculated by dividing 1,3-D exposure from shallow shank without tarp applicators to Pic exposure of the same scenario. The resulting adjustment ratio was applied for scenarios when Pic data was used (e.g., applicator exposure using shallow shank with tarp). An example of using this exposure adjustment ratio is demonstrated using the equation below:

$$\text{Applicator, shallow shank with tarp (1,3-}D\text{)} = \text{Applicator, shallow shank with tarp (Pic)} \times \frac{\text{Applicator, shallow shank without tarp (1,3-}D\text{)}}{\text{Applicator, shallow shank without tarp (Pic)}}$$

It is important to note that this adjustment method used in the 1,3-D exposure assessment document could not be used for the AITC exposure assessment because there are no AITC exposure monitoring data available to derive the adjustment ratio. One study measured AITC emissions from four different application and tarp methods (Ajwa *et al*., 2014). However this study could not be used to estimate handler exposures because human AITC exposures were not monitored.

Instead, exposure data from surrogate fumigants (1,3-D and Pic) were used with corrections for appropriate application rates, assuming that with the same application rates and application methods, handler exposures were similar. Accordingly, factors that may contribute to different handler exposures between AITC, 1,3-D, and Pic, such as different soil emission rates at the time of applications, were not considered. Table 21 compares the emission rates for the application periods for the three fumigants. The comparisons were done for four application types with the AITC emission data that were available, i.e., shallow shank with totally impermeable film (TIF) tarp, shallow shank with PE tarp, drip with TIF tarp and drip with PE tarp. Table 22 compares AITC air concentrations measured at adult breathing heights with those of 1,3-D or Pic concentrations from available studies.

AITC data is available for two application types, i.e. drip with TIF and drip with PE tarp. Tables 21 and 22 indicate that, at the time of application, AITC emission rates and air concentrations are comparable to 1,3-D and Pic. For broadcast shallow shank with PE tarp application, the estimated AITC emission was lower than those of 1,3-D or Pic. However, there is only one set of AITC emission data available for this application method, and the variations of emissions under different field, weather and application conditions cannot be evaluated. Therefore, based on the comparability for other application methods, this assessment determined 1,3-D and Pic data represented appropriate surrogate data to be used in the development of this exposure assessment considering that lack of AITC-specific monitoring data.

Table 21. Comparison of fumigant emission rates during the time of applications

Fumigant[a]	Application duration (hr)	Sampling duration (hr)	Emission[c] (μg/m²/s)
Broadcast shallow shank with TIF[b] tarp			
AITC	4.0	6	8.7
Pic	4.3	7	1.8
1,3-D	4.3	7	1.7
Pic	1.2	7	0.1
1,3-D	1.2	7	0.2
Pic	1.6	7	0.4
1,3-D	1.6	7	0.4
Pic	1.2	5	28.7
1,3-D	1.3	6	2.4
Pic	1.3	6	11.2
Broadcast shallow shank with PE tarp			
AITC	5.1	5	0.7
Pic	2.4	6	12.0
1,3-D	2.4	6	17.2
Pic	0.6	7	27.8
1,3-D	0.6	7	57.0
Pic	1.0	4	6.3
1,3-D	1.0	4	15.3
Pic	0.6	6	5.2
Pic	1.1	5	30.1
Shallow drip-TIF tarp			
AITC	1.8	6	7.7
Pic	3.0	6	5.7
1,3-D[d]	2.6	6	12.5
Pic[d]	2.6	6	19.5
1,3-D	2.5	6	5.3

Shallow drip-PE tarp			
AITC	3.9	4	54.9
Pic	1.0	4	23.0
Pic	3.0	6	86.8
Pic	4.7	5	48.8
1,3-D	4.7	5	73.6

a: AITC=allyl isothiocyanate, Pic=chloropicrin, 1,3-D=1,3-dichloropropene. Data was obtained from various sources (Knuteson and Dolder, 2000; van Wesenbeeck and Phillips, 2000; Rotondaro, 2004; Ajwa, 2008; Ajwa, 2009; Ajwa, 2010; Ajwa and Sullivan, 2010; Sullivan and Chellemi, 2010; Sullivan, 2012; Ajwa *et al.*, 2014; Ajwa, 2015);
b: TIF=totally impermeable film, PE=polyethylene;
c: the emission rates were normalized to 327 and 246 lbs/ac for shank and drip application respectively;
d: virtually impermeable tarp was used.

Table 22. Comparison of fumigant air concentrations measured near the breathing heights of applicators during the time of applications

Fumigant[a]	Application duration (hr)	Sampling duration (hr)	Concentration[b] (µg/m^3)
Drip with TIF tarp[c]			
AITC	1.8	6	28.7
Pic[d]	3.0	6	59.7
1,3-D[e]	2.6	6	97.4
Pic[e]	2.6	6	49.4
Drip with PE tarp			
AITC	3.9	4	317.9
Pic[d]	3.0	6	254.5
Pic	4.7	5	687.2
1,3-D	4.7	5	996.4

a: AITC=allyl isothiocyanate, Pic=chloropicrin, 1,3-D=1,3-dichloropropene. Data was obtained from various sources (Knuteson and Dolder, 2000; van Wesenbeeck and Phillips, 2000; Ajwa, 2010; Ajwa *et al.*, 2014);
b: TIF=totally impermeable film, PE=polyethylene;
c: the air concentrations were normalized to 246 lbs/ac;
d: the air concentration values may not be accurate as the actual sampling rates were not provided. Instead the target rate of 1000 mL/min was used for calculation;
e: virtually impermeable tarp was used.

This assessment considered exposure data from both 1,3-D and Pic as surrogates for AITC. For each of the assessed scenarios, exposure data are available from either 1,3-D or Pic with the exception of broadcast shallow shank without tarp application; in that scenario, both 1,3-D and Pic data are available for the applicators. Permutation test revealed a significant ($p < 0.05$) difference in emissions for the two fumigants. Nevertheless, application method is considered as the major factor determining applicator pesticide exposures. Also as discussed in the appended memo "Using allyl isothiocyanate (AITC)-specific and surrogate data to determine AITC soil emissions for residential and occupational bystander exposure assessments-revised", when 1,3-D and Pic were simultaneously applied to the same fields, their emission rates were comparable (Jiang, 2019b). Therefore, for the broadcast shallow shank without tarp application, this assessment combined 1,3-D and Pic exposure data together to estimate applicator exposures to AITC.

<u>Loader.</u> Available MITC data did not support loader exposure assessment to AITC, as monitored loaders were either from different application types (sprinkler applications), or only monitored for very short periods of time (4-17 min) during their workdays (Meyers, 1992). Loader exposures were assessed using monitoring data from a study that monitored loader exposures to 1,3-D during non-tarped applications (Houtman, 1993). In this study, 1,3-D breathing zone air concentrations were measured from loaders for their "*work period (or daily) exposures*", not just "*the period directly involved in product handling.*" In actual practice, applicators may also assist loading, connecting and unloading fumigant cylinders onto tractors, but they are not required to do so and they are not always around fumigant cylinders. This assessment considered loader exposures as a separate scenario assuming that they might experience great fumigant exposures, especially during their handling of fumigant cylinders. This assumption is consistent with the results in this assessment that loaders experienced higher AITC exposures than applicators and the periods of handling and loading cylinders accounted for a great portion of the loader exposures (median: 69%, N=15) during their work days (Houtman, 1993).

<u>Tarp cutter/remover/puncher.</u> There was no MITC available to support tarp remover exposure assessments. Exposures of this scenario were based on data that monitored tarp cutter exposures to Pic on the 6th day after applications (Beauvais, 2010). The use of Pic monitoring data on the 6th day is because of the following reasons. First, there was no study that monitored tarp cutter exposures from re-entry <6 days. Second, the Pic data represent the information available with the post-application entry interval closest to AITC's REI. Third, emission rates of AITC on the day of tarp-cutting and those the following day are comparable (0.25 *vs* 0.20 $\mu g/m^2/s$ for broadcast shallow shank with TIF tarp, and 6.0 *vs* 4.0 $\mu g/m^2/s$ for broadcast shallow shank with PE tarp, 12-hr TWA) (Ajwa *et al.*, 2014). This assessment also compared Pic exposures between tarp cutters and tarp removers who entered the treated field one day after the tarp cutting; their exposures were also comparable (Table 23) (Beard *et al.*, 1996; Rotondaro, 2004).

Table 23. Statistics of chloropicrin air concentrations (µg/m^3) measured from tarp cutters and tarp removers from fields with broadcast shallow shank applications with tarp

Occupation[a]	Day[b]	*N*[c]	Average	Std. Dev.[d]	Range
Tarp cutter	6	14	573	996	70-3959
Tarp remover	7	27	615	718	6-2925

a: Information was summarized from Beard *et al.* (1996); Rotondaro (2004). The application rate was normalized to the same 327 lbs/ac;
b: Number of days after application;
c: Number of applicator replicates;
d: Standard deviation;
e: Range: minimum-maximum.

B. Occupational and residential bystander

This analysis assessed occupational and residential bystander exposures for five application and tarp types, i.e., shallow shank with PE tarp, shallow shank without tarp, deep shank without tarp, drip with PE tarp and buried drip without tarp. These five application types were analyzed based on the application methods listed on the AITC product label, and three of them were also allowed for 1,3-D applications and included previously in the 1,3-D exposure assessment for bystander exposures (DPR, 2015a). For shallow shank with PE tarp application, bystander exposures were assessed because AITC-specific soil emission data is available for this application method and then used in this document. Lastly, but not the least, available data on buried drip without tarp indicates that this application type may cause greater bystander exposures than drip applications with PE tarp (Jiang, 2021b). Of the five assessed application types mentioned above, three of them (shallow shank without tarp, deep shank without tarp and drip without tarp) do not have AITC emission data, and 1,3-D or Pic data were used as surrogate. For each application type, multiple sets of 1,3-D or Pic emission data are available and this analysis selected the data with the highest emission rates as surrogate. For the remaining two application types (shallow shank with PE tarp, and drip with PE tarp), AITC-specific emission data were identified, but there is only one set of AITC data is available for each application type (Ajwa *et al.*, 2014).

This assessment gives preference to AITC data for bystander exposure assessment as they represent chemical-specific information. As there is only one set of AITC emission data available for each of the two application types, the variability of emission rates caused by different field conditions (soil type, weather, application equipment, etc.) is not known, suggesting that the characterization of bystander exposures may not be adequate. To address the emission variability issue, in this assessment, bystander exposures were estimated by extracting maximum emission rates from the AITC emission profiles and conducting AERMOD modeling in six different regions around the state. For each selected region, daily modeling was performed for five years and the upper-end values from the modeling results, i.e., maximum of daily 95th percentile value from all six regions and five years, were used to estimate the bystander exposures.

As the fumigant use of AITC has not been registered in California yet, its environmental monitoring data and use data in California is not available. Consequently, the intermediate- and long-term bystander exposures were not assessed in this document, but they are expected lower than short-term exposures.

C. Exposure to AITC degradates

This assessment did not estimate worker exposures to AITC degradates, as there is no study that monitored worker exposures to AITC degradates. In addition, there is no information on soil emission rates of AITC degradates under label-described application methods. Accordingly, the quantitative assessment of bystander exposures to AITC degradates cannot be performed.

The degradation pathway of AITC has been discussed previously (Borek *et al.*, 1995; Pechacek *et al.*, 1997; US EPA, 2013). In soils with pH ranging from 4.4 to 9.1, the half-lives of AITC were between 20-60 hr, and at near neutral pH (6-8), the primary degradates in aqueous solutions were allyl thiocyanate (ATC), allylamine (AA), carbon disulfide (CDS), allyl dithiocarbamate sodium salt (ADTC) and diallylthiourea (DATU)(Borek *et al.*, 1995; Pechacek *et al.*, 1997). For applicators and loaders with exposures occurring at the time of applications, they are not likely exposed to AITC degradates except ATC, as it is an isomerization product of AITC and that may exist in commercially prepared AITC products. Bystander exposures to ATC are also possible but the exposures are expected lower than AITC as ATC is more reactive than AITC in the environment. Bystanders may also get exposed to volatile AA and CDS. Although the quantitative assessment of these exposures is not feasible due to the lack of data, the exposures are not expected high as both AA and CDS rapidly react with photochemical radicals after releasing into the atmosphere (US EPA, 2013).

VII. CONCLUSION

This analysis assessed AITC exposures for occupational handlers, re-entry workers, occupational bystanders and residential bystanders. Based on the submitted product label from ISAGRO (Dominus), the primary route of AITC exposures is through inhalation. Due to the lack of AITC use information and exposure monitoring data as well as limited information on AITC soil emission rates, other soil fumigants (1,3-D, Pic, MeBr, MITC-Na and MITC-K) were used as surrogate to collect data for this assessment. A total of 93 exposure scenarios were assessed, and AITC inhalation exposures were estimated for four different exposure periods (short-term, seasonal, annual and life-time). These exposure values are calculated for the development of Risk Characterization Document of AITC.

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IX. APPENDICES

A. Appendix 1

Using allyl isothiocyanate (AITC)-specific and surrogate data to determine AITC soil emissions for residential and occupational bystander exposure assessments – revised

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SUBJECT: USING ALLYL ISOTHIOCYANATE (AITC)-SPECIFIC AND SURROGATE DATA TO DETERMINE AITC SOIL EMISSIONS FOR RESIDENTIAL AND OCCUPATIONAL BYSTANDER EXPOSURE ASSESSMENTS - REVISED

Executive summary:

This memorandum is prepared in response to a request for registering one product containing allyl isothiocyanate (AITC) for use in California as a soil fumigant. According to the submitted product label, AITC may be applied through shallow shank injection, deep shank injection, or drip chemigation, and the treated fields can be covered with or without tarp. Currently AITC soil emission data is only available for shallow shank w/ tarp and drip w/ tarp. Therefore, this analysis estimated AITC emissions for other application scenarios using 1,3-dichloropropene (1,3-D) and chloropicrin (Pic) field-monitored soil emission data as surrogates due to similar physiochemical properties, application methodologies and emission profiles, as well as availability of data for application scenarios without AITC-specific data. For each application scenario, maximum hourly AITC soil emission profiles were prepared for three time periods (i.e., 4, 8 and 24 hr) and summarized in Table 8. These hourly emission values will be further used to estimate short-term residential and occupational bystander exposure from AITC applications.

Background:

The California Department of Pesticide Regulation (DPR) received an application from ISAGRO USA, Inc (ISAGRO) to register a product containing AITC for use in California. The label of this product can be found on the U.S. Environmental Protection Agency (US EPA) website (submitted to US EPA on December 28, 2015; https://www3.epa.gov/pesticides/chem_search/ppls/089285-00002-20151228.pdf):

DPR track ID: 280548-N
Product name: Dominus®
US Environmental Protection Agency (US EPA) Registration No. 89285-2
Active ingredient: allyl isothiocyanate (96.3%)

Per the proposed label language, Dominus® can be used as a broad-spectrum pre-plant soil fumigant to control soil fungi, nematodes, and insects. Selected crops identified in the submitted labels include leafy vegetables (e.g., lettuce), root and tuber vegetables (e.g., carrot), fruiting vegetables (e.g., eggplant), strawberries, vineyards and nut crops, among others. Application methods are broadcast shank injection, bed/strip shank injection, or via drip irrigation systems. In addition, Dominus® may be used in post-plant crop termination applications. Details on application methods and tarp requirements are summarized in Tables 1.

It is DPR's practice that all field-use agricultural fumigants undergo comprehensive human health risk assessment before being registered for use in California. Occupational and bystander exposures to fumigant applications are evaluated in this process, necessitating fumigant emission data that quantify the rate and amount of fumigant escaping from treated soil. At present, DPR has identified one AITC emission study submitted by ISAGRO (Document No. 50544-0008). In this study, AITC emissions were measured for broadcast shallow application with totally impermeable film (TIF) tarp, broadcast shallow shank application with polyethylene (PE) tarp, shallow drip application with TIF tarp, and shallow drip application PE tarp (Ajwa *et al.*, 2014). However, AITC-specific emission data for other application and tarp conditions are not available. Therefore, fumigants with similar physiochemical properties as AITC are proposed for use as surrogates to bridge the data gap in order to complete the risk assessment and registration. This memorandum describes the method employed by the Exposure Assessment Section (EAS) of the Human Health Assessment (HHA) Branch to determine AITC emission values for bystander exposure assessment, using both AITC-specific and surrogate fumigant field emission studies.

Table 1. Application methods, injection depths and tarp requirements for Dominus® (US EPA Registration No. 89285-2)

Application method	Injection depth (in)	Tarp	Comment
Broadcast shank	4-15	Yes	PE, VIF, TIF[a]
		No[b]	Overhead sprinkler, water cap and/or roller/packer, close chisel traces
	>17	No	Roller/packer
Bed shank or strip	4-15	Yes	PE, VIF, TIF
		No	Overhead sprinkler, water cap and/or roller/packer, close chisel traces
Drip	subsurface[c]	Yes	N/A[d]
		No	>1 in buried drip tape

a: PE=polyethylene, VIF=virtually impermeable film, TIF=totally impermeable film;
b: tarp is not necessary, if alternative methods as described in the comment column are used;
c: drip emitters are placed at shallow subsurface positions;
d: tarp materials are not specified on the product label.

Determination of averaging periods for human exposure assessment:

AITC emission data from field studies need to be constructed based on the time periods used in bystander exposure assessment or the exposure periods from AITC toxicity studies, if warranted. In this assessment, 8- and 24-hour averaging periods are used to match default exposure times for occupational and residential bystanders (8 and 24 hr/day) respectively.

Review of AITC emission study:

Data volume 50544-0008, submitted by ISAGRO, is the only available AITC emission study (Ajwa *et al.*, 2014). This study was conducted in the central coast area of California. AITC was applied to four fields in this study using two different application methods (shallow shank and drip) and two different tarp materials (totally impermeable (TIF) or polyethylene (PE) film) (Table 2). AITC emission rates were calculated from on-field measurements of air concentrations except for the first period of the two shank applications where off-field air concentrations were used by AERMOD to back-calculate the emissions. AITC air concentrations were continuously monitored starting from the application, and the air sampling tubes were replaced every 6 hours within the first 48 hours. After that and before tarp cutting (for shank applications) or tarp punching (for drip applications), the tube was replaced every 12 hours.

An initial review of the submitted study report was conducted in 2015, and concerns were raised especially towards some findings in the Quality Control section (Barry, 2015). These concerns are (1) low recoveries were reported for quality control spike samples in Phase 1 (shank or drip applications with TIF tarp), (2) one field spike sample in Phase 2 (shank or drip applications with PE tarp) was reported with 51.5% recovery, but it was labeled as “Lost” without any explanation, and (3) field spike samples in both Phase 1 and 2 showed wide ranges of recoveries (Phase 1: 65.7-127.4%; Phase 2: 67.1-161.4%). Nevertheless, reevaluation of these concerns in this memorandum concluded that the emission data can be used for short-term bystander exposure assessment based on the following:

Table 2. Field layouts, application methods and tarp conditions of the four fields treated with allyl isothiocyanate[a]

Field layout	Treated acre	Application[b]	Tarp[c]	Gross application rate[d] (lbs/ac)
Bed	2.0	Drip (1 in)	TIF	209
Broadcast	1.9	Shank (8-10 in)	TIF	335
Bed	1.1	Drip (1 in)	PE	202
Broadcast	0.9	Shank (8-10 in)	PE	326

a: data were obtained from Document 50544-0008 (Ajwa *et al.*, 2014);
b: number in brackets indicates the application depth;
c: TIF= totally impermeable film, PE= polyethylene; d: actual AITC application amount per gross field acreage.

1) Low recoveries of quality control spike samples in Phase 1:

This refers to four 10 µg lab spike samples, labeled as QC (10 µg), on Pages 138-139 of the study report. According to the study report, these four spike samples had the same dates of preparation, extraction and analysis, and all showed similar amounts of AITC recovered (i.e., 0.9409, 1.1509, 1.2503 and 0.9098 µg/tube), that were about 10% of the target 10 µg/tube spiked amount. One most common cause for this low recovery in quality control spike samples is a different amount of AITC was spiked (e.g., 1 µg), through either using a wrong standard solution or spiking a different volume. Considering the fact that all other QC samples extracted and analyzed on the same dates, including both lab and field spiking samples, showed acceptable recoveries (average: 100.4%, range: 76.1-127.4%, *N*=16), this analysis determined the results analyzed on 10/12/2013 are still acceptable.

2) One field spike sample in Phase 2 was reported with 51.5% recovery, but it was labeled as "Lost" without any explanation provided in the study report:

This refers to a 0.2 µg field spike sample in Phase 2 that was prepared and analyzed together with AITC emission samples collected from Periods 23-28, but data from Periods 23-28 were not used in this analysis for bystander exposure assessments as AITC emissions during those periods were low. According to the study report, the maximum AITC emissions for drip-PE and shank-PE applications were from Periods 2 and 11 respectively, and recoveries of field spike samples for these two periods were all acceptable (>70%) as shown in Table 3.

Table 3. Summary of field spike recoveries in study 50544-0008 submitted by ISAGRO[a]

Application and tarp type[b]	Periods with highest AITC emission	Length of period[c] (hr)	Recoveries of field spikes for that period[d]	Comment

TIF-Drip	3[e]	5	80.4-120.0%	Field spikes were received, extracted and analyzed on the same dates as Period 3 samples
TIF-Shank	1	6	80.4-120.0%	Field spikes were received, extracted and analyzed on the same dates as Period 1 samples
PE-Drip	2	6	71.0-161.4%	Field spikes were received on the same date, but extracted and analyzed 1 day prior to the dates of Period 2 samples.
PE-Shank	11	12	84.4-108.9%	Field spikes were received, extracted and analyzed on the same dates as Period 11 samples

a: data were obtained from Document 50544-0008 (Ajwa *et al.*, 2014);
b: TIF=totally impermeable film, PE=polyethylene film;
c: rounded to the closest whole hour;
d: field spikes are not available for every period. The range here represents recoveries of field spike samples that are closest to the periods when the highest AITC emissions were measured; e: the period numbering system for TIF-Drip field starts with Period 2.

3) Field spike samples showed wide ranges of recoveries in both Phase 1 and 2:

> As discussed above, only periods with the highest AITC emissions were used for bystander exposure assessment as they represent the greatest exposure potential. As shown in Table 4, field spike recoveries of the periods with the highest AITC emissions were all >70%.

AITC emission profile within the first 5 days of applications, as well as the highest emissions of each treated field are summarized in Figure 1 and Table 4.

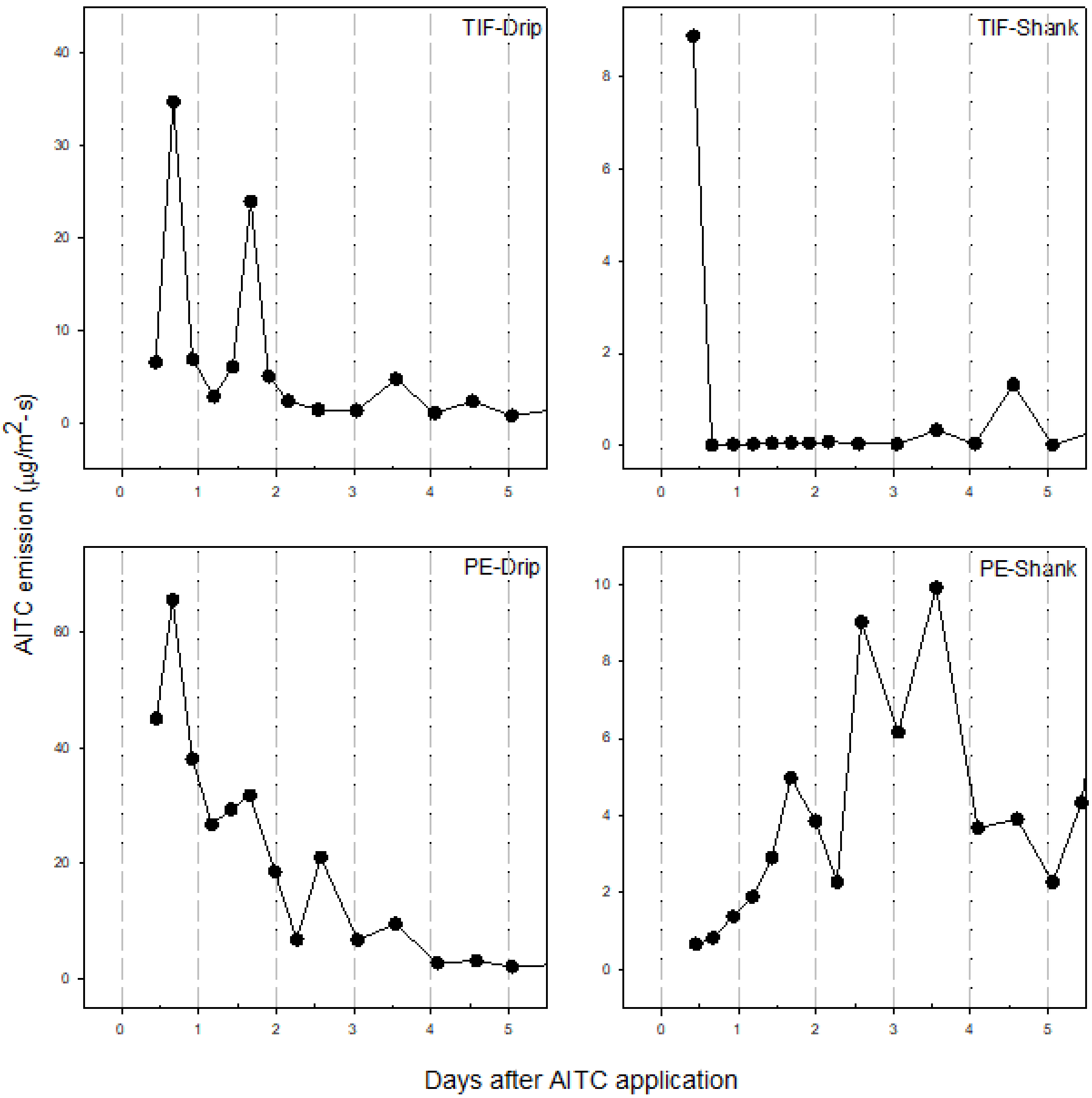


Figure 1. Allyl isothiocyanate (AITC) emissions from soil after different application methods and tarp conditions. AITC is applied through broadcast shank injection or drip irrigation, and the treated fields were covered with totally impermeable (TIF) or polyethylene (PE) film. Data were obtained from Document 50544-0008 (Ajwa *et al.*, 2014). The figure shows the original emissions without application rate adjustments. The figure only shows the emissions within the first 5 days which already included the maximum rates of the entire emission profiles. Five-day is also the restricted entry interval required on the Dominus® product label.

Table 4. Maximum allyl isothiocyanate soil emissions and the time when the maximum emissions were measured

Application method	Tarp type[a]	Maximum measured emission[b]	
		$\mu g/m^2/s$	Time[c]
Drip	TIF	40.9	1300-1900 (1st Day)
Broadcast shank	TIF	8.7	0900-1300 (1st Day)
Drip	PE	79.9	1300-1900 (1st Day)
Broadcast shank	PE	9.9	0700-1900 (4th Day)

a: the treated fields were covered with totally impermeable (TIF) or polyethylene (PE) film;
b: data were obtained from Document 50544-0008 (Ajwa *et al.*, 2014). The emissions were normalized to 327 (for broadcast shank) or 246 (for drip) lbs/ac application rate;
c: rounded to the closest whole hour.

For other application and tarp scenarios described on AITC product labels, such as deep shank without tarp, data from other soil fumigants were used as surrogates to estimate the emissions.

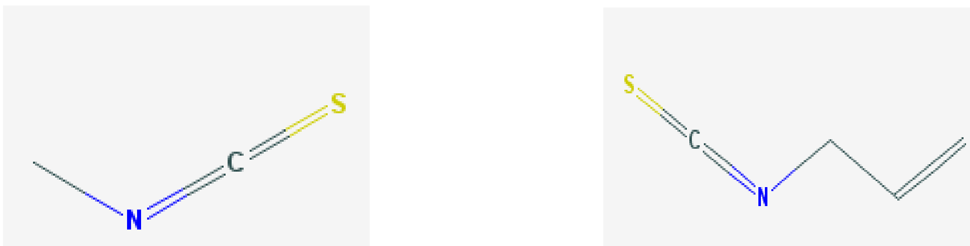
Selecting surrogate emission data:

This memorandum analyzed all fumigants registered in California and chosen five of them to consider as potential candidates of surrogate emission data. Based on DPR's Pesticide Use Reporting (PUR) database, these five fumigants, i.e., 1,3-dichloropropene (1,3-D), chloropicrin (Pic), methyl bromide (MeBr), metam-sodium (M-Na), potassium N-methyldithiocarbamate (M-K) and sulfuryl fluoride (SF), were the top 5 most used organic fumigant compounds in California, implying their extensive use data available in PUR and the likelihood of finding available emission data compatible with AITC application methods.

<u>Sulfuryl fluoride</u>. SF is primarily used for structural fumigation in California, thus was removed from being considered as surrogate data.

<u>Methyl isothiocyanate (MITC)</u>. Similar to AITC, M-Na and M-K are both used as soil fumigants. After application, M-Na and M-K degrade and produce methyl isothiocyanate

(MITC, Figure 2), which is responsible for the fumigation property. MITC is structurally similar to AITC and the physiochemical properties of MITC (boiling point, water solubility and hydrophobicity) are also similar (Table 5). Thus MITC was first considered as an ideal source of surrogate data.

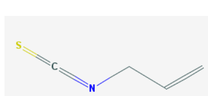
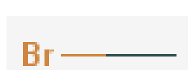
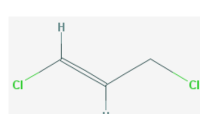
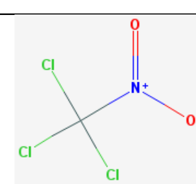
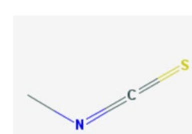


(a) MITC (b) AITC

Figure 2. Structure of methyl isothiocyanate (MITC, a) and allyl isothiocyanate (AITC, b). Images are copied from PubChem (NIH, 2019).

As shown in Table 6, applications of MITC products include methods such as soil-drenching or using overhead sprinklers, which are not allowed for Dominus® (DPR, 2015). MITC emission studies also often used "water cap" by irrigating the treated field once or multiple times, which was supposed to decrease MITC emissions. However "water cap" is not a required practice on Dominus® label. For application methods with no AITC emission data and in need of surrogate data (e.g., deep shank w/o tarp), there is no MITC emission data available. In addition, available MITC data often showed maximum MITC emissions at night, which is different from available AITC emission data which show maximum emissions during the day (Figure 3).

Table 5. Physiochemical properties of allyl isothiocyanate (AITC), methyl bromide (MeBr), 1,3-dichloropropene (1,3-D) and chloropicrin (Pic)

	AITC	MeBr	1,3-D	Pic	MITC
Structure					

Formula	C_4H_5NS	CH_3Br	$C_3H_4Cl_2$	CCl_3NO_2	C_2H_3NS
Molecular weight	99.2	94.9	111.0	164.4	73.1
Boiling point (°C)	148-154	3.5	108	112	119
Water solubility (g/L, at 20 °C)	2	18.5	2	1.9	7.6
K_{ow} (log)	2.2	1.2	2.0	2.1	0.94

Data obtained from Jones (2013) and PubChem.

Table 6. Application methods of metam sodium and metam potassium that produce methyl isothiocyanate after field applications

Application method #	Application method
2	metam sodium and metam potassium field soil fumigation recommended permit conditions for **drench** applications
3	metam sodium and metam potassium field soil fumigation recommended permit conditions for **drip** applications
4	metam sodium and metam potassium field soil fumigation recommended permit conditions for **flood** applications
5	metam sodium and metam potassium field soil fumigation recommended permit conditions for **power mulcher** and **rotary tiller (rototiller)** applications
6	metam sodium and metam potassium field soil fumigation recommended permit conditions for **rod bar** applications
7	metam sodium and metam potassium field soil fumigation recommended permit conditions for **shank** applications
8	metam sodium and metam potassium field soil fumigation recommended permit conditions for **spray blade with soil cap** applications
9	metam sodium and metam potassium field soil fumigation recommended permit conditions for **sprinkler** applications

This table was copied DPR (2015). The application methods are highlighted in bold.

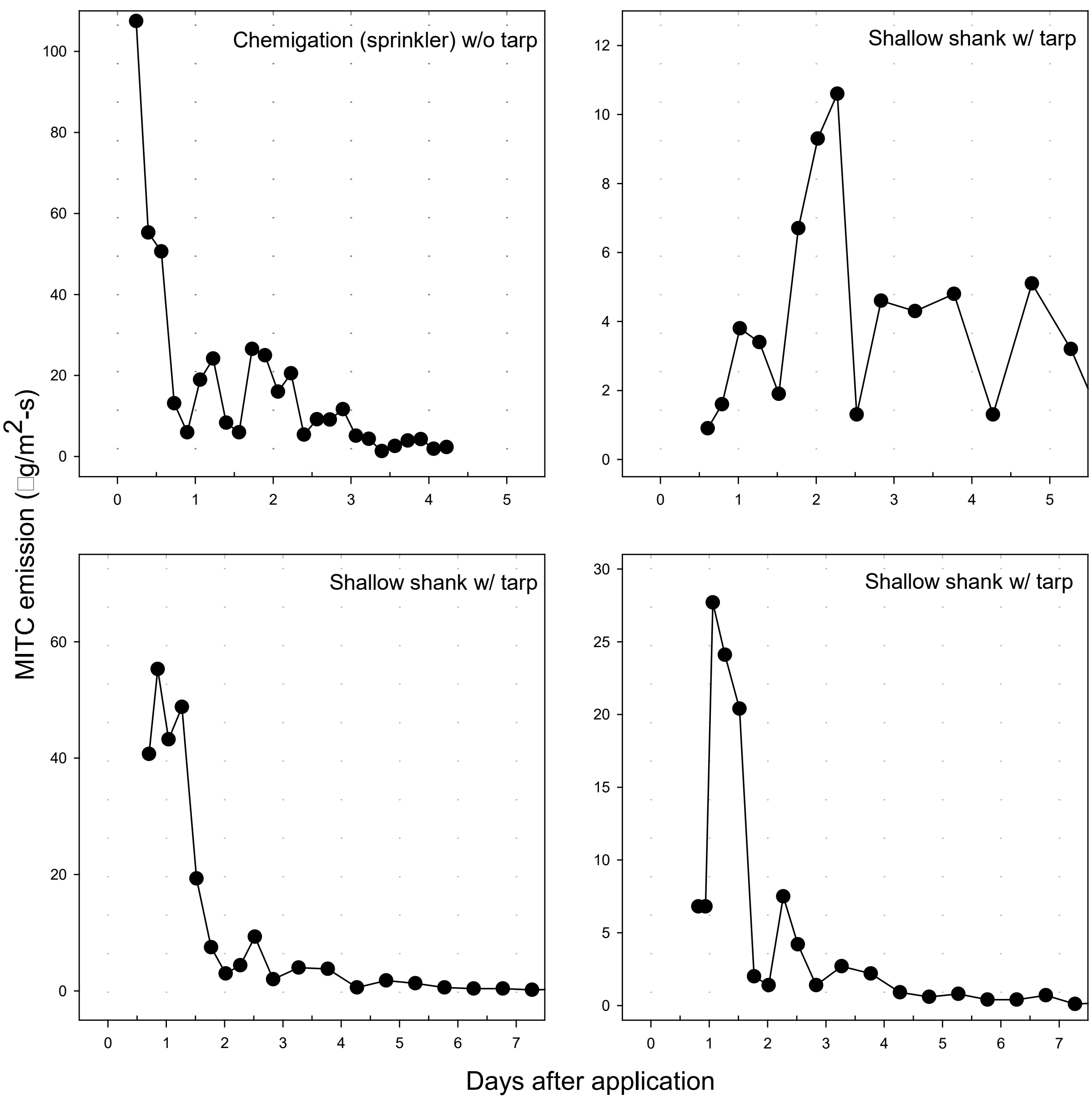


Figure 3. Methyl isothiocyanate (MITC) emissions from soil (Ajwa *et al.*, 2011; Sullivan, 2011). The figure only shows the emissions within the first 5 days from the day of application. Original emissions without application rate adjustments were used.

MeBr, 1,3-D and Pic. MeBr, 1,3-D and Pic are the other three soil fumigants with significant use in California. Table 6 shows their respective structures, and compared to MeBr, physiochemical properties of 1,3-D and Pic are more similar to AITC: 1). The octanol-water partition coefficient (K_{ow}) of 1,3-D and Pic are close to AITC, suggesting their similar affinity to soil particulates especially soil organic matter, 2). The water solubility of 1,3-D, Pic and AITC are similar, implying their similar transport potential to soil surface via soil water, and 3). 1,3-D and Pic have lower boiling points and higher vapor pressure than AITC, which means 1,3-D and Pic have greater volatility and higher emission potential from soil. All these reasons imply that compared to MeBr, 1,3-D and Pic are better surrogates of AITC emission data. In addition, for the application scenarios with available AITC data, we found similar emission rates between AITC and 1,3-D/Pic, which further supports using 1,3-D/Pic data as surrogate for applications without AITC data. Details on these comparisons will be provided in the latter appraisal section.

This assessment identified a total of 44 Pic and 1,3-D applications with complete soil emission data. Table A1 in the Appendix summarizes these applications and groups them based on their application methods and tarp conditions.

There were ten applications that treated soil simultaneously with both 1,3-D and Pic (Knuteson and Dolder, 2000; van Wesenbeeck and Phillips, 2000; Ajwa, 2009; Ajwa and Sullivan, 2010; Sullivan and Chellemi, 2010; Sullivan, 2012). These applications included broadcast shank with TIF-tarp, broadcast shank with PE-tarp, drip with virtually impermeable film (VIF)-tarp and drip with PE-tarp (Table 7). Most of these studies showed 1,3-D and Pic had comparable emission rates. Also, application method is considered as the major factor determining applicator pesticide exposures. Therefore, emission data from both 1,3-D and Pic are considered in this analysis.

Limited 1,3-D and Pic emission data was found for VIF-tarp applications. There were only one bed shank and one drip application with VIF-tarp, and no broadcast shank with VIF-tarp (Knuteson and Dolder, 2000; Rotondaro, 2004). The lack of data makes it difficult to analyze the emission variability of VIF-tarp applications among different studies. For instance, Pic emissions from a drip VIF-tarp field are about eight times that of Pic emissions from a drip TIF-tarp field. However, Pic emissions from a bed shank VIF-tarp field are comparable to the emissions from the TIF-tarp field. The U.S. Environmental Protection Agency (US EPA) often grouped VIF and TIF films together and assigned them the same buffer zone reduction credits (US EPA, 2018). For instance, for products containing 1,3-D and Pic, both Klerks VIF (1.30 mil) and Ginegar Ozgard T-Plus TIF (1.5 mil) were granted a 60% reduction in buffer zone distance. Considering the low number of VIF studies and US EPA's practice, emissions from VIF- tarp studies were grouped with TIF-tarp ones in the appended Table A1.

Table 7. Maximum emissions of 1,3-dichloropropene (1,3-D) and chloropicrin (Pic) from applications using both fumigants[a]

Application method	Tarp type[b]	Document No.	Field	Maximum measured emission[c] ($\mu g/m^2/s$)	
				1,3-D	Pic
Broadcast shank	TIF	50046-0198	1	9.2	6.2
			2	7.8	5.1
			3	6.3	4.0
			4	5.9	9.9
		199-0142	2	15.5	11.2
	PE	199-0143	1	106.1	65.5
			2	109.9	68.3
		199-0142	1	101.9	13.7
Drip	VIF	50046-0153	1	27.7	52.0
	PE	50046-0152	1	73.6	48.8

a: data were obtained from various sources (Knuteson and Dolder, 2000; van Wesenbeeck and Phillips, 2000; Ajwa and Sullivan, 2010; Sullivan and Chellemi, 2010; Sullivan, 2012);
b: the treated fields were covered with totally impermeable (TIF), virtually impermeable (VIF), or polyethylene (PE) film;
c: the emissions were normalized to 327 (for broadcast shank) or 246 (for drip) lbs/ac application rate.

Non-tarp applications are not common in California, but are allowed on AITC labels for both shank and drip applications (Spurlock, 2013). With the same application methods, non-tarp fields usually generate higher emissions than tarp fields, as the emitted fumigants can freely escape from the soil surface to the air. Therefore, to be consistent with label-permit conditions, emissions under non-tarp conditions were estimated in this analysis. AITC labels only allow deep (>1 in) drip non-tarp scenarios but permit both shallow and deep (>17 in) injections for shank applications. Therefore, emissions of shank injection with both injection depths will be developed.

Most maximum emissions in Table A1 were measured from periods shorter than 8 hours (range: 4-12 hours). This analysis used the maximum measured emissions as a conservative surrogate to represent the 8 hr-TWA emissions, except for the shallow shank w/ tarp application which observed the maximum emission from a 12-hr measurement period so the 8-hr TWA emission was estimated using a peak-to-mean adjustment method as described in Barry (2000) (Table 8). To determine emission rates for residential bystander exposure assessment, for each application scenario, rolling 24-hr periods with the maximum emission rates were extracted from the entire emission profiles and used to generate the hourly emission rates for 24 hours. The emission rates for 8- and 24-hr time periods are summarized in Tables 9. For each application scenario without AITC data, the emission rates in Table 9 were obtained from studies that showed the highest emissions of 1,3-D or Pic. The emission profiles of selected 1,3-D or Pic applications are presented in Figure 4. Also as noted in Table 9, for tarp applications, the emission rates were obtained from studies using PE tarps, as PE tarp applications generated higher emissions than TIF or VIF tarp applications.

Table 8. Durations of measured maximum emissions for different studies selected as allyl isothiocyanate (AITC) emission surrogate data

Application[a]	Fumigant[b]	Duration of measured max emission[c] (hr)
Shallow shank w/ tarp	AITC	12
Shallow shank w/o tarp	1,3-D	5
Deep shank w/o tarp	Pic	6
Drip w/ tarp	AITC	6
Deep drip w/o tarp	1,3-D	5

Data were obtained from various sources (Gillis, 1998; van Wesenbeeck, 1998; Ajwa, 2008; Ajwa *et al.*, 2014);
a: shank injection < 17 in is considered as shallow; Drip tape buried >1 inch is considered as deep;
b: Pic=chloropicrin, 1,3-D=1,3-dichloropropene;
c: rounded to the closest whole hour.

Table 9. Maximum emission rates for different application methods

Application scenario[a]	Source of data[b]	Maximum TWA emission[c] ($\mu g/m^2/s$)	
		8-hr	24-hr[d]
Shallow shank w/ tarp (PE[e])	AITC	12.1	8.1
Shallow shank w/o tarp	1,3-D	116.8	79.9
Deep shank w/o tarp	Pic	76.2	51.5
Drip w/ tarp (PE)	AITC	79.9	53.4
Drip w/o tarp	1,3-D	187.0	95.6

Data were collected from various sources (Ajwa, 2008; Ajwa et al., 2014; Gillis, 1998; van Wesenbeeck, 1998).

a: shank injection < 17 in is considered as shallow. Drip tape buried ⩽1 inch is considered as shallow. Emissions from PE tarp applications were used;

b: where data were cited. AITC=allyl isothiocyanate, 1,3-D=1,3-dichloropropene, Pic=chloropicrin;

c: maximum time-weighted average (TWA) emissions. The emission rates have been normalized to 327 (for shallow shank w/ tarp and deep shank w/o tarp) or 246 (for shallow shank w/o tarp, drip w/ tarp and drip w/o tarp) lbs/ac application rates. For shallow shank w/o tarp application, the emission rates were summarized from a study using bed applications. 327 and 246 lbs/ac respectively represent the maximum application rates allowed in the Dominus® product label for broadcast and bed/strip applications;

d: this represents the average of 24 hourly emission rates. Hourly rates for that 24-hour period will be used in the later air dispersion modeling for residential bystander exposure assessment;

e: emission data were summarized from applications using polyethylene (PE) tarp.

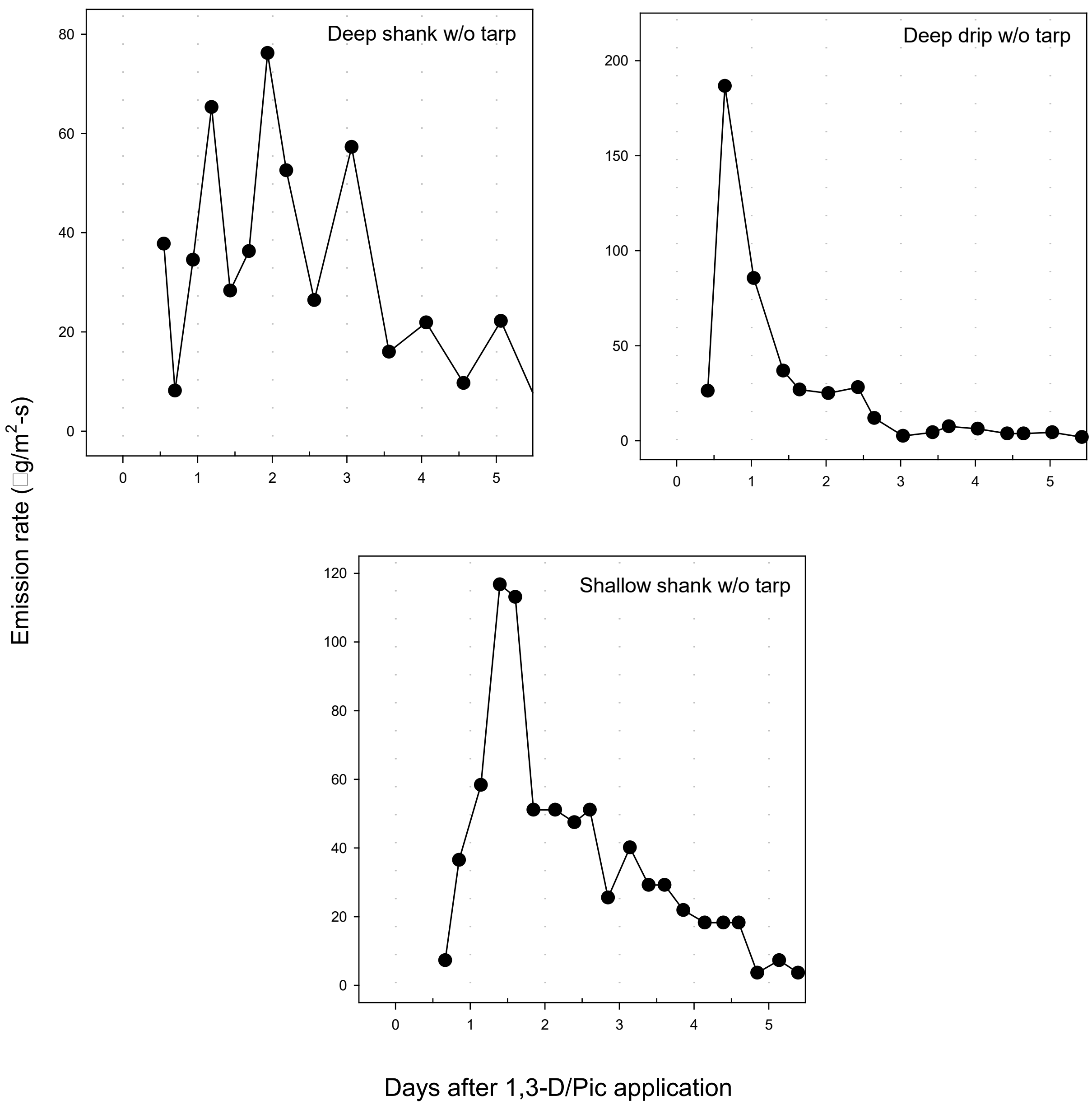


Figure 4. 1,3-Dichloropropene (1,3-D) and chloropicrin (Pic) emissions from soil. Data were obtained from various studies (Gillis, 1998; van Wesenbeeck, 1998; Ajwa, 2008). These applications were selected as surrogate data for scenarios without allyl isothiocyanate (AITC) emission data. The figure only shows the emissions within the first 5 days from the day of application. The emission rates have been normalized to 327 (for deep shank w/o tarp) or 246 (for shallow shank w/o tarp and deep drip w/o tarp) lbs/ac application rates. For shallow shank

w/o tarp application, the emission rates were summarized from a study using bed applications. 327 and 246 lb/ac respectively represent the maximum application rates allowed in the AITC product label for broadcast and bed/strip applications respectively.

Methodology appraisal:

This analysis employs all available information to estimate AITC emission data for bystander exposure assessment, and during this process, uncertainties have been identified. The section below addresses all uncertainties and the rationales underlying the selection and development of the proposed method.

Use of AITC emission study. This analysis reviewed and used the only AITC soil emission study submitted by the registrant, as this is the pesticide specific soil emission data (Ajwa *et al.*, 2014). However, this study only collected one set of emission data for each application and tarp scenario, so the variability of AITC emissions among different fields and weather conditions is not known. To account for the variability of bystander exposures under different meteorological and field conditions and for the short-term exposure assessment purpose, in a companion memorandum, bystander exposures were estimated by extracting maximum emission rates from the AITC emission profiles and conducting AERMOD modeling in six different regions around the state (Jiang, 2021). For each selected region, daily modeling was performed for five years and the upper-end values from the modeling results, i.e., maximum of daily 95th percentile value from all six regions and five years, were used to estimate the bystander exposures.

Using 1,3-D and Pic emissions as surrogate data. 1,3-D and Pic were selected as surrogate data to estimate AITC emissions for scenarios without AITC-specific data. Based on currently available information, 1,3-D and Pic are considered to be the two most suitable surrogates for estimating potential bystander exposure because of similar physicochemical properties, emission profiles, and application methodologies, as well as availability of emission data for application scenarios without AITC emission data. As shown in Table 5, 1,3-D and Pic have water solubility and hydrophobicity values close to AITC, implying their similar sorption potential to soil particles and upward transport to the soil surface via soil water. The vapor pressure of 1,3-D and Pic is greater than AITC, implying their emissions from soil could be greater than AITC.

AITC emission rates could be different from 1,3-D and Pic; however, this difference cannot be quantified by directly comparing AITC and 1,3-D (or Pic) emissions as there is only one set of AITC emission data for each application and tarp scenario and the variability of AITC field emissions is unknown. As shown in Table 10, for the four application and tarp scenarios with AITC data, AITC emissions are always within the range of Pic and 1,3-D emissions. Therefore, this analysis assumes the emission potential of AITC is the same as 1,3-D and Pic, and for the application scenarios without AITC data, this assessment used the studies that observed the highest 1,3-D or Pic emissions as the surrogate.

Table 10. Maximum emissions of 1,3-dichloropropene (1,3-D), chloropicrin (Pic) and allyl isothiocyanate (AITC) for different time-weighted average (TWA) periods[a]

Document No.	Field	Fumigant	Maximum TWA emission[b] ($\mu g/m^2/s$)	
			8 hr	24 hr
Broadcast shank with TIF or VIF tarp[c]				
50544-0008	2	AITC	8.7	2.1
50046-0198	1	1,3-D	9.2	5.8
50046-0198	1	Pic	7.5	3.5
50046-0198	2	1,3-D	7.8	7.0
50046-0198	2	Pic	6.3	3.6
50046-0198	3	1,3-D	6.3	2.9
50046-0198	3	Pic	4.9	1.7
50046-0198	4	1,3-D	7.1	3.1
50046-0198	4	Pic	12.1	9.2
199-0142	2	1,3-D	18.9	8.5
199-0142	2	Pic	11.2	6.3
123-0220	2	Pic	28.7	8.8

123-0220	5	Pic	10.7	5.2
Broadcast shank with PE tarp[d]				
50544-0008	4	AITC	12.1	8.1
199-0142	1	1,3-D	101.9	63.6
199-0142	1	Pic	13.7	8.4
199-0143	1	1,3-D	106.1	80.7
199-0143	1	Pic	65.5	44.6
199-0143	2	1,3-D	109.9	82.8
199-0143	2	Pic	68.3	46.9
199-0072	1	Pic	22.2	11.0
199-0072	2	Pic	54.6	27.9
199-0130	1	Pic	68.6	40.2
123-0220	1	Pic	53.7	29.1
Drip with TIF or VIF tarp				
50544-0008	1	AITC	40.9	13.8
199-0136	2	Pic	6.7	4.3
50046-0153	1	1,3-D	27.7	15.0
50046-0228	1	1,3-D	10.6	5.4
50046-0153	1	Pic	52.0	19.9
Drip with PE tarp				
50544-0008	3	AITC	79.9	53.4
199-0112	1	Pic	116.0	36.8
199-0136	1	Pic	95.6	55.5
199-0136	3	Pic	26.0	16.1
199-0136	4	Pic	62.0	34.7

50046-0152	1	Pic	48.8	18.0
50046-0152	1	1,3-D	73.6	30.1

a: emission data were collected from various sources (Gillis, 1998; Knuteson and Dolder, 2000; van Wesenbeeck and Phillips, 2000; Rotondaro, 2004; Ajwa, 2009; Ajwa, 2010a; Ajwa and Sullivan, 2010; Sullivan, 2012; Ajwa *et al.*, 2014; Ajwa, 2015);
b: emissions from different studies were normalized to the same 327 (for broadcast shank) or 246 (for drip) lbs/ac application rate;
c: TIF = totally impermeable film, VIF = virtually impermeable film;
d: PE = polyethylene film.

Comparison of field emission data with HYDRUS

Among the five application methods assessed in this document, three of them do not have AITC specific emission data. Hence, this assessment filled the emission data gaps using 1,3-D or Pic as surrogate. Alternatively, the data gaps can also be addressed by HYDRUS computer model that simulates fumigant fate and transport in soil column and estimates the rate and amount escaping from soil surface over time. If chemical-specific physiochemical parameters (e.g., water-air partitioning coefficient, soil-water partitioning coefficient, degradation half-life, etc.) are available, HYDRUS simulation is considered as a refinement method (i.e., higher Tier assessment) to estimate emission rates compared to the surrogate approach (i.e., lower Tier assessment). To provide support for the use of surrogate method, some HYDRUS modeling results on AITC applications are made available to the Human Health Assessment Branch by the Environmental Monitoring Branch (EM). For each of the application methods and each soil types, hourly AITC emission rates were modeled using the two-dimensional version of HYDRUS (HYRDUS-2D) and from the start of application to up to 10 days.

Tables 11 and 12 compare 8- and 24-hr emission rates collected from field studies with the rates estimated by HYDRUS-2D. Details on the HYDRUS-2D settings and validations will be provided elsewhere by EM. The comparisons in Table 11 are HYDRUS-2D results with AITC-specific emission data, whereas the comparison in Table 12 are between HYDRUS-2D and surrogate data using 1,3-D or Pic. These comparisons demonstrate that using 1,3-D or Pic as surrogate meets the need of AITC exposure assessment and the surrogate emission rates are comparable or higher than the rates generated by HYDRUS-2D. Among the scenarios in Table 11 and Table 12, both overestimation and underestimation of the modeled emission rates occurred, suggesting that further investigation is needed for assessing the advantage of HYDRUS-2D over surrogate data approach for assessing the AITC bystander exposures.

Table 11. Comparison of emission rates between field studies and HYDRUS-2D estimations for the four application methods with AITC-specific data available

Application method	Emission rates ($\mu g/m^2/s$)	
	from field studies	from HYDRUS-2D[a]
8-hr TWA[b] emission		
Shallow broadcast shank w/ TIF[c] tarp	8.7	1.3-2.0
Shallow broadcast shank w/ PE tarp	12.1	21.1-70.8
Drip with TIF tarp	41.0	1.9-3.3
Drip with PE tarp	79.9	60.5-100.2
24-hr peak emission		
Shallow broadcast shank w/ TIF tarp	2.1	0.7-1.1
Shallow broadcast shank w/ PE tarp	8.1	14.7-46.2
Drip with TIF tarp	13.9	1.1-2.1
Drip with PE tarp	53.4	31.8-66.3

a: HYDRUS-2D was used to model AITC emissions from 16 different types of soils. Correspondingly, results from HYDRUS-2D were expressed as a range (minimum – maximum) of the modeled results;
b: TWA=time-weighted average;
c: TIF=totally impermeable film, PE=polyethylene.

Table 12. Comparison of emission rates between field studies and HYDRUS-2D estimations for the two application methods using surrogate data from 1,3-dichloropropene or chloropicrin

Application method	Emission rates ($\mu g/m^2/s$)	
	from field studies	from HYDRUS-2D[a]

8-hr TWA[b] emission		
Deep broadcast shank w/o tarp	76.2	7.0-15.6
Drip w/o tarp	187.0	59.5-158.3
24-hr peak emission		
Deep broadcast shank w/o tarp	51.5	5.8-13.2
Drip w/o tarp	95.6	34.7-109.4

a: HYDRUS-2D was used to model AITC emissions from 16 different types of soils. Correspondingly, results from HYDRUS-2D were expressed as a range (minimum – maximum) of the modeled results;
b: TWA=time-weighted average.

Injection depth and other emission control practices. Increasing injection depth was considered as an emission mitigation measure and this is supported by previous modeling efforts using HYDRUS (Spurlock, 2013). However, this could not be verified using 1,3-D and Pic field emission data. For instance, for broadcast shank TIF-tarp scenarios, Pic emission from deep shank injection was comparable to shallow shank emissions (Ajwa, 2009; Ajwa and Sullivan, 2010; Sullivan, 2012). To be consistent with the label-permitted application scenarios for AITC, this analysis determined emissions for both shallow and deep shank un-tarp scenarios. However, the variabilities of the emission rates for those scenarios cannot be assessed in this analysis, as there are not enough 1,3-D and Pic non-tarp emission studies available.

AITC labels contain several "*non-tarped type sealing*" methods, including the use of overhead sprinklers to irrigate treated fields, and the use of roller/packers to compact soil surface and remove shank chisel traces. However, the efficacy of those methods on decreasing emissions is not well categorized or quantified under field conditions, and there is not enough 1,3-D or Pic emission data that used these practices. One study used a roller to compact soil surface after broadcast shallow shank injections and before PE-tarp, but the 1,3-D and Pic emissions from this application are comparable to other broadcast shallow shank PE-tarp applications (Sullivan and Chellemi, 2010). Therefore, those non-tarped sealing methods are not considered in this analysis.

Conclusion:

This memorandum describes a methodology of using 1,3-D and Pic soil emission data to determine AITC emissions for application and tarp conditions where AITC emission data is not available. This memorandum also describes why soil emission data from other surrogates are not appropriate for use in place of AITC, including metam sodium and metam potassium that generate MITC. 1,3-D and Pic were selected as surrogates because: 1) they have similar physiochemical properties to AITC, 2) their application methods are similar to AITC, 3) for application scenarios without AITC data, Pic and 1,3-D emission data are available, and 4) for application scenarios with available AITC emission data, 1,3-D and Pic showed similar emission patterns and comparable emission rates to AITC. The developed AITC emission data, as summarized in Table E1, will be further used for short-term bystander exposure assessment.

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Appendix:

Table A1. Summary of maximum chloropicrin (Pic) and 1,3-dichloropropene (1,3-D) soil emissions from studies used in this analysis[a]

Document No.	Field	Fumigant	Other application condition	Maximum measured flux[b]	
				$\mu g/m^2/s$	Time
Broadcast shank with totally impermeable film (TIF) tarp					
50046-0198	1	1,3-D		9.2	1245-1845 (2nd Day)[c]
		Pic		6.2	0645-1845 (3rd day)
	2	1,3-D		7.8	1245-1845 (2nd day)
		Pic		5.1	0645-1845 (4th day)
	3	1,3-D		6.3	1300-1900 (2nd day)
		Pic		4.0	1900-0700 (5th day)
	4	1,3-D	KTS[d]	5.9	0700-1900 (3rd day)
		Pic	KTS	9.9	0700-1900 (3rd day)
199-0142	2	1,3-D		15.5	0630-1830 (3rd day)
		Pic		11.2	1230-1830 (1st day)
123-0220	2	Pic		28.7	0830-1330 (1st day)
	5	Pic	Deep[e]	10.7	0030-0800 (3rd day)
Broadcast shank with polyethylene film (PE) tarp					
199-0142	1	1,3-D		101.9	1230-1830 (2nd day)
		Pic		13.7	1230-1830 (2nd day)
199-0143	1	1,3-D	Low disturbance[f]	106.1	1230-1830 (2nd day)
		Pic	Low disturbance	65.5	1230-1830 (2nd day)
	2	1,3-D		109.9	1230-1830 (2nd day)
		Pic		68.3	1230-1830 (2nd day)
199-0072	1	Pic		22.2	1230-1830 (3rd day)

	2	Pic		54.6	1200-1200 (2nd day)
199-0130	1	Pic		68.6	1330-1930 (2nd day)
123-0220	1	Pic		53.7	1330-1845 (1st day)
Broadcast shank without tarp					
50046-0067	1	1,3-D		26.4	1900-0700 (3rd Day)
50046-0127	1	1,3-D		99.5	1200-1720 (2nd Day)
199-0130	3	Pic		100.4	1930-0130 (2nd Day)
	4	Pic	Deep	76.2	1930-0130 (2nd Day)
Bed shank with totally impermeable (TIF) or virtually impermeable film (VIF) tarp					
199-0140	1	Pic	TIF	25.8	0700-1200 (1st Day)
123-0220	4	Pic	TIF, Deep	7.0	0800-1830 (3rd Day)
52971-0112	1	Pic	VIF	6.8	0330-0930 (3rd Day)
Bed shank with PE tarp					
52971-0112	2	Pic		47.5	1530-2130 (2nd Day)
	3	Pic		52.7	1530-2130 (2nd Day)
Bed shank without tarp					
50046-0088	1	1,3-D	Deep	35.9	1330-1930 (3rd Day)
50046-0127	2	1,3-D		113.1	1200-1700 (2nd Day)
Drip with TIF or VIF tarp					
50046-0153	1	1,3-D	VIF	27.7	1300-1900 (1st Day)
		Pic	VIF	52.0	1300-1900 (1st Day)
199-0136	2	Pic	TIF	6.7	1900-0100 (1st Day)
50046-0228	1	1,3-D	TIF	10.6	1300-1900 (1st Day)
Drip with PE tarp					
199-0112	1	Pic		116.0	1130-1530 (1st Day)
199-0136	1	Pic		95.6	1900-0100 (1st Day)

	3	Pic	KTS, water seal[g]	26.0	1300-1900 (1st Day)
	4	Pic	water seal	62.0	1300-1900 (1st Day)
50046-0152	1	Pic		48.8	1200-1700 (1st Day)
		1,3-D		73.6	1200-1700 (1st Day)
Drip without tarp					
50046-0179	1	1,3-D	Deep	187.0	1300-1800 (1st Day)
199-0131	1	Pic	Deep	144.3	1300-1900 (1st Day)

a: data were obtained from various sources (Knuteson *et al.*, 1992; Knuteson *et al.*, 1995; Beard *et al.*, 1996; Gillis, 1998; van Wesenbeeck, 1998; Knuteson and Dolder, 2000; van Wesenbeeck and Phillips, 2000; Rotondaro, 2004; Ajwa, 2009; Rotondaro, 2009; Ajwa, 2010b; Ajwa, 2010a; Ajwa and Sullivan, 2010; Sullivan and Chellemi, 2010; Ajwa *et al.*, 2011; Sullivan, 2012; Ajwa, 2015);
b: the emissions were normalized to 327 (for broadcast shank) or 246 (for drip) lbs/ac application rate;
c: start time, end time and the day after application when the maximum flux was measured;
d: Potassium thiosulfate (KTS) was applied to soil during application;
e: shank injection >17 inches and drip application >1 inch below soil surface are considered as deep application;
f: This application used a low disturbance application rig and a press pan to remove chisel traces and compact soil;
g: water was applied to soil in the furrows.

B. Appendix 2

Determination of allyl isothiocyanate air concentrations around fields fumigated using shank or drip applications – revised

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DATE: January 25, 2022

SUBJECT: DETERMINATION OF ALLYL ISOTHIOCYANATE AIR CONCENTRATIONS AROUND FIELDS FUMIGATED USING SHANK OR DRIP APPLICATIONS - REVISED

Executive summary:

The California Department of Pesticide Regulation (DPR) has received a request for the registration of allyl isothiocyanate (AITC) as a soil fumigant in California. This memorandum describes the use of the air dispersion model AERMOD to estimate AITC air concentrations around a treated field using application-specific emission information. AITC has not previously been used as a fumigant in California. Therefore, the pesticide use data needed for the modeling is not available. This analysis assumes that AITC use areas will be similar to other fumigants including 1,3-dichloropropene, chloropicrin, methyl bromide, metam-sodium and potassium N-methyldithiocarbamate. AITC air concentrations were modeled from emissions of five different application scenarios: shallow shank with tarp, shallow shank without tarp, deep shank without tarp, drip with tarp and deep drip without tarp, and three average time periods (4, 8 and 24 hr), using emission rates detailed in an companion memorandum (Jiang, 2021). This analysis also used 2013-2017 meteorological data from six counties (Merced, Kern, Santa Cruz, Ventura, Riverside and Siskiyou) with three different field sizes (i.e., 1, 40, and 100 acre) and three distances from the treated field edge (i.e., 0, 25 and 100 ft). At each distance, AITC concentrations were estimated at two heights corresponding to the breathing zone of adults and children (i.e., 5 and 1.7 ft). Estimated AITC air concentrations for the five modeled application scenarios can be found in the "Results section," Table 6 through 10. Values in these tables can be used to assess occupational and residential bystander exposures.

Background:

Background information of this analysis has been detailed in a previous memorandum (Jiang, 2021). Briefly, DPR received an application package from ISAGRO USA, Inc. (ISAGRO) to register a product containing AITC for use in California:

DPR track ID: 280548-N
Product name: Dominus®
US Environmental Protection Agency (US EPA) Registration No. 89285-2
Active ingredient: allyl isothiocyanate (96.3%)

The label of this product can be found on the U.S. Environmental Protection Agency (US EPA) website (submitted to US EPA on December 28, 2015; https://www3.epa.gov/pesticides/chem_search/ppls/089285-00002-20151228.pdf). ISAGRO is requesting that Dominus® be used as a soil fumigant and applied through broadcast and bed shank injections, or via drip irrigation systems.

DPR conducts a comprehensive human health risk assessment prior to the registration of a new fumigant. The health risk assessment includes bystander exposure to fumigants that have escaped from the soil of treated fields. As of April 2019, DPR had not received any studies from ISAGRO that monitored bystander exposure to AITC emissions or identified AITC air concentration data from open literature that can be used for the bystander exposure assessment.

A previous companion memorandum determined AITC soil emission rates under 5 different application and tarp conditions based on AITC specific and suitable surrogates identified (i.e., 1,3-dichloropropene (1,3-D) and chloropicrin (Pic)) data. In that memorandum, the AITC-specific data was used to determine the emission rates for shallow shank application with polyethylene (PE) tarp and drip application with PE tarp (Jiang, 2021). For the remaining three application scenarios when AITC-specific data were not available (shallow shank without tarp, deep shank without tarp and deep drip without tarp), 1,3-dichloropropene (1,3-D) and chloropicrin (Pic) emission data were used as surrogate. In addition, that memo also describes in detail why 1,3-D and Pic emission data were selected as appropriate surrogates compared to other active ingredients, such as methyl isothiocyanate (MITC), because of similar physiochemical properties, application methodologies and emission profiles, as well as availability of data for application scenarios in the absence of AITC-specific data. The emission rates of AITC were determined for two periods (8 and 24 hr), which are consistent with the time periods used in toxicity tests and the defaults for occupational and residential exposure assessment.

In the current analysis, the 8- and 24-hr emission rates were input into an air dispersion model (AERMOD) to estimate AITC air concentrations around a fumigated field. The resulting AITC air concentrations will be used in the exposure assessment document to assess both the occupational and residential bystander exposures through inhalation.

Method:

AITC use in California

Soil fumigant products containing AITC have not been registered in California. In the absence of information on the use pattern, this analysis assumes the use of AITC will be similar to other soil fumigants: 1,3-D, Pic, methyl bromide (MeBr), metam-sodium (M-Na) and potassium N-methyldithiocarbamate (M-K). Accordingly, the use data of these five fumigants were analyzed to project the AITC use regions and application acreage.

According to DPR's Pesticide Use Reporting (PUR) database, 35 counties in California reported agricultural use of at least one of the five fumigants from 2012-2017 (DPR, 2018). The highest use counties are Kern, Fresno, Monterey, Ventura, Merced and Santa Barbara, which account for > 60% of total use in the entire state. The other counties that accounted for > 1% of the entire state fumigant use include Stanislaus, Siskiyou, San Joaquin, Santa Cruz, Tulare, San Luis Obispo, Kings, Madera, Imperial, Riverside, and Los Angeles.

These counties represent different geographic regions of California and have distinctive meteorological conditions. This analysis selected six counties to represent the regions where AITC may be possibly used (Table 1). For each selected county, this analysis modeled AITC air concentration for 1, 40 or 100 acre applications, based on the use data of aforementioned fumigants from the PUR database (DPR, 2018).

Table 1. Counties selected for air concentration modeling and the fumigant use acreage in 2012-2017

County	Region	Application acreage per use[a]		
		Median	Average	95th %ile
Merced	Central Valley	18	28	93
Kern	Central Valley	45	52	105
Santa Cruz	Central coast	10	13	34
Riverside	Desert	27	28	71
Ventura	South Coast	22	30	92
Siskiyou	Northern	18	20	56

a: This information is retrieved from the DPR Pesticide Use Reporting (PUR) database, and is based on the use of five fumigants in 2012-2017, i.e., 1,3-dichloropropene, chloropicrin, methyl bromide, metam-sodium and potassium N-methyldithiocarbamate (DPR, 2018). Each use record in PUR may contain multiple-day applications, for which the acreage number below may reflect the total area fumigated on these days.

Model setup

The algorithm to model AITC air concentrations around application fields is shown in Figure 1. This analysis used AERMOD View™ version 9.9.0, and the modeling engine integrated in this software is AERMOD (version 19191) developed by American Meteorological Society and US EPA (Lakes Environmental, 2020a). This analysis also used AERMET View™ to prepare input files (surface and profile files) required by AERMOD (Lakes Environmental, 2020b). Required inputs for AERMET and AERMOD, are shown in square shapes in Figure 1 and described in detail below:

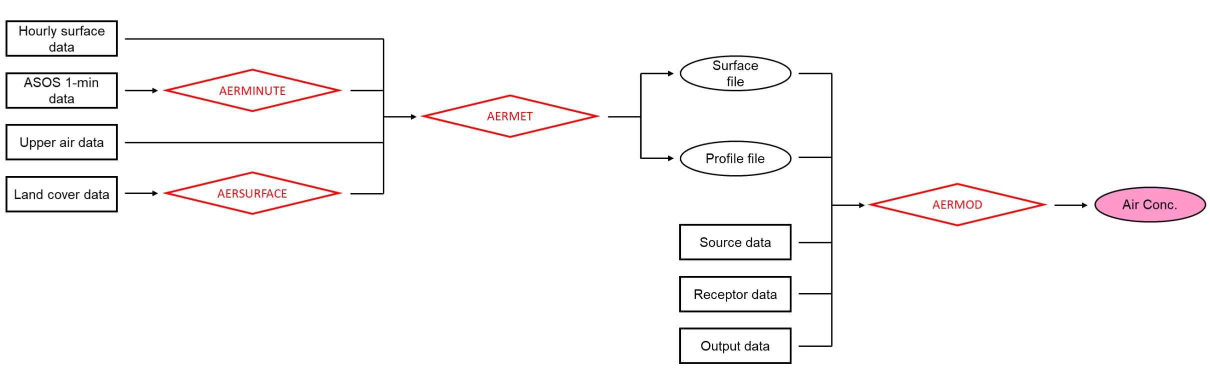

Figure 1. Modeling algorithm to estimate allyl isothiocyanate air concentration. Square, diamond and oval shapes respectively represent data inputs, processing models/tools and outputs. AERMINUTE and AERSURFACE are tools incorporated in AERMET. Surface and profile files, as outputs of AERMET, also serve as input files for AERMOD.

Hourly surface and *ASOS 1-minute data.* Hourly surface and automated surface observing system (ASOS) 1-minute data include information such as wind speed, wind direction, and cloud cover recorded from ground stations which are usually located at airports. Data used in this analysis was obtained from six airports located in the selected counties (Table 2). These airports were selected based on their distance to agricultural fields and whether ASOS 1-minute data were available. This analysis used 5-year meteorological data (2013-2017) which is the same practice done by other agencies such as California Air Resources Board and local air pollution control districts (ARB, 2019; Valley Air, 2019).

Upper air data. Upper air data is radiosonde soundings that measure meteorological parameters (e.g., temperature lapse rate, wind speed and direction, etc.) at different vertical layers of the atmosphere (USEPA, 2019). Depending on the location, each surface data station was paired with one of the three upper air stations in California or Oregon to obtain the required data (Table 2).

Table 2. Sources of surface and upper air data

County	Surface data[a]	Latitude	Longitude	Elevation (m)	Upper air[b]
Merced	KMCE	37.285N	120.512W	48	Oakland
Kern	KBFL	35.433N	119.050W	150	Vandenberg
Santa Cruz	KWVI	36.936N	121.788W	49	Oakland
Ventura	KCMA	34.217N	119.100W	23	Vandenberg
Riverside	KTRM	33.627N	116.159W	-35	Miramar
Siskiyou	KSIY	41.781N	122.468W	805	Medford

a: using airport 4-letter ICAO code;
b: Upper air data is obtained from Oakland International Airport (Oakland), Miramar naval station (Miramar), Vandenberg air force base (Vandenberg), or Medford Municipal Airport (Medford).

This analysis used AERMET to process the surface and upper air data and generate meteorological (surface and profile) files used in AERMOD to estimate AITC air concentrations. In California, AERMOD-ready meteorological files for certain areas are also available from some state and local government agencies including California Air Resources Board and local air districts. However, we did not use the meteorological files from these sources, as they either did not use the latest AERMET version for the data processing, did not have available files for analyzed areas (e.g., Siskiyou County), or did not use the most recent 5-year (2013-2017) meteorological data.

Two locations (Merced County and Riverside County) were selected to validate our meteorological data processing. At each location, air concentrations were modeled using self-processed meteorological files and then compared to the ones modeled using air pollution control district meteorological files. Some key settings in AERMET for meteorological data processing are summarized in Table 3.

Table 3. AERMET settings to prepare AERMOD-ready meteorological files

County	Merced		Riverside	
Source	DPR[a]	Valley Air[b]	DPR	South Coast AQMD[c]
AERMET Version	18081	18081	18081	16216
Year range	2013-2017	2013-2017	2012-2016	2012-2016
Surface data	KMCE[d]	KMCE	KTRM[e]	KTRM
ASOS station[f]	Yes	Yes	Yes	Yes
Upper Air	Oakland[g]	Oakland	Miramar[h]	Miramar
Use of Adj_U*	Yes	Yes	Yes	Yes
AERSURFACE setting	Airport site, average moisture, 12 sectors	unknown[i]	Airport site, average moisture, 12 sectors	unknown

a: AERMOD-ready meteorological files were generated in this analysis;
b: AERMOD-ready meteorological files were obtained from San Joaquin Valley Air Pollution Control District (Valley Air);
c: AERMOD-ready meteorological files were obtained from South Coast Air Quality Management District (AQMD);
d: Surface data is obtained from Merced Regional Airport;
e: Surface data is obtained from Jacqueline Cochran Regional Airport;
f: Whether this surface station has 1-min ASOS data;
g: Upper air data is obtained from Oakland International Airport;
h: Upper air data is obtained from Miramar Naval Air Station;
i: AERSURFACE settings were not disclosed.

Air concentrations were modeled for emissions occurring at different times and for different durations (8 and 24 hr). As shown in Figures 2 and 3, the plots followed a one-to-one correlation for both selected counties, indicating air concentrations estimated from using self-processed meteorological files are close to those from using air district AERMOD-ready files. This validates our meteorological processing method for modeling fumigant air dispersion.

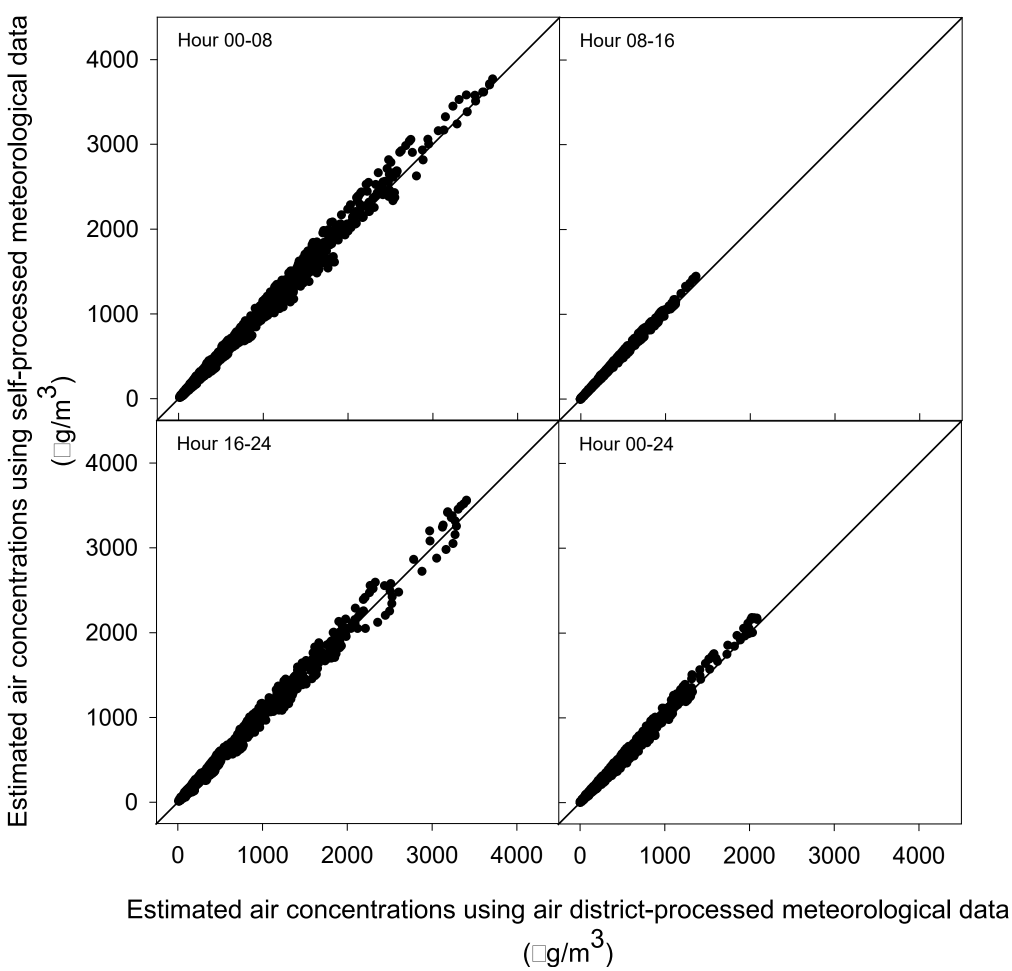

Figure 2. Correlation of estimated air concentrations in Riverside County from using self-processed or air district-provided meteorological files. The diagonal straight line represents a one-to-one correlation. Each dot represents the maximum AITC air concentration measured at one receptor around a 1 acre fumigated field with 2012-2016 meteorological data. The AITC emission rate is 100 μg/m^2/s.

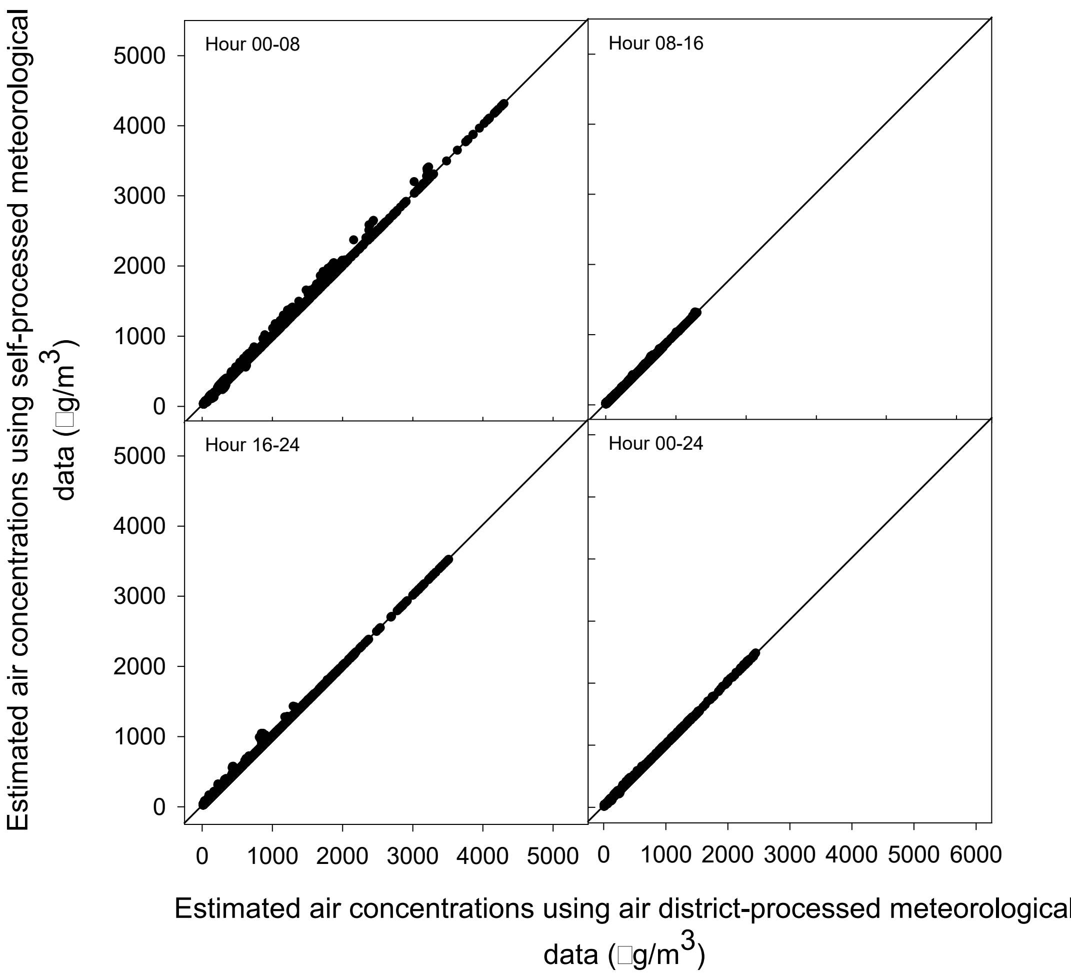

Figure 3. Correlation of estimated air concentrations in Merced County from using self-processed or air district-provided meteorological files. The diagonal straight line represents a one-to-one correlation. Each dot represents the maximum AITC air concentration measured at one receptor around a 1 acre fumigated field with 2013-2017 meteorological data. The AITC emission rate is 100 $\mu g/m^2/s$.

Land cover data. Land cover data is used to determine ground characteristics of the target area, i.e., surface roughness, albedo and Bowen ratio. This analysis used California data from National Land Cover Dataset 1992 (NLCD1992), which is the data format accepted by AERMET.

Source data. This includes data that define the time and rate of fumigant emissions from soil, as well as the size of the fields that emit fumigants. For each county mentioned above, this analysis modeled AITC air concentrations from 12 different emission scenarios (Table 4). These include two different emission durations (i.e., 8 and 24 hr), three different emission start times (i.e., Hour 00, 04, 08, 12, 16, and 20), and three different application acreages (i.e., 1, 40, and 100 ac).

Table 4. Summary of modeled emission scenarios

Emission period (hr)	Emission period (Hour)	Treated area (ac)
8	00-08, 08-16, 16-24	1, 40, 100
24	00-24	1, 40, 100

Receptor data. This defines the locations and heights where AITC air concentrations will be modeled. Dominus® label requires a minimum 25 ft from "*any occupied structure, such as a school, daycare, hospital, retirement home, business or residence.*" Therefore, occupational bystanders that works in a field adjacent to the fumigated area are not subjected to this 25 ft requirement. To understand potential bystander impacts, this analysis placed receptors at three different distances from the edge of a treated field: 0, 25, and 100 ft. At each distance, the receptors were placed about every 15 ft around the field (Figure 4). Receptors at field edge (i.e., 0 ft) were only placed at 5 ft high for occupational bystander exposure assessment; receptors at 25 and 100 ft from field edge were placed at two heights (i.e., 1.7 and 5 ft high), which respectively represent the breathing zones for children and adults.

a. Occupational bystander b. Residential bystander

Figure 4. Demonstrative illustration of receptor placement for (a). occupational bystanders and (b). residential bystanders

Output data. This analysis used 2013-2017 meteorological data, and AERMOD was set to generate for daily concentration values for each receptor. For each day, the 95th percentile value of air concentration was generated from receptors at the same distance (i.e., 0, 25 or 100 ft) from the field edge and at the same sampling height (i.e., 1.7 or 5 ft); among all the daily 95^{th} percentile air concentration values generated, the highest was used for bystander exposure assessment. Discussions on the use of 95^{th} percentile air concentration values will be provided in the appraisal section.

Results:

Effects of emission occurrence time and counties

Emission time of fumigant is critical for determining the air concentrations. A preliminary analysis was performed to model AITC air concentrations in a 4-hr emission interval at 100 $\mu g/m^2/s$ under six different times throughout a day: Hour 00-04, 04-08, 08-12, 12-16, 16-20, and 20-24. The assumption is that daytime solar radiation increases air turbulence which in turn favors pesticide dispersion and decreases the air concentration. This assumption is supported by modeling results that showed AITC air concentrations were higher from nighttime than daytime emissions when the same emission rate and duration were used (Figure 5). Considering this diurnal emission pattern, AERMOD modeling inputs preserved the time when the maximum emission rates were observed. Details and benefits of this method are discussed below and the modeled time-ranges for different application and tarp conditions are summarized in Table 5.

Instead of using the exact time when maximum emissions were observed in the field studies, this analysis incorporated wider time intervals within the modeling (Table 4). For example, by using data from an emission observed at Hour 13-19, two emission scenarios could be modeled for Hour 08-16 and 16-24. Whichever scenario resulted in a higher air concentration could then be selected for the exposure assessment, thereby providing a reasonable worst case exposure estimate. Emission data are dependent on a fixed set of field conditions (e.g., application time, injection depth, etc.) for each application scenario. However, actual fumigations can employ a variety of application settings and can occur under different field conditions. The method preserved not only the emission time observed in actual field conditions, but also allowed us to consider possible variations of emission time under diverse field use conditions.

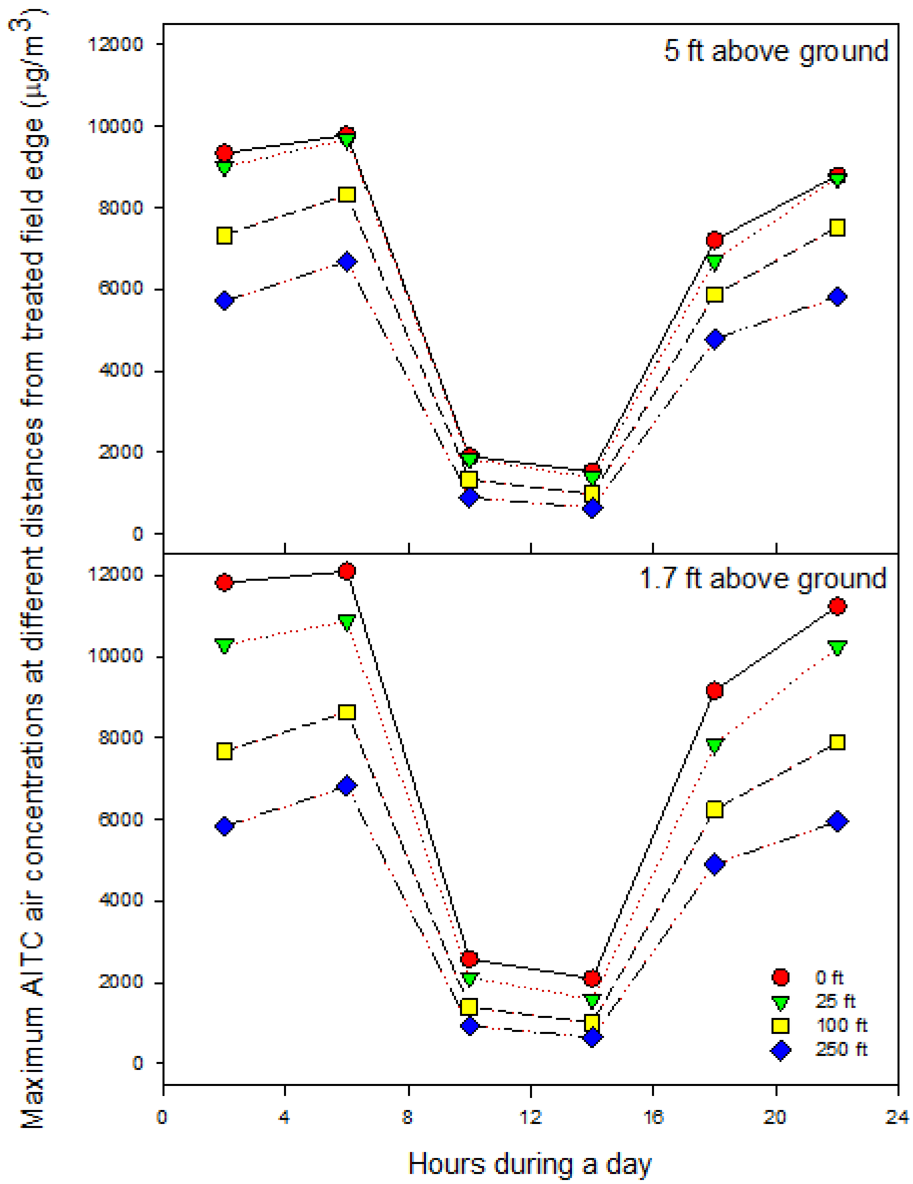

Figure 5. 4-hr averaging AITC air concentrations with different emission times. The modeled field is 40 acres and is located in Kern County. The emission rate is 100 $\mu g/m^2/s$ flux, and the emissions occur at six different times of a day (i.e., Hour 00-04, 04-08, 08-12, 12-16, 16-20 and 20-24).

Table 5. Summary of time periods modeled for air concentrations for different application and tarp conditions

Application & Tarp type	Time[a]	8-hr			24-hr
		00-08	08-16	16-24	00-24
Shallow shank with PE[b] tarp	07-19	X	X	X	X
Deep shank without tarp	19-02	X		X	X
Shallow shank without tarp	07-17[c]	X	X	X	X
Shallow drip without PE tarp	13-19		X	X	X
Deep drip without tarp	13-18		X	X	X

a: Sampling intervals (in hrs) when the maximum emission rates were measured in the field emission studies;
b: PE=polyethylene;
c: two periods (i.e., Hour 07-12 and 12-17) showed similar emissions, therefore both periods were considered for modeling.

<u>Estimated air concentrations for emissions from different application and tarp methods</u>

The estimated AITC air concentrations for 5 different application scenarios are summarized in Tables 6 through 10.

Table 6. Estimated 8-hr time weighted average air concentrations (µg/m^3) of AITC at field edge and 5ft sampling height[a]

Application scenario	1 ac[b]	40 ac	100 ac
Shallow shank with PE[c] tarp	330	982	1229
Shallow shank without tarp	3184	9481	11863
Deep shank without tarp	2077	6186	7739
Shallow drip with PE tarp	1788	5731	7148
Deep drip without tarp	4185	13412	16728

a: the application rate is 327 lbs/ac (for shallow shank with tarp and deep shank without tarp) or 246 lbs/ac (for shallow shank without tarp, drip with tarp and drip without tarp);
b: size of the fumigated field;
c: PE=polyethylene.

Table 7. Estimated 24-hr time weighted average air concentrations (µg/m^3) of AITC at 25 ft from field edge and 5 ft sampling height[a]

Application scenario	1 ac[b]	40 ac	100 ac
Shallow shank with PE[c] tarp	113	349	441
Shallow shank without tarp	1059	3425	4246
Deep shank without tarp	912	2965	3697
Shallow drip with PE tarp	732	2235	2824
Deep drip without tarp	1510	4769	5906

a: the application rate is 327 lbs/ac (for shallow shank with tarp and deep shank without tarp) or 246 lbs/ac (for shallow shank without tarp, drip with tarp and drip without tarp) lbs/ac;
b: size of the fumigated field;
c: PE=polyethylene.

Table 8. Estimated 24-hr time weighted average air concentrations (µg/m^3) of AITC at 25 ft from field edge and 1.7 ft sampling height[a]

Application scenario	1 ac[b]	40 ac	100 ac
Shallow shank with PE[c] tarp	158	404	497
Shallow shank without tarp	1393	3786	4613
Deep shank without tarp	1288	3336	4091
Shallow drip with PE tarp	1003	2591	3185
Deep drip without tarp	2016	5370	6590

a: the application rate is 327 lbs/ac (for shallow shank with tarp and deep shank without tarp) or 246 lbs/ac (for shallow shank without tarp, drip with tarp and drip without tarp);
b: size of the fumigated field;
c: PE=polyethylene.

Table 9. Estimated 24-hr time weighted average air concentrations (µg/m^3) of AITC at 100 ft from field edge and 5 ft sampling height[a]

Application scenario	1 ac[b]	40 ac	100 ac
Shallow shank with PE[c] tarp	66	282	368
Shallow shank without tarp	633	2542	3363
Deep shank without tarp	591	2367	3062
Shallow drip with PE tarp	407	1788	2367
Deep drip without tarp	864	3683	4888

a: the application rate is 327 lbs/ac (for shallow shank with tarp and deep shank without tarp) or 246 lbs/ac (for shallow shank without tarp, drip with tarp and drip without tarp);
b: size of the fumigated field;
c: PE=polyethylene.

Table 10. Estimated 24-hr time weighted average air concentrations (µg/m^3) of AITC at 100 ft from field edge and 1.7 ft sampling height[a]

Application scenario	1 ac[b]	40 ac	100 ac
Shallow shank with PE[c] tarp	75	296	381
Shallow shank without tarp	679	2617	3438
Deep shank without tarp	643	2495	3172
Shallow drip with PE tarp	462	1869	2452
Deep drip without tarp	948	3855	5067

a: the application rate is 327 lbs/ac (for shallow shank with tarp and deep shank without tarp) or 246 lbs/ac (for shallow shank without tarp, drip with tarp and drip without tarp);
b: size of the fumigated field;
c: PE=polyethylene.

Methodology appraisal:

Inclusion of 2018 meteorological data

This analysis was started in late-2018 when complete 2018 meteorological data was not available, thus the meteorological data from 2013-2017 was used. To determine whether using 2018 meteorological data generates greater air concentrations, this analysis randomly selected one of the modeled areas (Ventura County) and estimated the air concentrations for 2018. The maximum concentrations in 2018 were then compared with those using 2013-2017 meteorological data. As shown in Table 11, maximum AITC air concentrations in 2013-2017 are comparable (i.e., in the same order of magnitude) to those in 2018. Therefore, using 2013-2017 meteorological data is not expected to have a significant impact on the estimated AITC air concentrations.

Table 11. Comparison of estimated AITC air concentrations (μg/m^3) in Ventura County between 2013-2017 and 2018

Distance[b]	Estimated time-weighted average (TWA) air concentration[a] (μg/m^3)			
	8-hr		24-hr	
	2013-2017	2018	2013-2017	2018
		Adult		
0 ft	12698	11501	N/A[d]	N/A[d]
25 ft	N/A[c]	N/A[c]	3732	3215
100 ft	N/A[c]	N/A[c]	3059	2455
		Child		
25 ft	N/A[c]	N/A[c]	4276	3748
100 ft	N/A[c]	N/A[c]	3179	2573

a: The treated field is 40 ac and fumigated using deep drip application without tarp. The application rate is 246 lbs/ac;
b: distance from edge of treated field;
c: not available, 8-hr average air concentrations were only estimated for field edge for occupational bystander exposures;
d: not available, 24-hr average air concentrations were only estimated for 25 and 100 ft for residential bystander exposures.

Representativeness of weather stations

AERMOD relies on a single meteorological station to model air dispersion, thus selecting the representative station is critical to estimate AITC air dispersion after emissions from soil. All the selected stations in this analysis have automatically collected all available 1 min-ASOS data, which can help decrease the percentage of hours with missing data. These selected stations are also close to agricultural/unpaved fields where the surface characteristics are similar to areas where AITC may be applied with one exception. The meteorological data measured from Bakersfield Airport in Kern County may be influenced by the nearby urban/residential areas.

San Joaquin Valley Air Pollution Control District (Valley Air) provided modeled meteorological data for several agricultural locations within the Central Valley. The meteorological model used by Valley Air is the Fifth-Generation Penn State/National Center for Atmospheric Research (NCAR) Mesoscale Model (MM5), which is a weather-forecast mesoscale model. This analysis did not use this MM5 data as the latest available five-year data is 2007-2011. To assess the representativeness of the Bakersfield Airport data selected in this study, we modeled and compared 2007-2011 AITC air concentrations using either self-processed, airport meteorological data, or MM5-modeled meteorological data provided by Valley Air. As shown in Tables 12, using the airport and MM5-modeled meteorological data generated comparable air concentration estimates. Air concentrations from using the Bakersfield Airport meteorological data are lower (17-27%) than those from using the MM5-modeled meteorological data, but they are in the same order of magnitude. Considering data availability, this analysis concludes that using meteorological data measured from the Bakersfield Airport is appropriate for modeling air dispersions in agricultural areas of Kern County.

Table 12. Comparison of maximum AITC air concentrations (μg/m^3) in Kern County using either MM5-modeled (MM5) or self-processed airport (KBFL) meteorological data in 2007-2011

	Maximum time-weighted average (TWA) air concentration in[a] (μg/m^3)			
Distance[b]	8-hr		24-hr	
	KBFL	MM5	KBFL	MM5
		Adult		

0 ft	12581	17194	N/A[d]	N/A[d]
25 ft	N/A[c]	N/A[c]	3846	5178
100 ft	N/A[c]	N/A[c]	3254	4011
		Child		
25 ft	N/A[c]	N/A[c]	4521	5666
100 ft	N/A[c]	N/A[c]	3417	4095

a: The treated field is 40 ac and fumigated using deep drip application without tarp. The application rate is 246 lbs/ac;
b: distance from edge of treated field;
c: not available, 8-hr average air concentrations were only estimated for field edge for occupational bystander exposures;
d: not available, 24-hr average air concentrations were only estimated for 25 and 100 ft for residential bystander exposures.

Comparison with PERFUM3

As air concentrations from this analysis will be used for short-term bystander assessment, the 95th percentile values, as the "upper-bound" estimates of exposure, were derived from the estimated air concentrations output by AERMOD (Frank, 2009; Kwok, 2017).

In 2019, Exponent on behalf of US EPA developed the Probabilistic Exposure and Risk model for FUMigants, version 3.0 (PERFUM3). Similar to AERMET View^{TM}, PERFUM3 employs AERMOD as the dispersion modeling core. However, PERFUM3 is capable of generating distribution of air concentrations for a certain distance, using the whole field approach (Exponent, 2019). Details of the whole field approach have been discussed in the PERFUM3 user guide as well as a previous DPR memo (Barry, 2014; Exponent, 2019). DPR analyzed this approach and determined the 95th percentile air concentration values generated by PERFUM3 do not meet the purpose of this analysis and will cause underestimations of short-term bystander exposures, with the reason stated below.

The whole field approach derived the 95th percentile values from receptors at the same distance, the same height and most importantly, through the entire modeling domain (i.e., 5 years). For instance, for a 40 ac application, 332 receptors were set at 25 ft from the field edge. The whole field method would compile 605900 modeled air concentrations (332 receptors × 365 days × 5 years) into one distribution and generated a 95th percentile value. However, DPR define short-term exposures as "*exposures lasting seven days or less*", and the default exposure periods for occupational and residential bystanders are 8 and 24 hrs respectively. Therefore, it is inappropriate to derive the 95th percentile value using air concentrations from different days. This analysis, different from PERFUM3, only used air concentrations from the same day to generate the 95th percentile value. Using the same example above, this analysis set AERMOD to output daily air concentration value for each of the 332 receptor and then derived the 95th percentile value for that day. With 5 year modeling, a total of 1825 daily 95th percentile values were obtained and among them, only the day with meteorological conditions generating the highest 95th percentile air concentration value was chosen. To the best of our knowledge, similar results cannot be obtained from PERFUM3.

Table 13 below used a hypothetical 40 ac drip with tarp application in Santa Cruz as an example and compared the 95th percentile values estimated by PERFUM3 or by this analysis. As shown in Table 13, the PERFUM3 generated 95th percentile air concentrations were only equivalent to approximately 60th percentile values compared to those using the method of this analysis. For drip with PE tarp application, AERMOD estimated the greatest bystander exposures from applications in winter, and drip applications of fumigants in winter months (November and December) were indeed observed in Central Coast Counties (Monterey and Santa Cruz). Therefore, using PERFUM3 will underestimate bystander exposures during winter applications.

Table 13. Comparisons of 95th percentile air concentrations estimated by PERFUM3 or by this analysis

Bystander scenario	95th percentile of air concentration (μg/m^3)		Equivalent percentile rank of PERFUM3 value[b]
	PERFUM3	This analysis	
25 ft[a], adult	1000	2235	58th
25 ft, child	1200	2591	58th
100 ft, adult	790	1788	60th
100 ft, child	780	1869	59th

a: distance from field edge;
b: the equivalent percentile rank of the PERFUM3-estimated air concentration if using method of this analysis.

Conclusion:

AITC has not been used in California for soil fumigations, so its use pattern is unknown, and current knowledge on its soil emission profiles is limited. To address the lack of data, the current method was developed and modeling was conducted under various use scenarios, including different use areas in California, sizes of fields, application methods and tarp conditions. The breathing-zone air concentrations were estimated for both adults and children. The estimated air concentrations are summarized in Tables 6 through 10 and can be further used for assessing short-term bystander exposure.

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C. Appendix 3

Summary of air concentration tables

Summary of Air Concentration Tables

Table 1. 8-hr time weighted average allyl isothiocyanate air concentrations for applicators using shallow shank applications with tarp

Application	Air concentration	Short-term	Intermediate	Annual	Life-time
Broadcast	µg/m^3	130	53	14	7
	ppb[a]	32	13	3	2
Bed/Strip	µg/m^3	72	7	1	0.6
	ppb[a]	18	2	0.2	0.1

a: assuming at 25 ºC and 1 atm.

Table 2. 8-hr time weighted average allyl isothiocyanate air concentrations for applicators using shallow shank applications without tarp

Application	Air concentration	Short-term	Intermediate	Annual	Life-time
Broadcast	µg/m^3	291	82	21	11
	ppb[a]	72	20	5	3
Bed/Strip	µg/m^3	1149	103	17	9
	ppb[a]	283	25	4	2

a: assuming at 25 ºC and 1 atm.

Table 3. 8-hr time weighted average allyl isothiocyanate air concentrations for applicators using broadcast deep shank applications with and without tarp

Application	Air concentration	Short-term	Intermediate	Annual	Life-time
with tarp	µg/m^3	130	53	11	6
	ppb[a]	32	13	3	1
without tarp	µg/m^3	291	82	17	9
	ppb[a]	72	20	4	2

a: assuming at 25 ºC and 1 atm.

Table 4. 8-hr time weighted average allyl isothiocyanate air concentrations for applicators using drip applications

Air concentration	Short-term	Intermediate	Annual	Life-time
µg/m^3	44	15	2	1
ppb[a]	11	4	0.5	0.2

a: assuming at 25 ºC and 1 atm.

Table 5. 8-hr time weighted average allyl isothiocyanate air concentrations for loaders using shallow and deep shank applications

Air concentration	Short-term	Intermediate	Annual	Life-time
Broadcast shallow				
µg/m^3	7408	1426	371	198
ppb[a]	1826	351	91	49
Bed/Strip shallow				
µg/m^3	5573	423	71	38
ppb[a]	1374	104	17	9
Broadcast deep				
µg/m^3	7408	1426	293	156
ppb[a]	1826	351	72	38

a: assuming at 25 ºC and 1 atm.

Table 6. 8-hr time weighted average allyl isothiocyanate air concentrations for tarp cutter, remover and puncher

Air concentration	Short-term	Intermediate	Annual	Life-time
Broadcast shallow shank				
µg/m^3	1625	573	149	80
ppb[a]	401	141	37	20
Bed/Strip shallow shank				
µg/m^3	1222	170	28	15
ppb[a]	301	42	7	4
Broadcast deep shank				
µg/m^3	1625	573	118	63
ppb[a]	401	141	29	16
Drip				
µg/m^3	1222	431	58	31
ppb[a]	301	106	14	8

a: assuming at 25 ºC and 1 atm.

Table 7. 8-hr time weighted average allyl isothiocyanate air concentrations for re-entry workers

Air concentration	Short-term	Intermediate	Annual	Life-time
Broadcast shallow shank				
µg/m^3	167	145	38	20
ppb[a]	41	36	9	5
Bed/Strip shallow shank				
µg/m^3	125	43	7	4
ppb[a]	31	11	2	1
Broadcast deep shank				
µg/m^3	167	145	56	30
ppb[a]	41	36	14	7
Drip				
µg/m^3	125	109	18	9
ppb[a]	31	27	4	2

a: assuming at 25 ºC and 1 atm.

Table 8. 8-hr time weighted average AITC air concentrations for occupational bystanders

Short-term, µg/m^3	1 ac	40 ac	100 ac
Shallow shank w/ tarp	330	982	1229
Shallow shank w/o tarp	3184	9481	11863
Deep shank w/o tarp	2077	6186	7739
Drip w/ tarp	1788	5731	7148
Deep drip w/o tarp	4185	13412	16728

Short-term, ppb	1 ac	40 ac	100 ac
Shallow shank w/ tarp	81	242	303
Shallow shank w/o tarp	785	2337	2924
Deep shank w/o tarp	512	1525	1907
Drip w/ tarp	441	1413	1762
Deep drip w/o tarp	1031	3306	4123

assuming at 25 ºC and 1 atm.

Table 9. 24-hr time weighted average AITC air concentrations for residential adult bystanders

Short-term, μg/m^3	1 ac	40 ac	100 ac
25ft			
Shallow shank w/ tarp	113	349	441
Shallow shank w/o tarp	1059	3425	4246
Deep shank w/o tarp	912	2965	3697
Drip w/ tarp	732	2235	2824
Deep drip w/o tarp	1510	4769	5906
100ft			
Shallow shank w/ tarp	66	282	368
Shallow shank w/o tarp	633	2542	3363
Deep shank w/o tarp	591	2367	3062
Drip w/ tarp	407	1788	2367
Deep drip w/o tarp	864	3683	4888

Short-term, ppb	1 ac	40 ac	100 ac
25ft			
Shallow shank w/ tarp	28	86	109
Shallow shank w/o tarp	261	844	1047
Deep shank w/o tarp	225	731	911
Drip w/ tarp	180	551	696
Deep drip w/o tarp	372	1175	1456
100ft			
Shallow shank w/ tarp	16	70	91
Shallow shank w/o tarp	156	627	829
Deep shank w/o tarp	146	583	755
Drip w/ tarp	100	441	583
Deep drip w/o tarp	213	908	1205

Assuming at 25 °C and 1 atm

Table 10. 24-hr time weighted average AITC air concentrations for residential child bystanders

Short-term, µg/m³	1 ac	40 ac	100 ac
25ft			
Shallow shank w/ tarp	158	404	497
Shallow shank w/o tarp	1393	3786	4615
Deep shank w/o tarp	1288	3336	4091
Drip w/ tarp	1003	2591	3185
Deep drip w/o tarp	2016	5370	6590
100ft			
Shallow shank w/ tarp	75	296	381
Shallow shank w/o tarp	678	2617	3439
Deep shank w/o tarp	643	2495	3172
Drip w/ tarp	462	1869	2452
Deep drip w/o tarp	948	3855	5067

Short-term, ppb	1 ac	40 ac	100 ac
25ft			
Shallow shank w/ tarp	39	100	122
Shallow shank w/o tarp	343	933	1137
Deep shank w/o tarp	317	822	1008
Drip w/ tarp	247	639	785
Deep drip w/o tarp	497	1324	1624
100ft			
Shallow shank w/ tarp	18	73	94
Shallow shank w/o tarp	167	645	848
Deep shank w/o tarp	158	615	782
Drip w/ tarp	114	461	604
Deep drip w/o tarp	234	950	1249

Assuming at 25 °C and 1 atm