# Department of Pesticide Regulation Environmental Monitoring Branch 1001 I Street Sacramento, CA 95812

# Study #309: Monitoring of 1,3-Dichloropropene in Merced and Fresno Counties

Colin Brown December 12, 2016

#### **1** Introduction

1,3-Dichloropropene, also known as 1,3-D or Telone®, is a widely-used fumigant in California agriculture, used primarily for its nematicidal properties. It was first registered as a pesticide in the United States in 1954, and at present it is allowed as a soil fumigant for all vegetable, forage, fiber, nursery, fruit, nut, and tobacco crops. 1,3-D is normally applied to the soil through shank injection or chemigation as a mixture of *cis*- and *trans*- isomers at a maximum application rate of 24 gallons per acre for tarped fumigations and 35 gallons per acre for untarped applications (DPR 2014).

In April of 1990, the California Department of Food and Agriculture (CDFA)–then the state's pesticide regulatory agency–suspended use permits for 1,3-D following detections of high ambient air concentrations of the fumigant in Merced County. Commercial use of 1,3-D was reintroduced in 1994 following the development of new application methods by Dow AgroSciences (Dow), the primary manufacturer of 1,3-D. To mitigate cancer risk from 1,3-D the reintroduction included additional use restrictions, including limits on use within each township (6 x 6 mile area). As specified in the Department of Pesticide Regulation's (DPR's) 2016 risk management directive (DPR 2016), the use limit and other restrictions will be updated effective January 2017. Between 1995 and the present, the California Air Resources Board (ARB) and DPR have continued to monitor ambient 1,3-D in several high-use counties, including Fresno, Kern, Merced, and Monterey (Table 1).

Two statewide ambient air monitoring programs currently include 1,3-D among those substances sampled. Both isomers of 1,3-D are included in DPR's Air Monitoring Network (AMN), a long-term air study which began in February 2011 and measures ambient concentrations of pesticides in the communities of Ripon, Salinas, and Shafter. Additionally, ARB, at the request of DPR, collects 24-hour air samples every six days in 3 sites as part of DPR's Toxic Air Contaminant (TAC) monitoring program which includes 1,3-D. However, sites in the AMN were chosen for the purpose of capturing a broad selection of volatile pesticides, which does not necessarily include those areas with the greatest 1,3-D use. Similarly, ARB's TAC air monitoring does not specifically target areas of high 1,3-D use. A third monitoring program, ARB's Air Toxics Hot Spot program, includes an analysis for 1,3-D but samples in highly urbanized areas, far from the areas of highest use.

In the proposed study, DPR will monitor ambient air concentrations of 1,3-D in the communities of Delhi and Parlier for a period of at least 13 months, beginning December 1,

2016 and concluding December 31, 2017. DPR's evaluation indicates that Delhi and Parlier are consistently among those communities surrounded by the highest levels of 1,3-D use in the Northern and Southern San Joaquin Valley regions. Data collected in the study will complement ongoing monitoring along the Central Coast, where monitoring sites already operate in areas of heavy 1,3-D use. Study results will provide DPR with data useful in evaluating seasonal and annual 1,3-D exposure in populated areas located in those regions approaching the highest levels of 1,3-D use.

County	lbs 1,3-D	1,3-D Monitoring Studies
Fresno	7,963,100	Wofford et al. 2009, ARB 2016
Kern	5,894,800	Tuli et al. 2015; ARB 1996, 1997, 2000, 2002a
Monterey	4,676,100	Vidrio et al. 2014; Tuli et al. 2015; ARB 1994, 2001, 2002b
Merced	4,177,200	ARB 1991, 1995
Stanislaus	3,790,800	
Tulare	3,668,600	
Santa Barbara	3,259,500	Vidrio et al. 2014
San Joaquin	1,972,200	Tuli et al. 2015, ARB 2016
Ventura	1,942,000	Vidrio et al. 2014, ARB 2016
Santa Cruz	1,782,300	ARB 2001, 2002b

**Table 1:** Table of the sum of 1,3-D use data for 2011-2014 in the top 10 California counties. Related 1,3-D ambient air monitoring studies conducted in each county since 1990 are also shown.

#### **2** Objectives

- 1. Identify the presence and ambient concentration of 1,3-D in regions of high use;
- 2. Compare measured air concentrations to sub-chronic and chronic human health screening levels;
- 3. Evaluate the effectiveness of township use restriction on chronic ambient concentrations;
- 4. Determine correlation between pesticide use records and ambient concentrations.

#### **3** Personnel

The Environmental Monitoring Branch (EM) will conduct this study under the supervision of Edgar Vidrio, project supervisor. Key staff includes:

- Project supervisor: Edgar Vidrio
- Project leader: Colin Brown
- Field coordinator: Jazmin Gonzalez
- Sample collection: EM Air Unit Staff
- Chemical analysis: CDFA Center for Analytical Chemistry
- Laboratory liaison: Sue Peoples

All questions concerning this project should be directed to Edgar Vidrio at (916) 323-2778 or Edgar.Vidrio@cdpr.ca.gov.

#### **4** Study Plan and Sampling Methods

DPR selected two communities for 1,3-D monitoring based on a high relative amount of 1,3-D use in the surrounding area. Sites within selected communities were positioned as near-downwind of 1,3-D application sites as possible. Other overriding considerations for site placement included availability of a secure location meeting the criteria for unobstructed airflow in the immediate vicinity of the air sampler and availability of AC power. Selection criteria are further described, below.

### 4.1 Community Selection Criteria

### **4.1.1** 1,3-D Use

DPR referenced all 1,3-D use reports submitted for applications between 2012 and 2014 in order to identify communities surrounded by the highest amounts of 1,3-D use. The list of communities included all cities and census-designated places located within California and described by the 2010 United States Census, with the exception of communities within the urban counties of Los Angeles, Orange, San Diego, and San Francisco. Multiple queries of the California Pesticide Use Reports (PUR) Database provided 1,3-D usage data for every Public Land Survey System (PLSS) section<sup>1</sup> with a record of 1,3-D use between 2012-2014. Three non-overlapping spatial categories (or 'rings') were used to rank the level of use surrounding each community: use falling within the community boundary ('0 mile'), use between 0-1 mile out from the community boundary ('0-1 mile'), and use between 1-5 miles out from the community boundary ('1-5 mile'). In cases where a PLSS section was not fully contained by a ring, the use of that section was added to the total use in that ring in proportion to the area of the section falling within the ring (Figure 1).

Use was calculated in terms of total pounds applied, which differs from the calculation of adjusted total pounds<sup>2</sup> (ATP) in that it does not weight the actual application amount by an additional factor based on application method. A statewide ranking based on ATP, rather than total pounds, would likely change the rank order as application methods differ widely by region. For instance, use of totally impermeable film (TIF tarp) is more widespread along the Central Coast than it is in the Central Valley, and applications using TIF tarp would generate a lower ATP than would an application with conventional tarp.

The estimated use within each of a community's three rings was compared against those of every other community to generate a statewide ranking for each ring (Figure 1). The average of a community's three rings was used to generate an overall community ranking (Table 2), which was then used to inform community selection. The ranking was subset by county in order to identify top-ranking communities within each county.

<sup>&</sup>lt;sup>1</sup> PLSS sections are distinct 1 mi<sup>2</sup> areas used by the U.S. Bureau of Land Management for purposes of land survey. PLSS sections are arranged in a fixed grid and referenced to a principal meridian. Sections are used by DPR as a means of tracking the location of pesticide applications and applicators are required to report the section in which an application was made. A related concept is the PLSS township, which refers to a distinct 6x6 (36 mi<sup>2</sup>) arrangement of PLSS sections. DPR currently caps annual 1,3-D use per township.

<sup>&</sup>lt;sup>2</sup> Adjusted Total Pounds (ATP) is a method of standardizing the effect of 1,3-D applications on air quality by accounting for environmental conditions and application method. For additional details describing Adjusted Total Pounds and its calculation, please see DPR (2014), part 7.3.1, 'Calculating Adjusted Total Pounds'.

Merced and Fresno counties were prioritized for the purposes of this study as a means of placing monitoring sites in regions of high 1,3-D use that are not presently monitored. Merced and Fresno counties are among the highest-use counties in the state (Table 1), and each county is the highest-use county within its respective region of the San Joaquin Valley (SJV). Monitoring in California's coastal regions was not prioritized in this study, because despite heavy 1,3-D use in the coastal regions of Santa Cruz, Monterey, Santa Barbara, and Ventura counties, several high-use communities in these regions are already included in other monitoring studies conducted by DPR and ARB (Table 3).

Monitoring in the North SJV region (comprised of Merced, Stanislaus, and San Joaquin counties) was previously conducted in the community of Ripon (statewide 1,3-D rank #46), but monitoring at this location was terminated at the end of 2016. The highest-ranked monitoring location in the South SJV region (comprised of Madera, Fresno, Kings, Tulare, and Kern counties) was previously in Shafter (statewide 1,3-D rank #86). For 1,3-D specifically, there are several communities in both Merced and Fresno counties that rank more highly than those communities that have been monitored in the past. Monitoring for 1,3-D in these high-ranking communities should allow DPR to develop better estimates for the upper limits of ambient 1,3-D exposure in those regions (Table 3).

#### 4.1.2 Meteorology

Weather patterns were used to prioritize monitoring locations within each community. In areas where wind direction is not well-randomized over time, a monitoring site at the fardownwind margin of an urban boundary (i.e. a site located far from upwind applications) could theoretically return lower ambient concentrations than a site located further upwind due to the effects of plume dispersion over distance. With this possibility in mind, priority in site selection was given to sites located near the upwind margin of each community boundary.

Meteorological data for each community was obtained from the California Irrigation Management Information System (CIMIS), a network of automated weather monitoring stations managed by the California Department of Water Resources. Among these data are wind direction and wind speed measurements collected 2 meters above ground height. Data was downloaded in hourly format for the period between January 1, 2011 and December 31, 2015. Data was then aggregated and summarized as a wind rose, a graphical tool that provides a visual summary of the distribution of wind direction and speed at a monitoring location. The spokes on a wind rose indicate the strength and frequency with which a wind blows from a particular direction. The free WRPLOT View tool from Lakes Environmental Software was used to develop wind roses for each 5-year period.

-	Rank Categ 0 m 0 to 1 to	ories ile 9 1 mile 9 5 mile		0	3	6	mi.	
Community Name	County	0 mile (lbs/mi <sup>2</sup> )	0 mile rank	0-1 mile (Ibs/mi <sup>2</sup> )	0-1 mile rank	1-5 mile (Ibs/mi <sup>2</sup> )	1-5 mile rank	Overall Rank
Pajaro CDP Mettler CDP  Keves CDP	Monterey Kern  Stanislaus	10494.44 5848.561  5481.404	7 18  19	9346.931 15297.52  4143.803	7 1  55	7384.325 4122.704  2990.045	1 23  71	1 2  34
Ballico CDP Parlier city Del Rey CDP	Merced Fresno Fresno	4227.816 897.614 6705.965	29 105 15 	5994.074 5065.467 2425.463 	23 35 104 	2637.75 5091.927 3804.802 	94 9 34 	35 36 37 

**Figure 1:** Three non-overlapping spatial categories (or 'rings') were used to tabulate and rank 1,3-D use. Use records for those Public Land Survey System sections (1 mi<sup>2</sup> areas) partially contained within a ring are added to the total in accordance to the proportion of the section falling within the ring. The innermost ring is delineated by the community boundary, and the remaining two rings are determined by a fixed radius from the boundary edge. The total 1,3-D use in each ring for a given community is compared to those of all other California communities to determine its ranking for each ring and its overall rank, as shown by this example for the city of Parlier.

**Table 2:** Top 36 communities by unadjusted 1,3-D use in the state, subset by region. Communities are identified by their rank within each region in the locator maps. Ranks are calculated as the average of the statewide subrankings for each of the three rings, and two or more sites may receive the same ranking where the averages of the subrankings are equal. Existing sites are indicated on the list and locator map in red, and new monitoring sites as part of this study in green.

	Region	State			<u>0 Mi</u>	le	<u>0-1 N</u>	1ile	<u>1-5 N</u>	lile	
Region	Rank	Rank	Community Name	County	Use (lbs)	Rank	Use (lbs)	Rank	Use (lbs)	Rank	Images
	1	1	Pajaro CDP	Monterey	10,494	7	9,347	7	7,384	1	6 5
	2	4	Pajaro Dunes CDP	Santa Cruz	13,728	5	10,130	4	3,578	43	10 4
ist	3	9	Las Lomas CDP	Monterey	3,560	40	5,215	33	6,854	3	1
Соа	4	9	Watsonville city	Santa Cruz	3,214	46	10,180	3	3,976	27	2 9 3
itral	5	12	Interlaken CDP	Santa Cruz	7,730	13	5,604	28	3,665	39	
Cen	6	18	Amesti CDP	Santa Cruz	3,472	41	5,010	37	4,467	19	
orth	7	20	Boronda CDP	Monterey	3,865	33	3,350	68	6,349	4	
No	8	20	Castroville CDP	Monterey	3,656	39	5,033	36	3,837	30	
	9	27	Salinas city	Monterey	4,145	30	8,388	14	3,004	70	8
	10	32	La Selva Beach CDP	Santa Cruz	8,521	10	4,103	56	3,042	68	7 9
											0 2.25 4.5 Mile
t a i	1	8	El Rio CDP	Ventura	14,976	4	8,780	11	3,267	57	
Soutentra	2	24	Guadalupe city	Santa Barbara	3,106	49	4,995	38	4,023	24	
, g c	3	28	Santa Maria city	Santa Barbara	5,208	21	9,185	8	2,751	88	2 3
	Continued on next page										0 12.5 25 Miles

		Continued	from t	previous page								]
ſ		1	6	Westley CDP	Stanislaus	4,912	24	8,488	13	3,825	32	State State Barrier State
		2	15	Grayson CDP	Stanislaus	2,953	51	5,817	24	4,768	13	6
		3	16	Delhi CDP	Merced	3,964	32	5,077	34	3,885	29	4
		4	17	Salida CDP	Stanislaus	4,432	28	6,621	21	3,532	47	2
	orth SJ\	5	19	Livingston city	Merced	2,266	61	5,778	25	4,641	14	-
		6	22	Del Rio CDP	Stanislaus	7,976	11	5,754	27	3,032	69	0
	Z	7	30	Winton CDP	Merced	3,194	47	4,363	50	3,942	28	8 5 7
		8	31	Crows Landing CDP	Stanislaus	7,737	12	12,073	2	2,005	116	6
		9	34	Keyes CDP	Stanislaus	5,481	19	4,144	55	2,990	71	
		10	35	Ballico CDP	Merced	4,228	29	5,994	23	2,638	94	
												0 5 10 Miles
		1	2	Mettler CDP	Kern	5,849	18	15,298	1	4,123	23	8
		2	3	Biola CDP	Fresno	20,420	1	5,774	26	4,201	21	2 9 13 6
		3	5	Delft Colony CDP	Tulare	4,558	26	6,681	20	4,390	20	47
		4	7	Raisin City CDP	Fresno	2,454	55	9,915	5	4,896	10	12 0 (1)
		5	11	Edmundson Acres CDP	Kern	16,485	2	8,821	10	3,167	65	
	NLS	6	13	Reedley city	Fresno	2,084	69	9,524	6	5,430	6	
	uth	7	14	Caruthers CDP	Fresno	4,652	25	4,209	53	5,245	8	and the second second
	So	8	23	La Vina CDP	Madera	9,036	9	3,860	61	3,656	40	REAL PROPERTY
		9	24	Bowles CDP	Fresno	15,069	3	7,141	19	2,745	89	5
		10	26	Dinuba city	Tulare	2,107	68	8,895	9	3,778	35	1
		11	29	Farmersville city	Tulare	7,418	14	4,855	40	3,176	64	
		12	33	London CDP	Tulare	4,478	27	3,237	71	3,731	38	0 15 30 Miles
		13	36	Parlier city	Fresno	898	105	5,065	35	5,092	9	

**Table 3:** Regions of highest 1,3-D use in the state and the top-ranking communities for 1,3-D use within each region are provided alongside their statewide rankings, in parenthesis. Current monitoring sites in each region as of January 2017 are provided alongside its statewide rankings, in parenthesis.

Region	Counties	Top-Ranking Communities	Current Monitoring Sites
Northern SJV	San Joaquin, Stanislaus, Merced	Westley (6), Grayson (15), Delhi (16)	Delhi (16)
Southern SJV	Madera, Fresno, Kings, Tulare, Kern	Mettler (2)*, Biola (3)*, Delft Colony (5)*, Raisin City (7)*, Edmunson Acres (11)*	Parlier (36), Shafter (86), San Joaquin (163), Lindsay (193)
North Central Coast	Santa Cruz, Monterey	Pajaro (1), Pajaro Dunes (4), Watsonville (9), Las Lomas (9)	Watsonville (9), Chualar (224)
South Central Coast	Santa Barbara, San Luis Obispo, Ventura	El Rio (8), Guadalupe (26)	El Rio (8), Santa Maria (28), Cuyama (190)

\* No feasible monitoring site in these communities.

### **4.2** Communities Selected for Monitoring

## 4.2.1 Delhi, CA

Delhi is a small city (3.5 mi<sup>2</sup>) of 10,755 people located in Merced County and within the San Joaquin Valley. The nearest major cities are Merced, located approximately 18 miles to the southeast, and Modesto, located approximately 19 miles to the northwest. The city has an elevation of 118 feet. Merced Regional Airport, the closest major airport, reports average annual rainfall of 12.3 inches. Temperatures during the summer (May-September) reach an average daily maximum of 82.6-97.1°F and winter (November-February) temperatures reach an average daily maximum of 54.9-66.2 °F (Western Regional Climate Center 2016).

Delhi is surrounded by agricultural lands. Major crops include sweetpotatoes, almonds, and grapes. The times of heaviest application are expected to be during November-December, for pre-plant fumigation for sweet potatoes and pre-plant fumigation for almonds, and March-April for pre-plant fumigation of sweet potatoes. See Figure 2 for a year-by-year summary of reported applications by amount and day.

Delhi ranks 32nd in the state for 1,3-D use within community boundaries, 34th for use in a 1-mile radius surrounding the community, and 29th for use in a 1-to-5 mile ring surrounding the community based on 2011-2014 use data. Delhi ranks 16<sup>th</sup> in the state overall. Of the 98 selected sections, 68 contained record of 1,3-D usage between 2012 and 2014. Total use per section between 2012 and 2014 in the 5-mile area surrounding Delhi is shown in Figure 2. Between 2012 and 2014, the PUR reports applications of 1,3-D totaling 978,700 ATP in the 5 miles surrounding Delhi. On an annual basis, use in ATP ranged from a low of 302,100 ATP in 2014 to a high of 364,532 ATP in 2013. Normalized to a township (36 mi<sup>2</sup>) scale, use in the area ranged from a low of 111,000 ATP per township per year in 2014 to a high of 133,900 ATP per township per year in 2013. Delhi is also in the area of Merced County with historically high use of 1,3-D. Since 2014, four townships

in this region have been limited to 90,250 ATP annually. Beginning in January 2017, three of the townships will be able to use up to 136,000 ATP each year, and the fourth township will be able to use this amount beginning in 2018. Use in the Delhi area is expected to increase, which is why it is preferred over Westley and Grayson.

Winds in the Delhi region come mostly from the northwest, which favors the siting of the monitoring location somewhere near the northwestern margin of the Delhi city boundary. Wind patterns in Delhi were inferred from CIMIS Station #206, located in Denair, CA, approximately 8 miles north of Delhi, and station #148, located in Merced, approximately 23 miles ESE of Delhi (Figures 6 and 7). A third station—CIMIS Station #92—is located 14 miles SW of Delhi, in Kesterson, CA, but data gaps at this station preclude creation of a wind rose and the station was excluded from subsequent analysis.

The monitoring site in Delhi is located approximately 1 mile downwind of the city boundary. The site is housed on property owned by the Delhi County Water District and adjacent to Schendel Elementary School. The monitoring site is located approximately 0.3 miles downwind from the edge of a cluster of historically moderate-to-high-use sections, as indicated in Figure 4.

# 4.2.2 Parlier, CA

Parlier is a small city  $(2.2 \text{ mi}^2)$  of 15,138 people located in Fresno county and within the San Joaquin Valley. The nearest major city is Fresno, located 19 miles to the northwest. The city sits at an elevation of 344 feet above sea level. Meteorological data from the Fresno Yosemite International Airport indicates an average annual precipitation of 10.9 inches. Temperatures during the summer (May-September) reach an average daily maximum of 83.5-96.4 °F and winter (November-February) temperatures reach an average daily maximum of 54.6-65.3 °F (Center 2016).

Parlier ranks 105<sup>th</sup> in the state for 1,3-D use within community boundaries, 35th in the state for use in 1-mile radius surrounding the community, and 9th for use in a 1-to-5 mile ring surrounding the community based on 2011-2014 use data. The city ranks 36<sup>th</sup> overall.

Major crops around Parlier include peaches, nectarines, grapes, almonds, and other permanent crops. Applications of 1,3-D in the area historically show a brief peak in February followed by a longer application season between August and December. See Figure 3 for a year-by-year summary of reported applications by amount and day.

The monitoring site in Parlier is located at the Kearney Agricultural Research and Extension Center, located approximately 0.5 mile east of the city's urban boundary. The site is positioned within a section with historical 1,3-D use, and is adjacent to several other sections with historical 1,3-D use. A 5-mile radius surrounding the proposed monitoring location includes 101 sections, 85 of which report 1,3-D usage between 2012 and 2014. The three-year total use per section in a 5-mile radius surrounding the monitoring site is displayed graphically in Figure 5. Between 2012 and 2014, a total of 1,318,353 lbs ATP were applied in a 5-mile radius surrounding the monitoring site. Annual use during 2012-2014 ranged from a low of 422,300 lbs ATP in 2014 to a high of 452,700 lbs ATP in 2012. Normalized to a township (36 mi<sup>2</sup>) scale, use ranged between 150,523 and 161,358 lbs ATP per township per year in 2014 and 2012, respectively.

CIMIS Station #39, located in Parlier, CA, is located immediately adjacent (<0.1 mile) to the monitoring location at the Kearney Agricultural Research and Extension Center. This station will provide the most representative weather data for estimating conditions at the site due to its very close proximity and similar surrounding topography. Data from the station suggests a more varied distribution of wind directions that favors winds from the northwest (Figure 8). CIMIS station #80, located at Fresno State University, 20 miles to the northwest, shows a closer distribution of winds from the northwest (Figure 9). Data from CIMIS station #142, located in Orange Cove, 9 miles to the northeast, was not considered due to the station's positioning within mountainous topography.

### **5** Sampling Methods and Equipment

Each air monitoring station will have a minimum of 3 feet (ft) horizontal and vertical distance from its supporting structure, be at least 65 ft from trees, have a distance from obstacles at least twice the obstacle height, and have unobstructed airflow for 270° around the air sampling equipment. A protective shelter will be placed at each air sampling location. The shelter will house a SilcoCan® canister (Restek cat. no. 24142-65). The shelter will prevent damage to air sampling equipment from sunlight, rainfall, and fog during the monitoring study.

One 24-hour air sample will be collected per week at each of the two monitoring locations over the 13-month course of the study. Each week, sampling will begin on a randomly chosen day, Monday through Thursday, wherever possible. DPR anticipates that a total of 137 canister samples will be retrieved over the duration of the study, 13 of which will be duplicate samples taken for purposes of quality assurance and control.

Limited equipment availability at the beginning of the study will necessitate the use of passive sampling at the Delhi site until January 2017. Passive sampling involves the preevacuation of a SilcoCan® to a pressure of -30" Hg, after which air flow into the canister is controlled by a flow regulator calibrated to operate at a flow rate of  $3.0 \pm 0.3$  milliliters per minute (mL/min) for 24-hours. Valid samples will maintain a final vacuum of -5" Hg or below. A passive sampler assembly will require staff present to manually open and close flow to the canister at the beginning and end of the 24-hour sampling interval.

Active sampling will be used in Parlier and Delhi after the site is retrofitted in January 2017. Active sampling requires the pre-evacuation of a SilcoCan® to a pressure of -30" Hg. Ambient air is pumped into the can using a Xonteck Model 901 Automated Canister Sampler at a constant rate of  $7.5 \pm 0.5$  mL/min for 24 hours. Valid samples will maintain a final canister pressure of 6-16" Hg. Such active sampling will require access to AC power at the site. The active sampler eliminates the need for staff to manually start and stop flow to the canister as this functionality is programmable in the Xonteck unit.

Sample labels printed with the study number and a sample tracking number will be secured to the outside of all sample canisters. When air sampling commences at each monitoring site, the sample tracking number, date, time, staff initials, weather conditions, and air sampler flow rate will be documented on a chain of custody (COC) form as described in DPR Standard Operating Procedure (SOP) ADMN006.01 (Ganapathy 2004). At the end of each sampling period staff will record the date, time, staff initials, and ending flow rate on the COC form. Weather conditions and other pertinent information that may affect sample results will be recorded on the COC or in a field notebook.



**Figure 2:** Calendar heat map of 1,3-D applications in a 5-mile radius surrounding the Delhi air monitoring site between January 1, 2012 and December 31, 2014. Units of application are in adjusted total pounds (ATP) of 1,3-D per day. Data is displayed by day. There are clear seasonal peaks in 1,3-D use in November-December and February-April mostly associated with pre-plant fumigation of almond and sweetpotato. Data from DPR (2016).



**Figure 3:** Calendar heat map of 1,3-D applications in a 5-mile radius surrounding the air monitoring site at the Kearney Agricultural Research and Extension Center between January 1, 2012 and December 31, 2014. Units are in lbs ATP of 1,3-D per day. Data is displayed by day. Seasonal application peaks can be observed during the spring and winter months. Data from DPR (2016).



**Figure 4:** Map of the PLSS sections in a 5-mile radius surrounding the proposed study site in Delhi, CA. Point of origin is (37.429, -120.778). Sections are symbolized according to the total 1,3-D application in ATP between January 1, 2012 and December 31, 2014.



**Figure 5:** Map of the PLSS sections in a 5-mile radius surrounding the proposed study site in Parlier, CA. Point of origin is (36.597, -119.504), on property of the UC Kearney Agricultural Research and Extension Center and located in the periphery of Parlier, CA. Sections are symbolized according to the total 1,3-D application in ATP between January 1, 2012 and December 31, 2014.



**Figure 6:** Wind rose for CIMIS station #148 in Merced, located 23 miles ESE of Delhi. Data is presented for January 1, 2011 to December 31, 2015.



**Figure 7:** Wind rose for CIMIS station #206 in Denair, located 8 miles north of Delhi. Data is presented for January 1, 2011 to December 31, 2015.



**Figure 8:** Wind rose for CIMIS station #39 in Parlier, located 0.5 mile southeast of the Parlier monitoring station. Data is presented for January 1, 2011 to December 31, 2015.



**Figure 9:** Wind rose for CIMIS station #80 in Fresno, located 20 miles northwest of the Parlier monitoring station. Data is presented for January 1, 2011 to December 31, 2015.

Canister flow valves will be closed and a cap nut installed upon canister collection. Canisters will be transported under ambient conditions to DPR's West Sacramento facility where they will be checked-in and held until delivered to the laboratory for analysis. Sample handling-shipping and tracking procedures will be followed as described by DPR SOP QAQC004.1 (Jones 1999) and SOP QAQC003.02 (Ganapathy 2005), respectfully.

Co-located duplicate canister samples will be retrieved once per month as a quality control measure. The site from which the co-located sample is obtained will alternate monthly. Co-located samples are collected immediately adjacent to the primary samples and under the same conditions and time-frame. Pesticide recovery from the duplicate and primary samples is used to evaluate laboratory analytical precision; samples with greater than 50% difference in pesticide residue concentration will result in reassessment of the field and laboratory procedures.

## 6 Chemical Analysis

The California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry (CAC) will conduct chemical analysis of the air sampling media. Canisters will be analyzed for 1,3-D by directing a known volume of the sampled air through a sorbent resin and then extracting the analytes into a solution for us in gas chromatography mass spectrometry (California Department of Food and Agriculture 2008). The resulting mass of 1,3-D detected in this method is divided by the volume of air sampled to produce the average ambient concentration of 1,3-D over a 24-hour period (DPR 2011).

The method detection limit (MDL) for the air canister method will be 45.4 ng/m<sup>3</sup> (0.01 parts per billion by volume (ppbv)) for both *cis*- and *trans*-1,3-D. This value is determined by analyzing a standard at a concentration with a signal-to-noise ratio of 2.5 to 5. The spiked matrix is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail by U.S. EPA (1990).

The CDFA laboratory will follow DPR's standard laboratory quality control procedures as outlined in SOP QAQC001.00 (Segawa 1995). Prior to analysis of field samples, the laboratory will validate the method by analyzing a series of spikes (samples containing a known amount of pesticide) to document precision and accuracy of the methods. Storage stability tests will be performed to document the degradation of samples between the time of sample collection and the time of sample analysis. The laboratory will include quality control samples with each batch of field samples analyzed, including blank samples (samples containing no pesticides) to check for contamination, and spikes to check precision and accuracy.

For each analyte, upper and lower warning and control limits are set at  $\pm 2$  and  $\pm 3$  standard deviations derived from the average percent recovery, respectively, of the above mentioned replicates. During the analysis of field samples quality control samples will also be submitted for analyses. This includes pesticide-spiked samples to provide checks on analytical precision and accuracy, and blank samples to provide information on possible contamination. Corrective action will take place if spiked quality control recovery levels fall outside the established preset limits.

### 7 Data Analysis

Results from each air sample will be aggregated into a time series of all air samples for each sampling location. The maximum 24-hour, 28-day, and 1-year concentrations will provide indicators of maximum acute, subchronic, and chronic exposure, respectively. DPR will calculate potential health risks resulting from each level of exposure. DPR will compare results from this study to those from other air monitoring studies and analyze the concentration data for correlation with nearby 1,3-D applications. The data will expand the existing long-term fumigant monitoring datasets collated by DPR and ARB, and may provide additional insight into the process by which fumigant applications affect ambient concentrations.

DPR will publish an analysis of sampling results following completion of the study, in addition to the raw dataset. DPR will compare measured ambient air concentrations to human health screening levels to determine whether additional action is necessary. No state or federal agency has established regulatory health standards for pesticides in ambient air, but DPR has established human health screening levels for inhalation exposure to 1,3-D to provide context for acute, subchronic, and chronic air monitoring results. Exceedance of the screening level may signal a need for closer data evaluation, additional data collection, and possibly mitigation measures (DPR 2011).

## 8 Timetable

All sampling equipment will be installed and ready to sample by late November 2016. Weekly sampling will commence the week of December 1, 2016 and proceed through the week of December 31, 2017. A final study report will be published by end of 2018 alongside the complete air monitoring dataset.

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