

Monitoring of 1,3-Dicloropropene in Merced and Fresno Counties Results for 2018

Volume 2

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Report AIR 19-03

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1. Introduction

The soil fumigant 1,3-dichloropropene (1,3-D), also known as Telone[®], plays a critical role in California's agricultural industries by protecting soil from nematodes and soil-borne diseases. It continues to be the most used fumigant throughout the state. Due to the volatility of the chemical, a portion of the applied chemical can disperse into the atmosphere depending on the field fumigation method used during application. In 2017, the Department of Pesticide Regulation (DPR 2016) revised permit conditions which eliminated 1,3-D use in the month of December and restricted the total allotted application amount within a 6x6 square mile area to a maximum of 136,000 adjusted pounds (i.e., township cap) in a calendar year.

A goal of this air monitoring study is to evaluate the effectiveness of the current township cap and current permit conditions. As a result, DPR selected two communities characterized by relatively high levels of historical 1,3-D use which were not already included in monitoring conducted by DPR or the California Air Resources Board (ARB). DPR staff collected weekly 24-h air samples in an effort to monitor 1,3-D in the two communities of Delhi (Merced County) and Parlier (Fresno County) beginning in November, 2016. This report evaluates the results collected from January 1 through December 31, 2018.

2. Methods

2.1 Field and Lab Methods

From January 1 through December 31, 2018, one 24-hour ambient air sample was collected each week on a randomly assigned day of the week at Delhi and Parlier. Samples were primarily collected using 6-L vacuumed summa canisters placed on a Xonteck 901 automated canister sampler. In the event of equipment accessibility, malfunctions, or failures, Restek regulators were used to conduct the air sampling. A more in-depth sampling procedure is included in Appendix V. Collocated quality control samples were collected approximately once a month at the Delhi monitoring site, which was designated the quality control site. Fortified field spikes prepared by the Air Resources Board (ARB) Northern Branch Lab were collocated with primary samplers as part of the study's quality control procedures. All samples were collected using the same standard air sampling procedures. Samples were analyzed by the California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA CAC) using method EMON-SM-05-019 (Appendix VI). CDFA CAC followed DPR's standard lab quality control procedures and conducted lab blanks and lab spikes during each analytical run.

2.2 Methods of Data Analysis

DPR uses the data collected from this study to compare to current health based screening levels and regulatory targets for each year. DPR aggregates the laboratory results of 1,3-D isomers (cis and trans) per sample as the total 1,3-D concentration. Specifically, average concentrations of 1,3-D are determined for acute, subchronic, chronic, and lifetime periods (Table 1). In the absence of a 72-hr 1,3-D air sample, the maximum single 24-hr average concentration measured in this study is used to compare with the established 72-hr acute exposure. Rolling averages are used in subchronic exposure calculations, where the maximum 1,3-D concentration is determined for a period of 90 days (13 weeks). Concentrations are expressed as the average of results for a one-year period for chronic exposure. In the absence of 70 years' worth of 1,3-D monitoring data, DPR uses the average concentrations originating from the start of this study, beginning in December 2016 to calculate a lifetime exposure. For purposes of calculating averages, DPR substitutes non detections (ND) with a value of one-half the reporting limit (0.005 ppb) for the total 1,3-D. To determine the risk associated for each exposure period, DPR uses a Hazard Quotient (HQ). The HQ is calculated as a ratio of the measured 1,3-D to screening levels or regulatory target. A HQ over 1 indicates exceedance of the screening level and requires DPR to take action to further evaluate the data and look into possible mitigation measures (DPR 2011).

Exposure	Exposure Period	Screening Level (ppb)	Potential Health Effect
Acute	72 hour	110	Change in body weight
Subchronic	90 day	3	Tissue damage in nose and lung
Chronic	1 year	2	Tissue damage in nose and lung
Lifetime/Cancer	70 years	0.56	Cancer
Risk*			

Table 1: Screening Levels and Regulatory Target for 1,3-D

*Regulatory target rather than a screening level

3. Air Monitoring Results

In 2018, 101 valid primary samples were collected from the two sites (Appendix I and II). During this period, 1,3-D was detected in 76% of air samples collected from Delhi and Parlier.

3.1 Delhi

There were 50 valid primary samples collected at the Delhi site; one sample was invalidated due to low canister pressure. Detected air monitoring concentrations from the Delhi monitoring site were above the reporting limit (RL) in 68% of the samples in 2018 (34 out of 50 valid samples). Results from the Delhi monitoring site were characterized by a high proportion of detections; however, none of the detections exceeded established targets for acute, subchronic, chronic, or lifetime exposures. Quantifiable detections ranged from 0.012 to 1.80 ppb. The mean annual concentration for Delhi was 0.19 parts per billion (ppb) in 2018. A summary of maximum observed concentrations for each exposure period is included in Table 2. Results for acute, subchronic, and chronic exposure categories were below a hazard quotient of 1.0. The highest observed hazard quotient was 0.30 for the lifetime exposure.

Exposure	Exposure Period	Total 1,3-D (ppb)	Screening Level (ppb)	Hazard Quotient**
Acute	72 hour	1.80	110	0.02
Subchronic	90 day	0.48	3	0.16
Chronic	1 year	0.19	2	0.09
Lifetime*	70 years	0.17	0.56	0.30

Table 2: Delhi's Maximum Concentrations for Each Exposure period

*Calculated from available data Dec. 2016-Dec. 2018

**Hazard quotient is calculated as the ratio of measured concentration to screening level.

Figure 1 shows observed concentrations of 1,3-D as a function of time for Delhi in 2018. During the earlier and later parts of the year, 1,3-D concentrations are higher, the months of June through August, present a period of NDs and these months correspond with the region's low 1,3-D use pattern.





Data gaps are invalidated samples not sent for analysis

3.2 Parlier

Between January and December 2018, 1,3-D was detected in 84% of the air samples collected at the Parlier monitoring site (43 of 51 valid samples). One sample was invalid and not analyzed due to an inadequate ending canister pressure. Quantifiable detections ranged from 0.011 to 111 ppb with a median of 0.109 ppb and a mean of 2.94 pbb. Maximum concentrations for Parlier are presented in Table 3.

Measured 2018 air concentrations detected at the Parlier monitoring site exceeded established health screenings levels for acute, subchronic, chronic, and lifetime exposures. Subchronic, chronic, and lifetime concentrations were largely influenced by a single high detection of 111 ppb that was measured in October 2018. Due to how maximum subchronic and chronic exposures are calculated by DPR, the presence of the 111 ppb detection in the calculations increased the subchronic average concentration from 1.97 ppb to 10.53 ppb. Similarly, this high 111 ppb value almost quadrupled the 1-yr chronic concentration from 0.76 ppb to 2.94 ppb. As a result, the hazard quotients for all exposure periods were greater than 1.0.

For the acute exposure period, the maximum 24-hr concentration of 111 ppb measured at the site was compared to DPR's 72-hr acute screening level of 110 ppb. No 72-hr air sample was

collected in this study. It is unknown whether the 110 ppb 72-hr exposure target was exceeded during the 24-hr sampling period that included the 111 ppb air sample collected.

To address unacceptable exposures to ambient 1,3-D air concentrations, DPR is developing regulations to mitigate acute and lifetime exposures to 1,3-D.

Exposure	Exposure Period	Total 1,3-D (ppb)	Screening Level (ppb)	Hazard Quotient**
Acute	72 hour	111.29	110	1.01
Subchronic	90 day	10.53	3	3.51
Chronic	1 year	2.94	2	1.47
Lifetime*	70 years	1.71	0.56	3.05

Table 3: Parlier's maximum concentrations for each exposure period

*Calculated from available data Dec. 2016-Dec. 2018

** Hazard quotient is calculated as the ratio of measured concentration to screening level.



Figure 2: Observed 1,3-D air concentrations over time at Parlier

Data gaps are invalidated samples not sent for analysis

4. Quality Assurance Results

4.1 Collocated/Duplicate Samples

During 2018, 10 valid collocated paired air samples were collected from the Delhi site. Two pairs of sample results reported a ND for the primary sample and a quantifiable detection for the collocated sample. DPR was not able to calculate a relative percent difference for those two results. The additional eight pairs had measurable detections that resulted in an average relative percent difference of 21% (Standard Deviation [SD] = 18%). All samples were reviewed and determined valid by DPR based on DPR's acceptable sampling criteria of flow rate and ending canister pressure.

Sample Date	Primary Sample	Primary Result (ppb)	Collocated Sample	Collocated Result (ppb)	Relative % Difference
1/8/2018	309-A089	ND	309-A088	0.046	N/A
4/13/2018	309-A107	0.478	309-A108	0.483	1
4/26/2018	309-A111	0.063	309-A112	0.036	55
5/8/2018	309-A114	0.026	309-A115	0.022	17
8/3/2018	309-A132	0.033	309-A133	0.027	20
8/6/2018	309-A134	ND	309-A135	0.035	N/A
9/12/2018	309-A141	0.017	309-A142	0.022	26
10/13/2018	309-A147	0.055	309-A148	0.055	0
10/16/2018	309-A149	0.023	309-A150	0.024	4
11/19/2018	309-A157	1.705	309-A156	1.055	47

Table 4: Summary of collocated results and absolute relative percent difference

4.2 Fortified Field Spikes

In 2018, seven collocated field spikes were collected with the primary sample. These samples were collected using standard operating procedures for air sampling. Due to sampler availability, three were collected via a Restek regulator sampler and a Xonteck sampler. The other four were collected using two Xonteck samplers. The average percent recovery for the cis-1,3-D isomer was 70.7 % and 81.3% for the trans-1,3-D isomer. Table 6 highlights the results for each primary and fortified field spike. Two out of the seven field spikes fell below the lower control limits set by CDFA CAC for method EMON-SM-05-019 (*cis*: 61.6% and *trans*: 62%). DPR reached out to ARB and CDFA CAC labs to try to identify any unusual source of handling, but both confirmed that the samples were handled in the same manner.

Sample Date	Primary Sample	Primary Cis Result (ppb)	Primary Trans Result (ppb)	Primary Total 1,3-D (ppb)	Spike Cis Result (ppb)	Spike Trans Result (ppb)	Spike Total 1,3-D Result (ppb)	Percent Recovery: Cis	Percent Recovery: Trans
2/16/2018	309- A095	0.211	0.202	0.413	1.65	1.859	3.509	66.9	77.4
3/28/2018	309- A105	1.12	0.679	1.799	6.37	6	12.37	100.2	101.5
4/17/2018	309- A110	0.178	0.11	0.288	3.06	4.43	7.49	64.2	96.2
5/16/2018	309- A118	0.017	0.021	0.038	1.67	1.93	3.6	84.8	97.9
6/18/2018	309- A125	ND	ND	ND	0.657	0.92	1.577	37.1*	52*
8/20/2018	309- A138	ND	ND	ND	0.472	0.554	1.026	26.7*	31.3*
10/3/2018	309- A146	ND	ND	ND	1.09	1.07	2.16	114.7	112.6

Table 5: Summary of Fortified Field Spike Results

*Samples indicating below the lower control limits

4.3 Laboratory Spikes and Blanks

For quality assurance purposes, the CDFA CAC conducted 27 lab spikes when performing the air sample analysis. Spike recovery rates averaged 96.7% (SD = 5.8%) and 95.79% (SD = 5.1%) for the *cis-* and *trans-* isomers. None of the CDFA CAC lab blanks reported any contamination. Individual results of laboratory spikes and lab blanks are included in Appendices III and IV.

5. Discussion

5.1 December Air Concentrations

Current 1,3-D permit conditions do not allow for 1,3-D to be applied in the month of December. Detections of 1,3-D were present in most of the samples collected during this time period (6 out of 8 samples) although applications did not occur. For untarped applications of 1,3-D, studies have demonstrated that the fumigant's cumulative emission tends to stabilize roughly two weeks after application and in some cases beyond with low-level volatilization (Gao et al. 2008, Gao and Trout 2007). This may explain the low levels of detections during December even in the absence of applications.

5.2 Elevated Detection in Parlier

A sample collected on October 9, 2018 had the highest measured 1,3-D detection to date, 111 ppb. As a result of this detection, DPR conducted a detailed investigation into possible sources, including the precise locations of where applications of 1,3-D may have occurred. The Fresno County Agriculture Commissioner was notified and DPR requested notice of intent (NOI) and PUR records for applications in the area near the Parlier air monitoring site location. DPR also evaluated preliminary use data available from October 1 through October 10, 2018. The department determined that five applications were likely to be the sources of the onsite measured 1,3-D. Utilizing available field boundary information, DPR was able to identify the likely locations by matching field IDs. The field locations were mapped in ArcGIS Pro (version 2.2) and through spatial analysis results, it was determined that the distances of field boundaries of the five applications ranged from 0.1 to 1 miles away from the Parlier monitoring site.

The precise location of these applications could not be determined due to applications being smaller than the total acreage of the field boundary, but a general approximation was assumed for computer air modeling purposes. DPR used AERMOD, an air dispersion modeling computer program, in an attempt to simulate the measured 111 ppb detection level. Parameters that were included in the AERMOD modeling were weather/meteorological data from California Irrigation Management Information System (CIMIS) station #39, air data from the Fresno Airport weather station, and upper air data (30 m) from the Oakland Airport weather station. DPR simulated the five applications using all available modeling inputs. AERMOD modeling results estimated an average 24-hour concentration of 30.1-35.5 ppb (Appendix VII). Modeling results underestimated the observed measurements from the air sample collected, possibly due to several uncertainties as detailed in Tao (2019).

5.4 Comparisons to Previous Year

At both monitoring site locations, average concentrations increased for every exposure period in 2018 compared to 2017. In Delhi, the annual concentration increased by 46%. In contrast, in Parlier the annual concentration increased significantly (374%) from the previous year. This large increase was primarily driven by the 111 ppb detection that occurred in October. Data is summarized in Tables 7 and 8 below.

Monitoring Period	2017	2018
1 day	1.06	1.80
90 day	0.29	0.48
1 year	0.13	0.19
Lifetime	0.17	7

Table 6: Maximum Delhi Air Concentrations by Year

Table 7: Maximum Parlier Air Con	icentrations by	Year
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Monitoring Period	2017	2018
1 day	15.96	111.29
90 day	1.83	10.53
1 year	0.62	2.94
Lifetime	1.71	





Figure 4: Parlier Air Concentrations



6. References

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Appendix

Appendix I: Raw Results for Delhi

Start Date	Sample ID	Total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
1/8/2018	309-A089	0.005	ND	ND
1/20/2018	309-A090	0.092	0.049	0.043
1/23/2018	309-A091	0.037	0.019	0.018
2/1/2018	309-A093	0.166	0.085	0.081
2/4/2018	309-A094	0.455	0.254	0.201
2/15/2018	309-A096	0.413	0.211	0.202
2/23/2018	309-A097	0.322	0.18	0.142
2/28/2018	309-A098	0.185	0.102	0.083
3/4/2018	309-A099	0.229	0.112	0.117
3/15/2018	309-A101	0.263	0.143	0.12
3/19/2018	309-A103	1.445	0.878	0.567
3/28/2018	309-A104	1.799	1.12	0.679
4/1/2018	309-A106	0.137	0.06	0.077
4/13/2018	309-A107	0.478	0.27	0.208
4/17/2018	309-A109	0.288	0.178	0.11
4/26/2018	309-A111	0.063	0.033	0.03
4/29/2018	309-A113	0.037	0.017	0.02
5/8/2018	309-A114	0.026	0.011	0.015
5/16/2018	309-A116	0.038	0.017	0.021
5/20/2018	309-A119	0.005	ND	ND
6/1/2018	309-A120	0.046	0.02	0.026
6/5/2018	309-A121	0.005	ND	ND
6/10/2018	309-A123	0.005	ND	ND
6/18/2018	309-A124	0.005	ND	ND
6/30/2018	309-A126	0.005	ND	ND
7/2/2018	309-A127	0.005	ND	ND
7/14/2018	309-A128	0.005	ND	ND
7/17/2018	309-A129	0.005	ND	ND
7/24/2018	309-A131	0.005	ND	ND
8/3/2018	309-A132	0.033	0.014	0.019
8/6/2018	309-A134	0.005	ND	ND
8/17/2018	309-A136	0.005	ND	ND
8/20/2018	309-A137	0.005	ND	ND
8/29/2018	309-A139	0.013	0.013	ND
9/6/2018	309-A140	0.179	0.089	0.09
9/12/2018	309-A141	0.012	0.012	ND
9/21/2018	309-A143	0.242	0.116	0.126
9/23/2018	309-A144	0.074	0.033	0.041
10/3/2018	309-A145	0.005	ND	ND

Start Date	Sample ID	Total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
10/13/2018	309-A147	0.055	0.031	0.024
10/16/2018	309-A149	0.023	0.012	0.011
10/22/2018	309-A151	0.084	0.041	0.043
11/1/2018	309-A152	0.054	0.022	0.032
11/7/2018	309-A153	0.091	0.048	0.043
11/15/2018	309-A155	0.274	0.154	0.12
11/19/2018	309-A156	1.705	0.987	0.718
11/30/2018	Invalid(Low			
12/4/2018	209-0159	0 158	0.1	0.058
12/4/2010	300 A1CO	0.138	0.1	0.008
12/10/2018	309-A160	0.241	0.108	0.133
12/19/2018	309-A161	0.005	ND	ND
12/27/2018	309-A162	0.005	ND	ND

Results listed as "0.005" are Non Detections substituted for one-half of the Method Detection Limit (0.01)

Start Data	Sample ID	Total 1 2 D (mmh)	$cis_1 2 D (conh)$	trans 1 2 D (mmb)
		(ppb)	(ppb)	(ppb)
1/3/2018	309-B063	0.082	0.043	0.039
1/10/2018	309-B064	0.005	ND	ND
1/17/2018	309-B065	0.056	0.034	0.022
1/27/2018	309-B066	Invalid	Invalid	Invalid
1/28/2018	309-B067	0.124	0.069	0.055
2/7/2018	309-B068	0.973	0.528	0.445
2/12/2018	309-B069	1.167	0.605	0.562
2/23/2018	309-B071	0.374	0.196	0.178
2/27/2018	309-B072	0.783	0.466	0.317
3/5/2018	309-B073	0.416	0.209	0.207
3/14/2018	309-B074	0.167	0.084	0.083
3/22/2018	309-B075	0.005	ND	ND
3/26/2018	309-B076	0.01	0.01	ND
4/4/2018	309-B077	0.037	0.019	0.018
4/9/2018	309-B078	0.026	0.011	0.015
4/16/2018	309-B079	0.005	ND	ND
4/24/2018	309-B080	0.005	ND	ND
5/3/2018	309-B081	0.016	0.011	ND
5/7/2018	309-B082	0.099	0.048	0.051
5/14/2018	309-B083	0.005	ND	ND
5/25/2018	309-B085	0.005	ND	ND
5/29/2018	309-B084	0.011	0.011	ND
6/6/2018	309-B086	0.030	0.018	0.012
6/14/2018	309-B087	2.440	1.34	1.1
6/19/2018	309-B088	0.073	0.03	0.043
6/25/2018	309-B089	0.129	0.056	0.073
7/5/2018	309-B090	4.183	2.005	2.178
7/9/2018	309-B091	0.082	0.032	0.05
7/18/2018	309-B092	0.860	0.491	0.369
7/26/2018	309-B093	0.293	0.121	0.172
7/31/2018	309-B094	0.005	0.005	0.005
8/8/2018	309-B095	0.061	0.033	0.028
8/13/2018	309-B096	0.042	0.024	0.018
8/23/2018	309-B097	0.032	0.016	0.016
8/28/2018	309-B098	0.005	0.005	0.005
9/5/2018	309-B099	0.042	0.023	0.019
9/10/2018	309-B100	0.157	0.068	0.089
9/20/2018	309-B101	0.523	0.253	0.27
9/25/2018	309-B102	1.924	1.141	0.783
10/1/2018	309-B103	0.049	0.027	0.022

Appendix II: Raw Results for Parlier

Start Date	Sample ID	Total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
10/9/2018	309-B104	111.290	72.35	38.94
10/18/2018	309-B105	9.080	5.22	3.86
10/24/2018	309-B106	5.530	3.3	2.23
10/30/2018	309-B107	3.300	1.66	1.64
11/5/2018	309-B108	2.140	1.06	1.08
11/14/2018	309-B109	1.407	0.617	0.79
11/18/2018	309-B110	0.874	0.466	0.408
11/29/2018	309-B111	0.109	0.067	0.042
12/3/2018	309-B112	0.437	0.252	0.185
12/12/2018	309-B113	0.257	0.125	0.132
12/18/2018	309-B114	0.351	0.162	0.189
12/27/2018	309-B115	0.087	0.041	0.046

Results listed as "0.005" are Non Detections substituted for one-half of the Method Detection Limit (0.01)

Appendix III: Lab Spike Recovery Rates

Analysis Date	cis- 1,3-D	trans-1,3-D	Sample
Analysis Date	recovery (%)	recovery (%)	Туре
1/11/2018	101.30	94.70	lab spike
1/23/2018	100.00	100.00	lab spike
2/8/2018	97.30	96.00	lab spike
2/22/2018	94.00	92.70	lab spike
3/8/2018	99.30	100.00	lab spike
3/22/2018	103.00	101.00	lab spike
4/3/2018	101.00	98.70	lab spike
4/16/2018	86.70	86.70	lab spike
5/3/2018	97.30	98.00	lab spike
5/24/2018	95.00	99.30	lab spike
6/7/2018	91.30	87.30	lab spike
6/21/2018	99.30	95.30	lab spike
7/5/2018	99.30	96.70	lab spike
7/19/2018	96.00	94.00	lab spike
8/3/2018	96.70	96.00	lab spike
8/28/2018	95.30	94.70	lab spike
9/10/2018	102.00	102.00	lab spike
9/21/2018	96.70	96.00	lab spike
11/8/2018	96.00	102.00	lab spike
11/9/2018	103.00	84.70	lab spike
11/15/2018	88.00	89.30	lab spike
11/16/2018	99.00	103.00	lab spike
11/29/2018	93.30	88.00	lab spike
11/30/2018	101.00	104.00	lab spike
12/6/2018	82.70	94.70	lab spike
12/10/2018	109.00	94.70	lab spike
12/27/2018	87.30	96.70	lab spike

Appendix IV: Lab Blank Recovery Rates

Analysis Date	cis 1,3-D recovery (%)	trans-1,3-D recovery (%)	Sample Type
1/11/2018	ND	ND	lab blank
1/23/2018	ND	ND	lab blank
2/8/2018	ND	ND	lab blank
2/22/2018	ND	ND	lab blank
3/8/2018	ND	ND	lab blank
3/22/2018	ND	ND	lab blank
4/3/2018	ND	ND	lab blank
4/16/2018	ND	ND	lab blank
5/3/2018	ND	ND	lab blank
5/24/2018	ND	ND	lab blank
6/7/2018	ND	ND	lab blank
6/21/2018	ND	ND	lab blank
7/5/2018	ND	ND	lab blank
7/19/2018	ND	ND	lab blank
8/3/2018	ND	ND	lab blank
8/28/2018	ND	ND	lab blank
9/10/2018	ND	ND	lab blank
9/21/2018	ND	ND	lab blank
11/8/2018	ND	ND	lab blank
11/9/2018	ND	ND	lab blank
11/15/2018	ND	ND	lab blank
11/16/2018	ND	ND	lab blank
11/29/2018	ND	ND	lab blank
11/30/2018	ND	ND	lab blank
12/6/2018	ND	ND	lab blank
12/10/2018	ND	ND	lab blank
12/27/2018	ND	ND	lab blank

Appendix V: Study #309: Monitoring of 1,3-Dichloropropene in Merced and Fresno Counties (Document Attached)

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 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.

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.

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

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) section¹ 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 pounds² (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.

¹ PLSS sections are distinct 1 mi² 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 mi²) arrangement of PLSS sections. DPR currently caps annual 1,3-D use per township.

² 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.

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	Rank Categ	ories						
	0 m	ile			7			
					-			
	0 to	1 mile		0	3	6	mi	
	1 to	5 mile		120				
Community		0 mile	0 mile	0-1 mile	0-1 mile	1-5 mile	1-5 mile	Overall
Name	County	(lbs/mi ²)	rank	(lbs/mi ²)	rank	(lbs/mi ²)	rank	Rank
Pajaro CDP	Monterey	10494.44	7	9346.931	7	7384.325	1	1
Mettler CDP	Kern	5848.561	18	15297.52	1	4122.704	23	2
 Keves CDP	 Stanislaus	 5481 404	 19	 4143 803	55	 2990 045	 71	34
Ballico CDP	Merced	4227,816	29	5994.074	23	2637.75	94	35
Parlier city	Fresno	897.614	105	5065.467	35	5091.927	9	36
Del Rey CDP	Fresno	6705.965	15	2425.463	104	3804.802	34	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 mi² 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			0 Mi	ile	0-1 N	1ile	1-5 N	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
ıst	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 0 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	
N	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 Miles
tt al	1	8	El Rio CDP	Ventura	14,976	4	8,780	11	3,267	57	and the second sec
Sout entr Coas	2	24	Guadalupe city	Santa Barbara	3,106	49	4,995	38	4,023	24	
0 -	3	28	Santa Maria city	Santa Barbara	5,208	21	9,185	8	2,751	88	2 3
	Continue	d on nex	t page								0 12.5 25 Miles

1	1. 1.5.1 7.64	8.8	26.								1
	Continue	d from p	previous page								
-	1	6	Westley CDP	Stanislaus	4,912	24	8,488	13	3,825	32	and the second
	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
h SJ	5	19	Livingston city	Merced	2,266	61	5,778	25	4,641	14	9
lort	6	22	Del Rio CDP	Stanislaus	7,976	11	5,754	27	3,032	69	3 00
2	7	30	Winton CDP	Merced	3,194	47	4,363	50	3,942	28	8 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 0 10 -
	4	7	Raisin City CDP	Fresno	2,454	55	9,915	5	4,896	10	12 11
	5	11	Edmundson Acres CDP	Kern	16,485	2	8,821	10	3,167	65	
SJV	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	A STREET
Sol	8	23	La Vina CDP	Madera	9,036	9	3,860	61	3,656	40	
	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 mi²) 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 16th 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 mi²) 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 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 105th 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 36th 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 mi²) 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 ± 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 ± 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/m³ (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 ± 2 and ± 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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Appendix VI: Determination of Bromomethane, Carbon Disulfide, cis-1,3 Dichloropropene and trans-1,3-Dichloropropene in air samples collected in summa canisters (Document Attached)

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Determination of Bromomethane, Carbon Disulfide, cis-1,3 Dichloropropene and trans-1,3-Dichloropropene in air samples collected in summa canisters.

1. Scope

This section method (SM) is for the analysis of the selected compounds collected in summa canisters. The canisters are pressurized after receipt at the lab and analyzed using GC/MSD in the SIM mode. The reporting limits for all the compounds are 0.01 ppbv.

2. Principle:

Air samples are collected in a summa canister that has been cleaned and under vacuum at 0.05 torr. The air sample is pressurized allowing the contents to flow into the sample concentrator through a mass flow controller and collected on an absorbent tube. The collected compound are then heated and flushed off the absorbent tube into the GC/MSD for analysis. The confirmation of compound identity with GC/MSD is achieved by the ratio of selected ions.

- 3. Safety:
 - 3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.
 - 3.2 All solvents should be handled with care in a ventilated area.
- 4. Interferences:

Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses.

Whenever a high concentration (>10 ppbv) sample is encountered, it should be followed by an analysis of humid zero air to check for carryover contamination.

- 5. Apparatus and Equipment:
 - 5.1 Silco steel summa air canisters (Restek # 24142-650)
 - 5.2 Mass flow controller

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- 5.3 Air concentrator auto sampler (Wasson-ECE)
- 5.4 Gas chromatograph (Agilent Model 7890) equipped with a mass spectrometer (Agilent model 5975) or equivalent.
- 5.5 Analytical column: Wasson-ECE proprietary 60m x 0.32mm 1.8µm film.
- 5.6 Canister cleaning system (Wasson-ECE TO-Clean)
- 5.7 Tedlar bags (various sizes)
- 6. Reagents and Supplies: (All reagents shall meet the minimum requirement in residue and pesticide analysis.
- 6.1 Nitrogen gas UHP He gas UHP Medical air
 - 6.2 Standards: An air mixture of the following compounds at 100 ppbv was prepared for calibration.

Bromomethane	CAS Number 74-83-9
Carbon disulfide	CAS Number 75-15-0
Cis-1,3 dichloropropene	CAS Number 10061-01-5
Trans-1,3 dichloropropene	CAS Number 10061-02-6

- 7. Calibration Standards Preparation:
 - 7.1 Make a 1:100 dilution of the 100 ppbv standard for the calibration standards.
 - 7.2 Use the Wasson-ECE auto sampler to load varying volumes of the 0.01 ppbv air mixture for the instrument calibration
- 8. Sample Preservation and Storage:

All samples shall be stored in the laboratory at ambient temperatures.

- 9. Test Sample Preparation:
 - 9.1 Sample Preparation
 - 9.1.1 Total sample volume for all samples using the stated calibration curve will be 1000 mL's.

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- 9.1.2 Sample volumes less that 1,000 mL's will be used for high concentration samples or samples with interfering matrices.
- 10 Instrument Calibration:
 - 10.1 The calibration standard curves consist of five levels. The lowest level must be at or below the corresponding reporting limits. (The current working standard levels are 0.01 ppbv, 0.05 ppbv, 0.15 ppbv, 0.25 ppbv and 0.5 ppbv.
 - 10.2 The calibration curves for the GC-MS are generally obtained using linear regression. Quadratic fit may be used if the response of certain compounds exhibited quadratic behavior.
 - 10.3 The following amounts of the 1.0 ppbv air mixture will be loaded through the Wasson auto sampler to generate the 5 point calibration curve.

Calibration amounts assuming 1000 mL's for all samples

Calibration	Calibration	1.0 ppb air mixture	Sampling time@
Level	Amount	Volume (mL)	30 mL's /min
Level 1	0.01 ppb	10 mL's	20 seconds
Level 2	0.05 ppb	50 mL's	100 seconds
Level 3	0.15 ppb	150 mL's	300 seconds
Level 4	0.25 ppb	250 mL's	500 seconds
Level 5	0.50 ppb	500 mL's	1000 seconds

All samples are loaded using 1000 mL's which takes 2,000 seconds

11 Analysis:

11.1 Injection Scheme

The GC-MS may need to be conditioned with a matrix sample or a humidified air blank before running the following sequence: A set of calibration standards, an air blank, an air spike, a set of up to 12 test samples, then another set of calibration standards.

11.2 GC-MSD Instrumentation:

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- 11.3.1 Agilent GC-MSD model HP7890 with a Wasson-ECE air concentrator auto sampler.
- 11.3.2 Column: Wasson propriarity 60m x 032mm x 1.8µm film
- 11.3.3 Temperature program

Injector Temperature: 250 °C Oven Temperature:

Oven Ramp	Program (°C/min)	Temperature (°C)	Hold (min)	
initial		45		4
Ramp 1	15	200		2
Ramp 2	15	250		2

11.3.4 Retention times and ions selected for SIM acquisition:

Compound name	Retention time	Selected ions	Starting time
Bromomethane	4.2	94, 96	3
Carbon Disulfide	5.9	76, 78	5
cis-1,3 dichloropropene	10.5	75, 110	10
trans-1,3 dichloropropene	11.0	75, 110	10

- 12. Quality Control:
 - 12.1 Each set of samples shall have a humid blank and minimum of one spike sample. Each set contains up to 12 samples.

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- 12.2 The blank shall be free of target compounds above the reporting limit.
- 12.3 The recoveries of the spike should be within the control limits.
- 12.4 The retention time shall be within \pm 20 seconds of that of the standard.
- 12.5 The sample volumes will be reduced if results fall outside the linear range of the standard curve.
- 12.6 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate air samples at 1.0 ppbv are analyzed. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.7 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. In general, the RL is chosen in a range 1-5 times the MDL. The response reproducibility of each compound is also considered to determine the RL

MDL data and the RL are tabulated in Appendix 1.

- 12.8 Method Validation Recovery Data and Control Limits:
 - 12.8.1 The method validation consisted of five sample sets. Each set included 5 levels (0.01, 0.05, 0.15, 0.25 and 0.50 ppbv)
 - 12.8.2 Upper and Lower warning and control limits are set at \pm 2 and \pm 3 standard deviations of the average % recovery, respectively.
 - 12.8.3 Method validation results and control limits are tabulated in appendix 2.

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- 13. Calculations:
 - 13.1 The quantification is based on the sum of area count of the quantitation ion of the compound analyzed. The calculation is based on external standard (ESTD).
 - 13.2 The correlation coefficient, slope, intercept of the linear regression line are calculated once the calibration standards are defined. The equation for calculating analytes using a linear calibration is as follows:

y= mx+b

Where: y = peak response m = slope b = intercept x = concentration of compound

When the unit and the dilution factor are entered correctly in the analysis sequence, the software will then correctly generate the results.

13.3 Results can be manually calculated by a single point standard. The unit is ppbv (parts per billion volume).

The general equation is as follows:

13.4 Calculating the pressurization factor (PF) when pressurizing the canister before Analysis.

14.7 *psig*+ analysis pressure *psig*

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- 14. Reporting Procedure:
 - 14.1 Perform Quantification with Enhanced Data Analysis software:
 - 14.1.1 Load a standard data file Integrate the data file
 Edit compounds based on retention time and identity
 Review the window range of each compound and adjust it as needed.
 Reintegrate the data file based on the new method
 Update levels
 View the calibration curves
 Save as a new method
 - 14.1.2 Load a sample data file Do quantification with this new method with new calibration curves Review each compound and do integration correction if necessary Save this reviewed file Print this reviewed data file
 - 14.2 Acceptance Criteria:
 - 14.2.1 Peak retention time between standards, QC spikes and unknowns shall be within 20 seconds. If there is a known reason for retention time shifting, an explanation memo shall be included.
 - 14.2.2 Peak response shall be within the calibration range
 - 14.2.3 The R² of calibration curve or overlay calibration curves shall be 0.990 or better.
 - 14.2.4 Recoveries of spike QC shall be within the established control range, otherwise a rerun of the entire set shall be performed. If problems remain, an explanation memo shall be included.
 - 14.2.5 The ratio of product ion and precursor ion between standard and unknown shall be consistent and the variation of the ratio between standard and unknown shall be within ±20 %.

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- 14.2.6 Manual single point calculation result is acceptable with explanation
- 14.3 Reporting:
 - 14.3.1 Sample results are reported out according to the client's analytical laboratory specification sheet.
 - 14.3.2 Fill out COC, QC sheet, and control chart.
 - 14.3.3 Prepare data package. Peer review. Report.
- 15 Canister cleaning and certification
 - 15.1 All canisters must be clean and free of any contamination before sample collection.
 - 15.2 All canisters are leak tested by pressurizing them to 30 psig with zero-air or nitrogen. The pressure should not vary by more than 2 psig over a 24 hour period.
 - 15.3 Canister cleaning

15.3.1The canister valve is opened in a fume hood to release the pressurized air in the canister. Place canister in cleaning oven and start up the vacuum pump.

- 15.3.2 The canister is evacuated to 0.05mTorr for 30 minutes.
- 15.3.3 The canister is then pressurized with humid air to 30 psig.
- 15.3.4 Repeat steps 15.3.2 and 15.3.3 2 more times for a total of three evacuations/pressurizations for each canister.
- 15.3.5 At the end of the evacuation/pressurization cycles, pressurize the canister to 30 psig with humid zero air.
- 15.3.6 The canister is then analyzed by the GC/MS system. The canister is clean when there are no detected targeted VOC's > 0.5 ppbv.

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- 15.3.7 After the canister passed the analysis return the canister to the cleaning system and evacuate the canister to 0.05 mTorr. Close the valve and remove the canister from the cleaning system.
- 15.3.8 The canister is now ready for collection of an air sample.

16 References

Method TO-14A U.S. EPA Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268 January 1999

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Appendix 1

Method Detection Limit (MDL) data

Compound	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7
Bromomethane	0.04412	0.04107	0.04477	0.04020	0.04308	0.04301	0.04126
Carbon disulfide	0.04652	0.04571	0.04612	0.04590	0.04414	0.04404	0.04400
cis-1,3 dichloropropene	0.04923	0.04645	0.04626	0.04439	0.04881	0.04691	0.04950
trans-1,3							
dichloropropene	0.04960	0.04769	0.04780	0.04466	0.04690	0.04833	0.04741

⁽MDL = 3.14 X SD)

						0.01
Bromomethane	SD	0.0017	MDL	0.0051	RL	ppbv
						0.01
Carbon disulfide	SD	0.0011	MDL	0.0033	RL	ppbv
						0.01
cis-1,3 dichloropropene	SD	0.0019	MDL	0.0056	RL	ppbv
trans-1,3						0.01
dichloropropene	SD	0.0015	MDL	0.0045	RL	ppbv

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Compound	ppbv	Day 1	Day 2	Day 3	Day 4	Day 5	SD	14.18
Bromomethane	0.01	100	81.5	95.0	90.3	74.8	Mean	95.17
	0.05	84.2	93.4	90.1	70.1	77.3	UCL	137.71
	0.15	90.6	105	100	87.5	82.9	UWL	123.53
	0.25	96.0	88.1	99.5	95.2	100	LWL	66.81
	0.5	96.7	117	126	125	113	LCL	52.63

Compound	ppbv	Day 1	Day 2	Day 3	Day 4	Day 5	SD	3.34
Carbon								
disulfide	0.01	89.3	86.0	90.3	87.4	86.7	Mean	89.85
	0.05	97.3	92.0	90.1	98.8	86.0	UCL	99.87
	0.15	90.3	89.5	87.5	92.2	84.5	UWL	96.53
	0.25	90.6	90.1	87.8	91.3	85.8	LWL	83.17
	0.5	91.0	93.4	90.7	89.7	88.0	LCL	79.83

Compound	ppbv	Day 1	Day 2	Day 3	Day 4	Day 5	SD	4.03
c-1,3-D	0.01	91.6	82.5	98.2	93.6	88.3	Mean	92.34
	0.05	94.7	96.8	97.3	102	93.2	UCL	104.43
	0.15	89.6	92.0	92.6	93.8	88.0	UWL	100.40
	0.25	89.9	89.5	92.5	93.0	88.3	LWL	84.28
	0.5	89.6	93.9	96.7	91.0	89.9	LCL	80.25

Compound	ppbv	Day 1	Day 2	Day 3	Day 4	Day 5	SD	5.22
t-1,3-d	0.01	90.1	83.3	109	89.7	93.6	Mean	93.27
	0.05	99.0	93.5	101	102	91.3	UCL	108.94
	0.15	91.6	91.0	93.0	94.4	87.7	UWL	103.72
	0.25	91.8	90.4	92.6	93.1	87.9	LWL	82.83
	0.5	91.8	94.9	97.3	90.9	90.9	LCL	77.60

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Author:

Original Signed by

12/4/2013

Date

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Revision Log:

Date	What was revised? Why?
5/15/2012	Changed RL to 0.1 ppbv and updated with new MDL and validation results.
11/6/13	Changed RL to 0.01 ppbv, updated with new MDL and validation results.

Appendix VII: Modeling 1,3-Dichloropropene Applications at Parlier, CA on October 9, 2018 (Document Attached)



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

Modeling 1,3-Dichloropropene Applications at Parlier, CA on October 9, 2018

Jing Tao

March 15, 2019

Introduction

The Department of Pesticide Regulation (DPR) has been monitoring ambient air concentrations of 1,3-dichloropropene (1,3-D) at Parlier (Fresno County) since December 2016 (Brown, 2016). A concentration of 111 ppb ($504 \mu g/m^3$) was measured at this monitoring site during a 24-hr sampling period on October 9-10, 2018. This air concentration of 1,3-D is the highest concentration measured in ambient air monitoring studies conducted by DPR. Although the 24-hr concentration of 111 ppb does not necessarily indicate that DPR's acute human health screening level of 110 ppb for a 72-hr period was exceeded, the measured value could cause the annual average concentrations were measured over several years. Therefore, an evaluation of this detection was conducted with use data information from preliminary 2018 pesticide use reports (PUR). Based on the use data, there were five possible 1,3-D applications on October 9, 2018 that likely could have been the sources that led to the high detection. Computer modeling using the AERMOD air dispersion model was employed to simulate these 1,3-D applications and examine if the measured concentration could be modeled under the weather conditions recorded by nearby meteorological stations.

1,3-D Applications

Table 1 listed the information of five reported applications. The sampling site and the fields were shown in Figure 1. The field areas ranged from 3.2 to 5.45 acres, which were larger than the treated areas.

Site ID	5355	5237	5115	5354	5236
Source Group	1	1	2	2	3
Start Time (hr)	1030	1030	900	900	1200
1,3-D (lbs)	478.09	478.09	848.67	848.67	648.02
Treated Area (ac)	1.45	1.45	2.6	2.6	2
Field Fumigation	1210	1210	1210	1210	1210
Method (FFM)					
Application Rate	330	330	326	326	324
(lbs/ac)					

Table 1. Preliminary application information of pesticide use report (PUR)



Figure 1. Location of 1,3-D monitoring site at Parlier and agriculture fields where the applications were conducted on 10/09/2018.

AERMOD Configuration and Post-Processing

Although PUR contains field information, the exact treated area of each field is unknown. Therefore, an area close to the monitoring site and within the reported field was configured as each source location (Figure 2). A receptor was set at the Parlier monitoring site with height of 4 m to match the monitoring site (Figure 2). A uniform grid receptor network at the same height with spacing of 50 m was also used to output contour plots. DPR developed flux profiles for all 1,3-D field fumigation methods (FFMs) applied in 16 soil types using HYDRUS modeling (Brown, 2018). All the applications around the sampling site on 10/9/2018 were reported use of FFM 1210 but the soil information was unknown. This modeling used the flux of soil #5 because this flux produces the highest emission among the 16 examined soil types. The flux was developed for a nominal rate of 100 lbs/ac and had units of ug/m²s. It was accordingly converted to the flux profiles for the different application rates starting at the reported application hours.

The air sampling started at 16:37 and lasted for 24 hours so the modeling period was first set as hour 17 of 10/09/2018 to hour 16 of 10/10/2018 to estimate the 24-hr average concentration of this period. In addition, the model outputted hourly concentrations from 10/09/2018 to 10/15/2018. The results were used to estimate the rolling 24-hr and 72-hr average concentrations after applications.



Figure 2. Diagram of modeling sources and the receptor at the Parlier site

Meteorological Data

Meteorological files used in the AERMOD modeling are processed by MetProc. MetProc is an interface of AERMET, the meteorological data processer of AERMOD developed by the United States Environmental Protection Agency (USEPA). DPR developed MetProc to process weather data for AERMOD modeling of pesticide uses (Luo, 2017). For this modeling, the upper air soundings used data of the station WBAN 23230 at Oakland International Airport. The surface weather data was from the station at Fresno Airport (WBAN 93193), which is about 17 miles away from the monitoring site. A station of the California Irrigation Management Information System (CIMIS) at Parlier (#39) is located 0.5 mile southeast of the monitoring site and was considered for use as an onsite station. However, since CIMIS stations measure weather conditions at 2 m above the ground, their wind measurements are only considered to be valid and compiled into the AERMOD meteorological files by AERMET in the hours when the surface roughness is lower than 1/7 of the anemometer height 2 m (USEPA, 2018). For the 24-hr period from hour 17 of 10/09/2018 to hour 16 of 10/10/2018, 22 hours of CIMIS hourly records were valid. Figure 3 compared the wind roses of the AERMOD ready meteorological file compiled from the WBAN 93193 data only and the data including CIMIS 39 as an onsite station during the sampling period. CIMIS 39 recorded more low wind speeds at 0.5 - 1 m/s and less variation of wind directions than WBAN 93193. No calms hours were recorded at both stations.



Figure 3. Wind roses of AERMOD ready meteorological files compiled with surface station (A) WBAN 93193 and (B) CIMIS #39 + WBAN 93193 during the 24-hr period between hour 17 of 10/09/2018 to hour 16 of 10/10/2018.

Results and Discussion

Average Concentration during Sampling Period

The two sets of meteorological files, (A) WBAN 93193 and (B) CIMIS #39 + WBAN 93193, estimated 24-hr average concentrations as 35.5 and 30.1 ppb at the sampling site during the sampling period (Table 2). The estimated concentrations were about 32% and 27% of the sampling result 111 ppb. Although two sets of data closely estimated the concentrations, contour plots showed that the spatial distribution of concentrations in the modeling domain area were different (Figure 4). Table 2 listed the contribution of three source groups to the concentrations estimated at the sampling site. CIMIS #39 had more low wind speed and estimated a higher concentration contributed by the nearby sources (Source Group 1). Higher wind speed recorded by WBAN 93193 might convey higher amount of 1,3-D from farther sources to the sampling site. WBAN 93193 estimated that the contributed concentrations from Source Group 2 and 3 were about 9 and 2 times of the estimates of CIMIS #39.

Contour plots of both meteorological files showed that the 1,3-D air concentrations traveled from the treated fields towards the sampling site in the west and could lead to high concentrations near the sampling site during 10/9 - 10/10 (Figure 4).

	Weath	ner A: WBAN	93193	Weather B: CIMIS #39 + WBAN 93193			
Source	$\frac{\text{Conc}}{(\mu q/m^3)}$	Conc (ppb)	%	$\frac{\text{Conc}}{(\mu q/m^3)}$	Conc (ppb)	%	
1 010up	(μg/m) 118.6	26.1	74	(μg/m) 131.5	29.0	06	
2	40.5	20.1	25	131.3	29.0	90	
Z	40.3	8.9	23	4.5	1.0	3	
3	2.1	0.5	1	0.9	0.2	1	
Sum	161.3	35.5	100	136.7	30.1	100	

Table 2. Time weighted average concentrations at Parlier monitoring site during the samplingperiod.



Figure 4. Contour plots of 1,3-D 24-hr average concentrations (µg/m³) estimated by AERMOD using meteorological data compiled with surface station (A) WBAN 93193 and (B) CIMIS #39 + WBAN 93193 during the sampling period .

Model Uncertainties

Several uncertainties in this modeling case could cause the discrepancy between the estimated and monitored results:

(1) Representative weather station.

As shown in Figure 3, wind conditions recorded by the two stations were different. WBAN 93193 is 17 miles away from the site. While CIMIS #39 is located closer, its anemometer height is only 2 m. The anemometer height of 10 m is usually required for the air dispersion modeling (USEPA, 2018). Neither of them may perfectly represent weather condition of the modeling domain area.

(2) Wind condition.

AERMOD uses hourly weather data and its output has a minimal interval of an hour. The wind direction shown in Figure 2 was an average or an observation of an hour, which did not reflect accurate instantaneous wind direction and could cause uncertainty in the magnitude and location of the estimated concentrations. In addition, under stable light wind conditions, modeling results do not perform well to match the monitoring concentration paired in space because of potential high degree of variability existing in the modeling domain and the microscale influences on air transport and dilution (USEPA, 2017). Figure 4(A) shows that the concentration of a location near the site and about the same distance from Source Group 1 was estimated at 234 μ g/m³ (52 ppb), which was 1.5 times of the estimate at the site and could occur at the site.

(3) Flux profile.

The actual 1,3-D emission fluxes of the applications are unknown. The flux profiles generated by HYDRUS used soil characteristics of 16 types of agricultural soils sampled in previous fumigant field studies conducted by DPR. These soils types may not represent the actual soil conditions of the treated fields on 10/09/2018. Different soil conditions could cause variation of the fluxes and subsequently the air concentrations. For example, if reducing the organic matter content of soil #5 to 0, which was possible especially when turning over older orchards for replant, the new flux values would lead to 41 ppb estimated at the sampling site. In addition, the flux was generated for the application time at 8 AM and could change for the applications at noon because of the effect of diurnal temperature fluctuation on emission rates.

(4) Application information.

The exact location and shape of the treated area is unknown. Sometimes the application time recorded in PUR may be inaccurate. For example, the applicators may input an incorrect application time; or they input a planned start time, instead of the actual application completion time that was used by the modeling as flux starting time. Five treatments had recorded application time between 10 AM - 1PM, when the flux estimated the lowest concentrations. Assuming that the flux profile would not change for different application time, the estimated concentrations of the sampling site were around 41 ppb for applications completed in the early morning at 5AM or in the afternoon at 4 PM.

All the above factors could interact with each other and bring more complexity to this case.

Rolling Average Concentrations

Hourly concentrations and their rolling averages were calculated and plotted on Figure 5. Although results of two sets of meteorological data had different temporal patterns, they both estimated the highest 24-hr average concentrations during the sampling period. The highest 72-hr average concentrations were estimated at 14.5 ppb (65.7 μ g/m³) and 12.3 ppb (55.9 μ g/m³), about 13% and 11% of DPR acute health screening level of 110 ppb for 1,3-D. For the meteorological data of WBAN 93193, a 72-hr period ending at 1AM of 10/13/2018 produced the highest concentrations. Results of the meteorological data including CIMIS #39 presented five continuous 72-hr periods producing the same highest concentration. Figure 6 presents the contour plots for the 72-hr period that estimated the highest concentration.



Figure 5. Hourly and rolling average concentrations estimated at sampling sites using meteorological data compiled with surface station (A) WBAN 93193 and (B) CIMIS #39 + WBAN 93193



Figure 6. Contour plots of 1,3-D maximum 72-hr average concentrations (μg/m³) estimated by AERMOD using meteorological data compiled with surface station (A) WBAN 93193 and (B) CIMIS #39 + WBAN 93193.

Conclusion

This analysis used AERMOD to simulate five 1,3-D applications near the Parlier sampling site of DPR Study 309 on 10/09/2018. With the available application and meteorological data, the modeling estimated the average concentration as 30.1 - 35.5 ppb during the sampling period, about 27% - 32% of the monitoring result. Several uncertainties are discussed regarding the discrepancy between the modeling and monitoring estimates. Despite the underestimated concentrations, the modeling results showed that the 1,3-D traveled from the treated fields towards the sampling site and could cause high concentrations collected at the site. In addition,

this analysis estimated 24-hr and 72-hr rolling averages for 7 days following the reported applications. The sampling on 10/9/2018 - 10/10/2018 appeared to be one of the 24-hr periods that collected the highest 1,3-D concentrations after these particular applications. The modeling estimated the highest 72-hr average concentration as 12.3 - 14.5 ppb, about 11 - 13% of the DPR target concentration 110 ppb.

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