Monitoring of 1,3-Dicloropropene in Merced and Fresno Counties
Results for 2019

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TABLE OF CONTENTS

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 as well as environmental conditions. In 2017, the California Department of Pesticide Regulation (CDPR) revised permit conditions which eliminated 1,3-D use in the month of December and restricted the total allotted application amount within each township - a 6x6 square mile area - to a maximum of 136,000 adjusted pounds (a weighting method to account for emissions based on application method, month, and region) in a calendar year (CDPR 2016).

In 2016, CDPR conducted an evaluation on reported 1,3-D pesticide use to rank communities surrounded by highest 1,3-D use. CDPR prioritized regions outside the coverage area of CDPR's Air Monitoring Network and the California Air Resources Board's (CARB) Toxic Air Contaminant programs. As a result, CDPR selected two communities in the Central Valley; Delhi (Merced County) and Parlier (Fresno County). This monitoring study aims to identify the presence of ambient air concentrations of 1,3-D in regions of high use, compare measured air concentrations to sub-chronic and chronic human health screening levels, evaluate the effectiveness of the current township cap on chronic ambient concentrations, and determine correlation between pesticide use records and ambient air concentrations. CDPR staff collected weekly 24-h air samples to monitor 1,3-D in these two communities beginning in November, 2016.

This report evaluates the results of samples collected from January 1, 2019 through December 31, 2019 and is the third report for this multi-year study.

2. Methods

2.1 Field and Lab Methods

From January 1, 2019 through December 31, 2019, one 24-h ambient air sample (primary sample) was collected each week on a randomly assigned day of the week at Delhi and Parlier. Sample start times varied as they were left to the discretion of individual field staff. Samples were collected using a 6-Liter SilcoCan® canister (Restek cat. no. 24142-65) pre-evacuated to a pressure of -30" Hg placed on a Xonteck 901 Model automated active sampler. As a backup process depending if the Xonteck 901 sampler malfunctioned or was unavailable a Veriflow SC423XL flow controller attached to the SiloCan ® canister was used to conduct the air sampling. A more in-depth sampling procedure is included in Appendix V. Approximately once a month, a collocated sample was collected which is placed adjacent to primary samples. Delhi was designated the collocated site and was used as the quality control monitoring station. 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 CDPR's standard lab quality control procedures and conducted lab blanks and lab spikes during each analytical run.

2.2 Data Analysis

CDPR aggregates the laboratory results of 1,3-D isomers (cis and trans) per sample as the total 1,3-D concentration and compares the data collected with current health-based screening levels and regulatory targets for each year. For purposes of calculating averages, CDPR substitutes non detections (ND) with a value of one-half the reporting limit (0.005 ppb) for the total 1,3-D. However, if either cis or trans isomers of 1,3-D concentration were detected, then the total 1,3-D result would equal the value of that detection and no substitution is used for the other ND isomer. Average concentrations of 1,3-D are determined for acute, sub-chronic, chronic, and lifetime periods (Table 1). In the absence of a 72-h 1,3-D air sample, the 24-h average concentration measured in this study is compared against the established 72-h acute exposure level. Rolling averages of 90 days (13 weeks) are calculated to determine sub-chronic exposures. One-year average concentrations are calculated to determine the chronic exposure. In the absence of 70 years' worth of 1,3-D monitoring data, CDPR uses the average concentrations originating from the start of this study, beginning in December 2016, to calculate a lifetime exposure. To determine the risk associated for each exposure period, CDPR uses a Hazard Quotient (HQ). The HQ is calculated as a ratio of the measured 1,3-D concentrations to screening levels or a regulatory target. A HQ of greater than one (HQ > 1) indicates exceedance of the screening level and requires CDPR to take action to further evaluate the data and look into possible mitigation measures (CDPR 2011).

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

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

*Regulatory target rather than a screening level

3. Air Monitoring Results

In 2019, a total of 103 valid primary samples were collected from the two sites (Appendices I and II). During this period, 1,3-D was detected in 80% of air samples collected from Delhi and Parlier.

3.1 Delhi

Fifty-one (51) valid primary samples were collected at the Delhi site. One sample was invalidated due to a low ending canister pressure during the week of May 10 and CDPR was not able to make up another sample. Detected 1,3-D concentrations from the Delhi monitoring site were above the reporting limit (RL) in 78% of the samples in 2019 (40 out of 51 samples). Results from the Delhi monitoring site were characterized by a high number of detections; however, none of the detections exceeded established targets for acute, sub-chronic, chronic, or lifetime exposures. Quantifiable detections (above the reporting limit of 0.01 ppb) ranged from 0.017 to 2.04 parts per billion (ppb). The mean annual concentration for Delhi was 0.151 ppb and a median of 0.06 ppb in 2019. A summary of maximum observed concentrations for each

exposure period are included in Table 2 for Delhi. Results for acute, sub-chronic, and chronic exposure categories were below a HQ of 1.0. The highest observed HQ was 0.29 for lifetime exposure.

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

Exposure	Exposure Period	1,3-D (ppb)	Screening Level (ppb)	Hazard Quotient**
Acute	24 hour	2.04	110	0.02
Sub-chronic	90-day	0.42	3	0.14
Chronic	1 year	0.15	2	0.08
Lifetime*	70 years	0.163	0.56	0.29

*Calculated from available data Dec. 2016-Dec. 2019

**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 2019. Concentrations of 1,3-D were consistent toward the early and later months of the year. The months of July and August are presented more NDs, which coincides with the region's low 1,3-D use pattern.

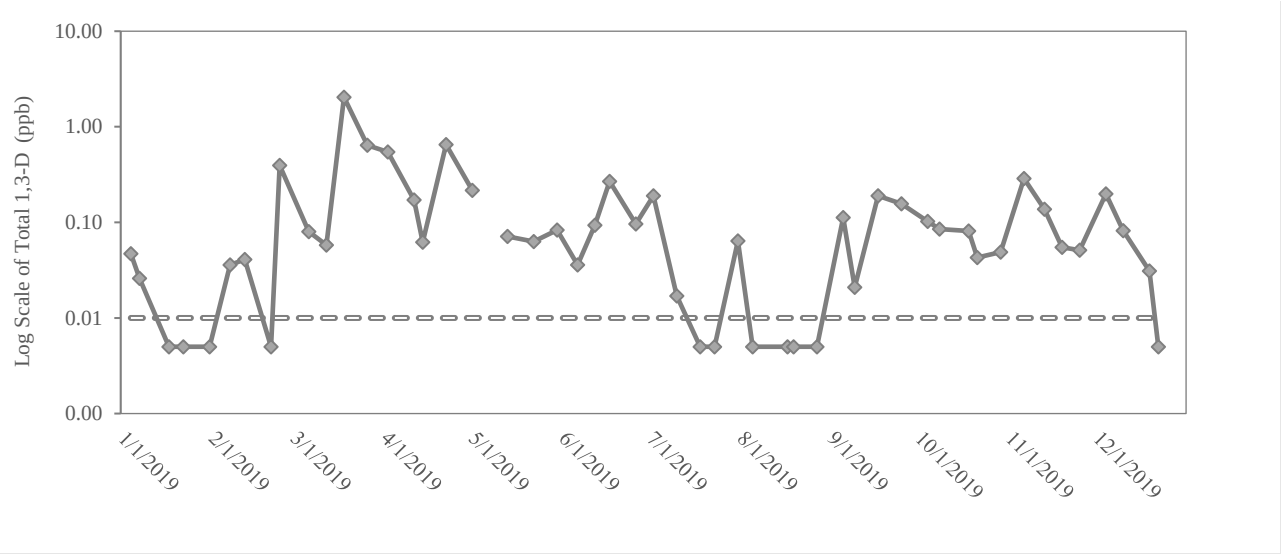

Figure 1: Observed 1,3-D air concentrations over time at Delhi. The data gap represents the invalidated sample from the week of May 10. The dashed horizontal line represents the reporting limit (RL).

3.2 Parlier

In Parlier, all 52 air samples collected between January and December 2019 were valid. 1,3-D was detected in 82% of the air samples collected at the Parlier monitoring site (43 of 52 samples). Parlier results are characterized by a large number of detections, but no exceedances for acute, sub-chronic and chronic targets were observed in 2019. Quantifiable detections in 2019 ranged from 0.011 to 2.07 ppb with the annual mean and median concentration of 0.27 ppb and 0.0945 ppb, respectively in Table 3 for Parlier.

Aggregating the measured air concentrations at the Parlier monitoring site from December 2016 through December 2019 revealed an exceedance of the established regulatory target for

lifetime exposures. The exceedance was largely due to a single high detection of 111 ppb in October 2018 and not a result of concentrations from 2019 (Gonzalez, 2019). To address unacceptable exposures to ambient 1,3-D air concentrations, CDPR is developing regulations to mitigate exposures to 1,3-D.

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

Exposure	Exposure Period	1,3-D (ppb)	Screening Level (ppb)	Hazard Quotient**
Acute	72 hour	2.07	110	0.02
Sub-chronic	90-day	0.78	3	0.26
Chronic	1 year	0.27	2	0.14
Lifetime*	70 years	1.24	0.56	2.21

*Calculated from available data Dec. 2016-Dec. 2019

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

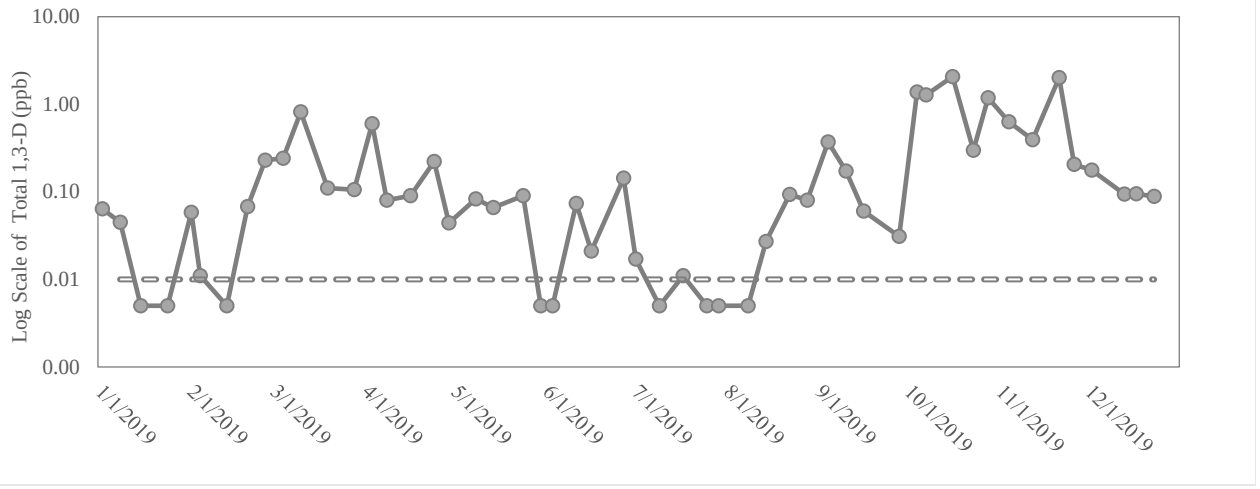

Figure 2: Observed 1,3-D air concentrations over time at Parlier. The dashed horizontal line represents the reporting limit (RL).

4. Quality Assurance Results

4.1 Collocated Samples

During 2019, 10 out of 10 scheduled collocated paired air samples were valid and collected from the Delhi site. A pair of sample results reported NDs for the primary sample and the collocated sample; thus, CDPR was not able to calculate a relative percent difference for that pair. The other nine pairs had measurable detections above the detection limit resulting in an average relative percent difference of 43% (standard deviation [SD] = 43). All samples were reviewed and determined valid by CDPR based on CDPR's acceptable sampling criteria of flow rate and ending canister pressure.

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

Sample Date	Primary Sample	Primary Result (ppb)	Collocated Sample	Collocated Result (ppb)	|Relative % Difference|
2/12/2019	309-A172	0.041	309-A173	0.052	24
3/6/2019	309-A177	0.08	309-A178	0.033	83
4/2/2019	309-A183	0.544	309-A184	0.658	19
4/11/2019	309-A186	0.171	309-A185	0.224	27
4/22/2019	309-A188	0.653	309-A189	0.668	2
5/1/2019	309-A190	0.216	309-A191	1.149	137
8/27/2019	309-A216	ND	309-A217	ND	N/A
9/17/2019	309-A221	0.189	309-A222	0.211	11
11/13/2019	309-A235	0.137	309-A236	0.146	6
12/4/2019	309-A240	0.199	309-A239	0.089	76

4.2 Laboratory Spikes and Blanks

For quality assurance purposes, the CDFA CAC conducted 24 laboratory spikes when performing the air sample analysis. Spike recovery rates averaged 95.4% (SD = 6.7) and 96% (SD = 5.0) for the *cis*- and *trans*- isomers, respectively. Out of the 24 the lab blanks, there were no reports of cross contamination in these samples. 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 the application of 1,3-D during the month of December. Detections of 1,3-D were present in most of the samples collected from Delhi and Parlier during the month of December (7 out of 8 samples). Delhi experienced low-level detections for the first three weeks followed by a non-detection during the last sampling event in December. In Parlier, four low 1,3-D detections were present in the month of December. For untarped applications of 1,3-D, studies have demonstrated that the fumigant's cumulative emission tends to stabilize roughly two weeks after application (Gao et al. 2008, Gao and Trout 2007). This may be one of the contributing factors to the low levels of detections observed during December even in the absence of 1,3-D applications during that month.

5.2 Comparisons to Previous Year

Delhi's maximum sub-chronic exposure decreased 13% while the annual average showed a 21% reduction from the previous year. Over a one-year period, the maximum acute exposure increased slightly from 1.80 to 2.04 ppb (13%). Annual summaries are presented in Table 5.

In Parlier, maximum concentrations of acute decreased 98%, sub-chronic decreased 92%, and chronic concentration were reduced 90% over the last year. Annual summaries are presented in Table 6.

Table 5: Maximum Delhi Air Concentrations by Year

Monitoring Period	2017	2018	2019
1 day	1.06	1.80	2.04
90 day	0.29	0.48	0.42
1 year	0.13	0.19	0.15
Lifetime	0.16		

Table 6: Maximum Parlier Air Concentrations by Year

Monitoring Period	2017	2018	2019
1 day	15.96	111.29	2.07
90 day	1.83	10.53	0.78
1 year	0.62	2.94	0.27
Lifetime	1.24		

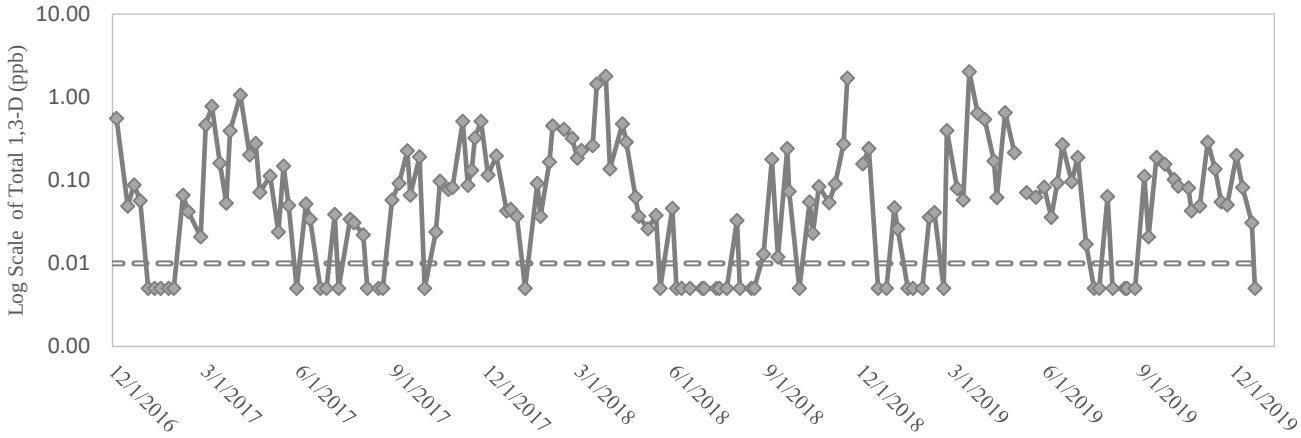

Figure 3: Log scale of Delhi air concentrations since the beginning of the study from December 2016-December 2019. The dashed horizontal line represents the reporting limit (RL).

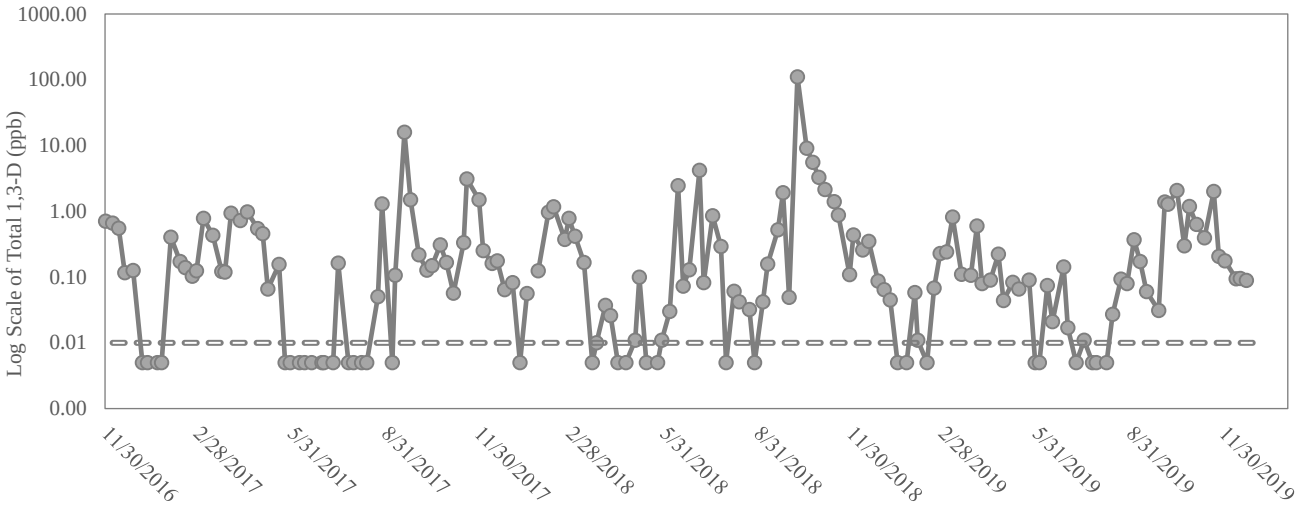

Figure 4: Log scale of Parlier air concentrations since the beginning of the study from December 2016-December 2019. The dashed horizontal line shows the reporting limit (RL).

5.3 Study Updates

In late October 2019, CDPR began to monitor onsite meteorological data at the Parlier monitoring location. The newly installed weather station is situated adjacent to the monitoring station with sensors at 2 and 10 meters high. The sensor at 2 meter height is an ATMOS 41 all-in-one system manufactured by Meter Group, Inc. It measures solar radiation, precipitation, air temperature, barometric pressure, vapor pressure, relative humidity, wind speed, wind direction. The meteorological variables monitored at 10 m height are wind speed (Met One Instruments, 10C), wind direction (Met One Instruments, 20C), relative humidity, and temperature (Met One Instruments, 083E). These meteorological variables are recorded and stored in the Zentra ZL6 (2 meter) and CR 23X (10 meter) data loggers. CDPR will be able to utilize the collected onsite weather data to assist in future ambient air monitoring studies.

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Appendix

Appendix I: Raw Results for Delhi

Sample Date	Sample ID	Total 1,3-D (ppb)	Cis 1,3-D (ppb)	Trans 1,3-D (ppb)
1/4/2019	309-A163	0.047	0.026	0.021
1/7/2019	309-A165	0.026	0.014	0.012
1/17/2019	309-A167	0.005	ND	ND
1/22/2019	309-A168	0.005	ND	ND
1/31/2019	309-A169	0.005	ND	ND
2/7/2019	309-A171	0.036	0.02	0.016
2/12/2019	309-A172	0.041	0.025	0.016
2/21/2019	309-A174	0.005	ND	ND
2/24/2019	309-A176	0.396	0.24	0.156
3/6/2019	309-A177	0.08	0.032	0.048
3/12/2019	309-A179	0.058	0.025	0.033
3/18/2019	309-A180	2.04	1.191	0.849
3/26/2019	309-A182	0.639	0.37	0.269
4/2/2019	309-A183	0.544	0.311	0.233
4/11/2019	309-A186	0.171	0.09	0.081
4/14/2019	309-A187	0.062	0.028	0.034
4/22/2019	309-A188	0.653	0.348	0.305
5/1/2019	309-A190	0.216	0.119	0.097
5/13/2019	309-A194	0.071	0.023	0.048
5/22/2019	309-A193	0.063	0.031	0.032
5/30/2019	309-A195	0.083	0.036	0.047
6/6/2019	309-A197	0.036	0.011	0.025
6/12/2019	309-A201	0.093	0.041	0.052
6/17/2019	309-A202	0.268	0.14	0.128
6/26/2019	309-A204	0.096	0.045	0.051
7/2/2019	309-A205	0.189	0.123	0.066
7/10/2019	309-A206	0.017	0.017	ND
7/18/2019	309-A208	0.005	ND	ND
7/23/2019	309-A209	0.005	ND	ND
7/31/2019	309-A211	0.064	0.025	0.039
8/5/2019	309-A212	0.005	ND	ND
8/17/2019	309-A214	0.005	ND	ND
8/19/2019	309-A215	0.005	ND	ND
8/27/2019	309-A216	0.005	ND	ND
9/5/2019	309-A218	0.112	0.036	0.076
9/9/2019	309-A220	0.021	ND	0.021
9/17/2019	309-A221	0.189	0.098	0.091
9/25/2019	309-A225	0.156	0.063	0.093

Sample Date	Sample ID	Total 1,3-D (ppb)	Cis 1,3-D (ppb)	Trans 1,3-D (ppb)
10/4/2019	309-A226	0.102	0.037	0.065
10/8/2019	309-A227	0.085	0.02	0.065
10/18/2019	309-A228	0.081	0.034	0.047
10/21/2019	309-A230	0.043	0.018	0.025
10/29/2019	309-A232	0.049	0.02	0.029
11/6/2019	309-A234	0.288	0.161	0.127
11/13/2019	309-A235	0.137	0.057	0.08
11/19/2019	309-A237	0.055	0.021	0.034
11/25/2019	309-A238	0.051	0.025	0.026
12/4/2019	309-A240	0.199	0.105	0.094
12/10/2019	309-A241	0.082	0.037	0.045
12/19/2019	309-A242	0.031	0.013	0.018
12/22/2019	309-A243	0.005	ND	ND

Results listed as “0.005” are Non Detections (ND) substituted for one-half of the Reporting Limit (0.01)

Appendix II: Raw Results for Parlier

Sample Date	Sample ID	Total 1,3-D (ppb)	Cis 1,3-D (ppb)	Trans 1,3-D (ppb)
1/2/2019	309-B116	0.064	0.033	0.031
1/8/2019	309-B117	0.045	0.019	0.026
1/15/2019	309-B118	0.005	ND	ND
1/24/2019	309-B119	0.005	ND	ND
2/1/2019	309-B120	0.058	0.036	0.022
2/4/2019	309-B121	0.011	0.011	ND
2/13/2019	309-B122	0.005	ND	ND
2/20/2019	309-B123	0.068	0.039	0.029
2/26/2019	309-B124	0.229	0.111	0.118
3/4/2019	309-B125	0.241	0.113	0.128
3/10/2019	309-B126	0.815	0.447	0.368
3/19/2019	309-B127	0.11	0.045	0.065
3/28/2019	309-B128	0.106	0.04	0.066
4/3/2019	309-B129	0.601	0.31	0.291
4/8/2019	309-B130	0.08	0.036	0.044
4/16/2019	309-B131	0.09	0.042	0.048
4/24/2019	309-B132	0.222	0.116	0.106
4/29/2019	309-B133	0.044	0.017	0.027
5/8/2019	309-B134	0.083	0.036	0.047
5/14/2019	309-B135	0.066	0.026	0.04
5/24/2019	309-B136	0.09	0.036	0.054
5/30/2019	309-B137	0.005	ND	ND
6/3/2019	309-B138	0.005	ND	ND
6/11/2019	309-B139	0.074	0.045	0.029
6/16/2019	309-B140	0.021	0.021	ND
6/27/2019	309-B141	0.143	0.083	0.06
7/1/2019	309-B142	0.017	0.017	ND
7/9/2019	309-B143	0.005	ND	ND
7/17/2019	309-B144	0.011	0.011	ND
7/25/2019	309-B145	0.005	ND	ND
7/29/2019	309-B146	0.005	ND	ND
8/8/2019	309-B147	0.005	ND	ND
8/14/2019	309-B148	0.027	0.027	ND
8/22/2019	309-B149	0.093	0.037	0.056
8/28/2019	309-B150	0.08	0.033	0.047
9/4/2019	309-B151	0.37	0.183	0.187
9/10/2019	309-B152	0.172	0.072	0.1
9/16/2019	309-B153	0.06	0.022	0.038
9/28/2019	309-B154	0.031	ND	0.031
10/4/2019	309-B155	1.38	0.709	0.671

Sample Date	Sample ID	Total 1,3-D (ppb)	Cis 1,3-D (ppb)	Trans 1,3-D (ppb)
10/7/2019	309-B156	1.277	0.578	0.699
10/16/2019	309-B157	2.07	1.03	1.04
10/23/2019	309-B158	0.298	0.132	0.166
10/28/2019	309-B159	1.187	0.554	0.633
11/4/2019	309-B160	0.632	0.276	0.356
11/12/2019	309-B161	0.394	0.181	0.213
11/21/2019	309-B162	2.006	0.942	1.064
11/26/2019	309-B163	0.206	0.096	0.11
12/2/2019	309-B164	0.177	0.08	0.097
12/13/2019	309-B165	0.094	0.035	0.059
12/17/2019	309-B166	0.095	0.042	0.053
12/23/2019	309-B167	0.089	0.019	0.07

Results listed as “0.005” are Non Detections (ND) substituted for one-half of the Reporting Limit (0.01)

Appendix III: Lab Spike Recovery Rates

Analysis Date	Cis 1,3-D Recovery (%)	Trans 1,3-D Recovery (%)
1/10/2019	99.3	100.0
1/28/2019	90.7	89.3
2/14/2019	98.0	95.3
2/26/2019	94.0	92.7
3/22/2019	100.0	100.0
4/12/2019	94.0	94.7
4/25/2019	92.0	93.3
5/9/2019	81.3	97.3
5/17/2019	93.3	94.0
6/12/2019	92	98.7
6/14/2019	90.7	90.0
7/2/2019	109	100
7/18/2019	111	102
7/26/2019	89.3	86.0
8/12/2019	94.7	97.3
8/26/2019	86.7	90.7
9/6/2019	93.3	93.3
9/26/2019	104	99.3
10/14/2019	94	101
10/21/2019	95.3	96
11/7/2019	100	102.7
12/6/2019	86.7	86
12/16/2019	100	105
1/2/2019	101	98.7

Appendix IV: Lab Blank Recovery Rates

Analysis Date	Cis 1,3-D Recovery (%)	Trans 1,3-D Recovery (%)
1/10/2019	ND	ND
1/28/2019	ND	ND
2/14/2019	ND	ND
2/26/2019	ND	ND
3/22/2019	ND	ND
4/12/2019	ND	ND
4/25/2019	ND	ND
5/9/2019	ND	ND
5/17/2019	ND	ND
6/11/2019	ND	ND
6/14/2019	ND	ND
7/2/2019	ND	ND
7/18/2019	ND	ND
7/26/2019	ND	ND
8/12/2019	ND	ND
8/26/2019	ND	ND
9/6/2019	ND	ND
9/26/2019	ND	ND
10/14/2019	ND	ND
10/21/2019	ND	ND
11/7/2019	ND	ND
12/6/2019	ND	ND
12/16/2019	ND	ND
1/2/2019	ND	ND

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

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)