Monitoring of 1,3-Dichloropropene in Merced and Fresno Counties

2016-2017 Annual Report

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By

Colin Brown, Senior Environmental Scientist

Jazmin Gonzalez, Environmental Scientist

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Summary

Department of Pesticide Regulation (DPR) staff collected weekly 24-h air samples for the purpose of measuring ambient concentrations of 1,3-dichloropropene (1,3-D) in the high-use regions of Merced and Fresno counties over a period of 13 months from the beginning of December 2016 to the end of December 2017. Monitoring sites in each region were located in communities characterized by relatively high levels of historical 1,3-D use and that were not currently included in other monitoring studies being conducted by DPR or the California Air Resources Board (ARB). The monitoring site in the city of Delhi, located in Merced County, was characterized by a high percentage of detections with air concentrations falling below regulatory targets for acute, subchronic, chronic, and lifetime exposure. The monitoring site outside of Parlier, in Fresno County, was characterized by a high proportion of detections. Measured air concentrations at Parlier did not exceed human health screening levels for acute, subchronic, or chronic exposures. An annual concentration of 0.62 ppb was measured at the Parlier sampling site, a one-year average concentration that, were it to continue for 70 years, would exceed DPR's regulatory target of 0.56 ppb for the mitigation of lifetime cancer risk. Monitoring at both sampling sites will continue at least to the end of 2018.

1. Background

1,3-Dichloropropene, also known as 1,3-D or Telone®, is a widely-used pre-plant fumigant in California agriculture, used primarily for its nematicidal properties. 1,3-D, a highly volatile liquid, is typically applied to the soil through shank injection or chemigation as a roughly equal mixture of *cis-* and *trans-* isomers at a maximum rate of 332 lbs per acre (DPR 2017a). Once applied to the soil, 1,3-D quickly volatilizes and re-dissolves into an aqueous film surrounding soil particles. Some proportion of 1,3-D that is not re-dissolved, degraded, or otherwise contained in the soil column (possibly by use of mitigation measures such as surface tarpaulins) will then emit into the atmosphere.

1,3-D is listed as a known human carcinogen under California's Proposition 65 (OEHHA 2017) and as a "likely" human carcinogen by the United States Environmental Protection Agency (US EPA 2008). Use of 1,3-D in California is restricted by usage caps on the basis of discrete 6x6 mile areas known as 'townships' as a method of mitigating the cancer risk associated with long-term inhalation exposure (DPR 2015). The California Department of Pesticide Regulation (DPR) periodically reevaluates the human health risks associated with 1,3-D to determine regulatory targets for ambient air concentration, which were updated most recently in 2016 (DPR 2016). Those regulatory targets are used to develop usage caps, which are then included in a revised set of 1,3-D permit conditions. Usage caps from 1,3-D are quantified in terms of 'adjusted total pounds' (ATP), which weights 1,3-D applications by method type, location, and season.

The most recent revision of 1,3-D application permit conditions became effective January 2017 (DPR 2017b). The change followed the development of updated reference concentrations for acute, subchronic, chronic, and lifetime exposures (DPR 2015). An analysis of past 1,3-D monitoring data (Tao 2016), as well as computer modeling (Barry and Kwok 2016), was used to estimate a township cap that would maintain mean lifetime (70-year) ambient air concentrations below the 0.56 parts per billion by volume (ppb) regulatory target. The resulting permit conditions established a 1,3-D township cap of

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136,000 lbs ATP per township per year while eliminating the previous practice of township banking whereby usage caps could be exceeded in townships where use in prior years had fallen below the cap. Additionally, the new permit conditions disallowed applications in December, which monitoring data had shown to consistently impact ambient air quality to a greater degree than applications occurring during other months of the year for reasons that are not well-understood.

While the California Air Resources Board (ARB) and DPR perform additional air monitoring for volatile pesticides throughout the state, those studies are designed to capture a broad selection of pesticides rather than any specific active ingredient. As a result, monitoring in the San Joaquin Valley does not always include communities associated with the greatest 1,3-D use. Monitoring is an important component of the continuous evaluation that DPR must perform to ensure the effectiveness of regulation, and monitoring in high-use communities is one of the most direct ways to evaluate whether regulatory targets are being met.

In this study, we performed ambient air monitoring of 1,3-D in the communities of Delhi and Parlier for a period of 13 months, from November 30, 2016 to December 31, 2017. Sampling involved the collection of one 24-h air sample from each monitoring location on a random day of the week during each week of the 13-month period. The primary objectives of the study were to collect monitoring data for the purpose of assessing ambient 1,3-D concentrations in regions of high use; to compare those measured air concentrations to subchronic, chronic, and lifetime human health screening levels; to evaluate the effectiveness of the township use restriction on chronic ambient concentrations; and to evaluate the effectiveness of a December ban in mitigating high subchronic ambient concentrations.

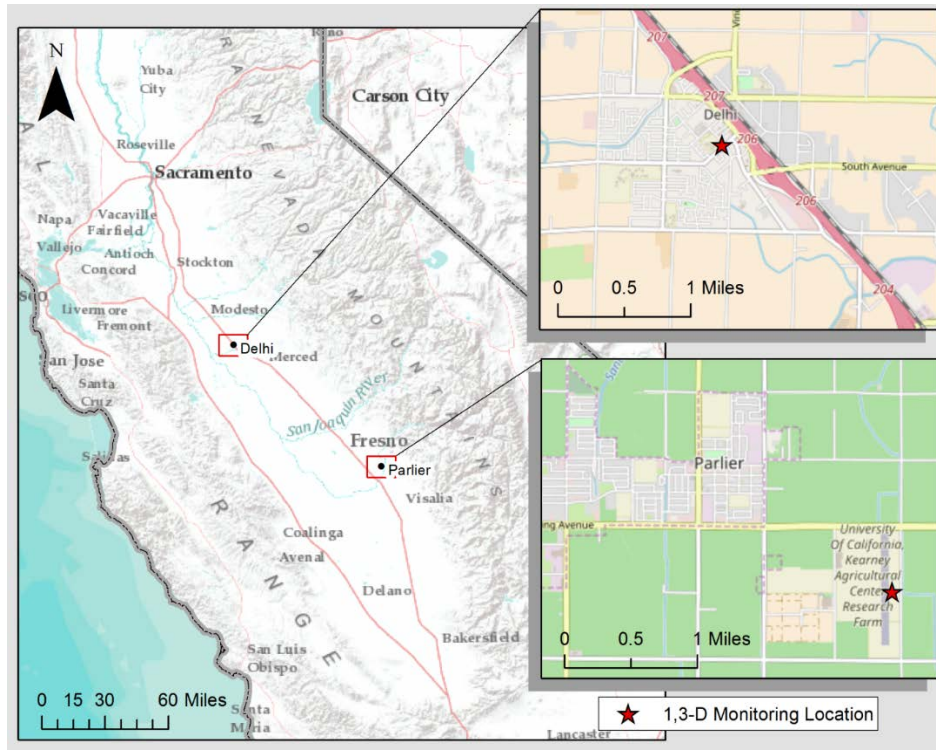## 2. Communities and Monitoring Site Locations

Air monitoring was performed in communities of high use located within the high-use regions of Merced and Fresno counties. The highest-use communities (based on historical use data) within each region were prioritized wherever possible, contingent on the availability of adequate air monitoring sites and the permission of site stewards. Additional consideration was given to the location of monitoring sites within each community and its position relative to the prevailing winds and nearby fields with historical 1,3-D usage. Brown (2016) provides a detailed description of the site selection process for this study.

2.1 Delhi

Delhi is a small (3.5 mi^2) city located in Merced County (Figure 1). Delhi is surrounded by agricultural lands where major crops include sweet potatoes, almonds, and grapes. Delhi ranked 16th for statewide 1,3-D use and 3rd for 1,3-D use in Merced County according to the prioritization scheme used in this study. Historic use typically occurred in two peaks, one occurring from March-April and a second peak occurring November-December. The monitoring site in Delhi is located in the interior of the city approximately 1 mile downwind of the community boundary. The monitoring site is housed on property leased from a local utility and is located adjacent to Schendel Elementary School.

2.2 Parlier

Parlier is a small (2.2 mi^2) city located in Fresno County (Figure 1). The city ranked 36th for statewide 1,3-D use and 13th for 1,3-D use in the region of Fresno County according to the prioritization scheme used in this study. Parlier is located in an agricultural region where major crops include permanent crops such as peaches, nectarines, grapes, and almonds. Historically, 1,3-D use peaks twice throughout the year, once in February and again in August-December. The monitoring site at Parlier is located at the eastern margin of Parlier on property of the Kearney Agricultural Research and Extension Center, an agricultural research facility operated by the University of California.

Figure 1. Location of communities selected for 1,3-D monitoring (left) and placement of monitoring locations within the communities of Delhi and Parlier (right).

3. Methods

3.1 Air sampling locations

Monitoring stations were located in secure, relatively flat, open areas with a 3 foot horizontal and vertical clearance between the sample intake and its supporting structure. Monitoring stations were placed to allow unobstructed airflow from at least 270° surrounding the sampling location. Other criteria included a minimum 65 foot setback from trees and a setback of at least double the height of nearby obstacles. A shelter at each location protected sampling equipment from tampering, as well as sunlight, rainfall, fog, and heat over the course of the monitoring study. AC power was available at each site to provide power to air monitoring equipment and active cooling within each shelter during equipment operation.

3.2 Air sampling equipment

From November 2016 through January 2017, passive flow regulators were used to control flow into 6L SilcoCan® canisters (Restek cat. No. 24142-65) pre-evacuated to a pressure of -30" Hg. Flow regulators were calibrated with a Bios Defender 510® flow standard to a flow rate of 3.0 ± 0.3 milliliters per minute (mL/min) for 24-h and valid samples were those with a final vacuum of -5" Hg or below. Regulator flow rates were verified with a flow standard at the beginning and end of each sample period. Regulator valves were manually opened and closed by sampling personnel at the beginning and end of each 24-h sampling period.

Beginning in late January 2017, the Xonteck Model 901 Automated Canister Sampler ('Xonteck 901') replaced regulators as the primary sampling tool. Like regulators, samples retrieved with the Xonteck 901 are collected in a 6L SilcoCan® pre-evacuated to a pressure of -30" Hg. Each Xonteck 901 was equipped with an internal mass flow controller programmed to target a constant flow of 7.5 ± 0.4 mL/min (± 5%). The flow of the Xonteck 901 was calibrated against readings from a Bios Defender 510® flow standard at the beginning of each sample period. A discrepancy greater than 0.4 mL/min resulted in re-calibration of the Xonteck 901. Valid samples obtained with the Xonteck 901 were those with a final canister pressure of 6-16" Hg at the end of the 24-h sampling period.

3.3 Sampling procedures

One 24-h air sample was collected each week at each of the two monitoring locations over the 13-month course of the study. Sampling began on a randomly-chosen day each week where possible.

Sample labels including the study number and sample tracking numbers were secured to the outside of all sample canisters. At the time of sampling, staff recorded sample tracking number, date, time, staff initials, weather conditions, sampler flow rate, and starting canister pressure on a chain of custody (COC) form as described by Ganapathy (2004). At the end of each sampling period, staff recorded the date, time, staff initials, ending flow rate (or average flow for the Xonteck 901), and ending canister pressure on the COC form.

Canister flow valves were closed and a cap nut was installed upon collection of each canister sample. Collected samples were stored and transported under ambient conditions to DPR's West Sacramento facility where they were checked-in and held until delivery to the California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA CAC) laboratory for analysis. Samples were stored for no longer than 28 days between sample collection and laboratory analysis. Jones (1999) and Ganapathy (2005) describe sample handling-shipping and tracking procedures utilized in this study, respectively.

4. Laboratory methods

CDFA CAC laboratory conducted chemical analysis of the air sampling media. Canisters were analyzed for the presence of 1,3-D by directing a known volume of sampled air through a sorbent resin and then extracting the analytes into a solution for use in gas chromatography-mass spectrometry (CDFA 2010).

The resulting mass of 1,3-D detected by this method was divided by the volume of air sampled to estimate the average ambient concentration of 1,3-D over a 24-h period (DPR 2011).

The reporting limit (RL) for the air canister method is 0.01 ppb for both *cis-* and *trans-* 1,3-D isomers. This value was determined by analyzing a standard at a concentration with a signal-to-noise ratio of 2.5 to 5. The spiked matrix was analyzed at least seven times, and the RL was determined by calculating the 99% confidence interval of the mean. US EPA (1990) further describes this procedure. Note that for air canister samples, the RL, method detection limit (MDL), and limit of quantitation (LOQ) are equivalent values. Where the sample concentration of an analyte fell below the RL, it was categorized as a 'non-detection' and the analytical result was substituted with a value of one-half the RL (0.005 ppb) for the purposes of determining subchronic, chronic, and lifetime average concentrations.

CDFA CAC laboratory followed DPR's standard laboratory quality control procedure (Segawa 1995). Prior to analysis of field samples, the laboratory validated the method by analyzing a series of laboratory spikes (samples containing a known amount of pesticide) to document precision and accuracy of the analytical method. Storage stability tests were performed to document degradation of samples between the time of sample collection and the time of sample analysis. CDFA CAC laboratory's analysis included quality control samples with each batch of field samples. Quality control samples included laboratory blank samples (samples containing no pesticide) to check for contamination and laboratory spikes to check method precision and accuracy. Recovery warning and control limits were set at ±2 or ±3 standard deviations from the average percent recovery, respectively.

Co-located duplicate canister samples were retrieved approximately once per month as a quality control measure. Co-located duplicate samples were primarily obtained from the Delhi location due to equipment availability. Co-located duplicate samples were collected with an air intake probe directly adjacent (i.e. within 1 m) to the intake for the primary sample and under the same environmental conditions and time-frame. Due to limited equipment availability, co-located duplicate samples were retrieved with a different type of flow regulator than used for the primary sample (i.e. Xonteck 901 vs. passive flow regulator) although sampling and laboratory methods for the two methods operate under the same principles. The difference in the calculated air concentration between the primary and duplicate samples was used as one measure of laboratory analytical precision.

5. Health Evaluation Methods

Air samples collected between January 1, 2017 and December 31, 2017 are considered in the evaluation of 2017 annual concentrations against the regulatory target of 0.56 ppb for lifetime (70-year) exposure, and cancer risk estimates are calculated based on 2017 annual concentrations. Although cancer risk estimates are based on 70-year of exposure, DPR (2016) specifies that the 0.56 ppb regulatory target for lifetime exposure can be evaluated on an annual or longer period basis as an additional measure of safety. In addition to the 0.56 ppb regulatory target, DPR established a 0.27 ppb trigger point that, when exceeded, suggests the need for additional evaluation and possible revised mitigation measures. Data from December 2016 was not considered in these calculations (i.e., for determination of the maximum

12-month concentration) because this data represents pre-revision management practices; therefore, it does not satisfy the objective of evaluating the revised permit conditions implemented in January 2017.

This study additionally compares measured air concentrations to acute, sub-chronic, chronic human health screening levels to place results in a health-based context for non-cancer risk (Table 1). Monitoring results are evaluated on the basis of a rolling average to identify the maximum acute (24-h), subchronic (90-d), and chronic (1-yr) concentrations. Only 2017 (post-revision) data is considered in these calculations. The screening levels used in this study are identical to the 1,3-D reference concentrations for children described in DPR (2015), wherein a reference concentration is an estimate of inhalation exposure in humans that is likely to be without appreciable risk of deleterious effects.

Table 1. Screening levels and regulatory target for 1,3-dichloropropene.

Exposure period	Screening level (ppb)	Potential health effect
Acute (24-h)	110	Body weight change
Subchronic (90-d)	3	Tissue damage in nose and lung
Chronic (1-yr)	2	
Lifetime (70 years*)	0.56	Cancer

*This is a regulatory target rather than a health screening level.

The risk of measured concentrations over each period of exposure is summarized in the format of a hazard quotient (HQ), calculated as the ratio of measured 1,3-D concentration to each health screening level (or regulatory target). An HQ of greater than 1 indicates that air concentrations have exceeded the screening level. Exceedance of any screening level may signal the need for closer data evaluation, additional data, collection, and possibly mitigation measures (DPR 2011).

6. Air Monitoring Results

6.1 Delhi Results

Detailed monitoring results from Delhi are included in Table A-1 (appendix). Monitoring results at Delhi were characterized by a high proportion of detections (78%) over the course of the study, including several low concentrations during the summer period when 1,3-D applications are typically infrequent, and low-level detections throughout the entirety of December 2017 despite a statewide ban on December applications. The timing of seasonal peaks and troughs in ambient 1,3-D concentration appears consistent with historical use patterns (Figure 2).

Table 2 summarizes the maximum observed concentration for each exposure period compared to health screening levels. Hazard quotients in Delhi were below 1.0 in every exposure category, and below 0.1 in the case of acute, subchronic, and chronic exposures. The greatest observed HQs were 0.23 and 0.25 for one-year (2017) and 13-month (all samples) exposure periods for cancer risk based on mean period concentrations of 0.13 ppb and 0.14 ppb, respectively.

Table 2. Summary of maximum measured air concentrations by exposure period for monitoring performed at Delhi, 2016-2017.

Exposure Period	Total 1,3-D (ppb)	Screening level (ppb)	Hazard Quotient[*]
Acute (24-h)[†]	1.06	110	0.01
Subchronic (90-d)[†]	0.29	3	0.10
Chronic (2017)[†]	0.13	2	0.07
Cancer risk (2017)[‡]	0.13	0.56	0.23

[†]Screening levels for acute, subchronic, and chronic concentrations are reference concentrations for child inhalation exposure described in DPR (2015).
[‡]Cancer screening level is the 0.56 ppb regulatory target for 70-year inhalation exposure.
[*]Hazard quotient is calculated as the ratio of measured concentration to screening level.

6.2 Parlier Results

Table A-2 (appendix) includes detailed monitoring results for Parlier. Monitoring results at Parlier were characterized by a high proportion of detections (69%) over the course of the study. Detections around Parlier occurred in seasonal peaks separated by several weeks of non-detections in a pattern consistent with historical use (Figure 2). As in Delhi, detectable concentrations of 1,3-D were measured throughout December despite a statewide ban on December applications.

The maximum observed concentration for each exposure period is summarized and compared to health screening levels in Table 3. The greatest observed HQ was 1.11 for the one-year (2017) exposure period for cancer risk based on a mean period concentration of 0.62 ppb. Hazard quotients for acute, subchronic, and chronic non-cancer exposures were each below 1.0.

The high ambient concentrations of 1,3-D at the Parlier location were heavily influenced by a single measurement of 15.96 ppb retrieved on September 20, 2017. A possible source for this elevated measurement is described in Section 7.2. Although the 24-h detection did not exceed DPR's acute human health screening level of 110 ppb, the detection did result in a doubling of the annual average concentration to 0.62 ppb.

Table 3. Summary of maximum measured concentrations by exposure period for monitoring performed at Parlier, 2016-2017.

Exposure Period	Total 1,3-D (ppb)	Screening level (ppb)	Hazard Quotient
Acute (24-h)	15.96	110	0.15
Subchronic (90-d)	1.83	3	0.61
Chronic (2017)	0.62	2	0.31
Cancer risk (2017)	0.62	0.56	1.11
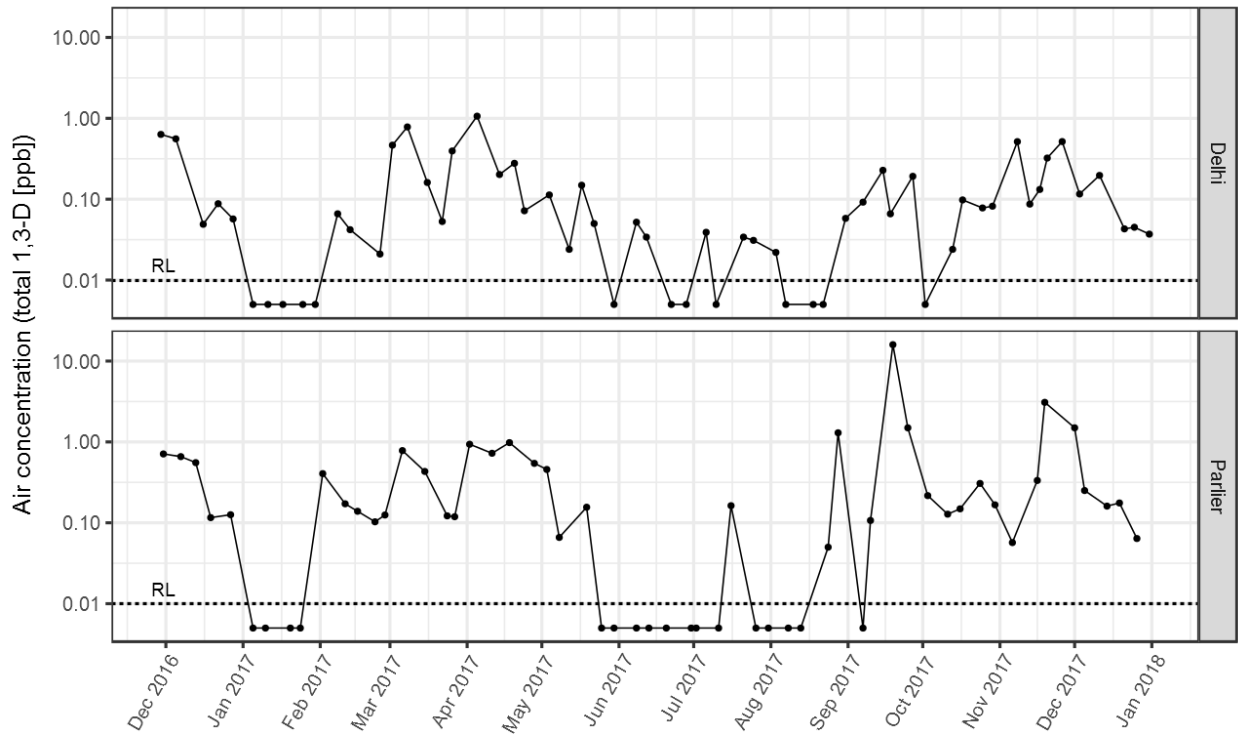
Figure 2. Summary of measured air concentration results collected in Delhi and Parlier from December 2016 to December 2017. Bolded points represent 24-h air sample concentration of total 1,3-D (combined cis- and trans-).

6.3   Cancer Risk Estimates

1,3-D is classified as a human carcinogen by both US EPA and under California Proposition 65. The purpose of the 1,3-D township cap is to manage cancer risk associated with long-term inhalation exposure to 1,3-D (DPR 2015). Cancer risk is typically expressed as the estimated probability of developing cancer over a 70-year lifetime (e.g., 1 in 100,000 or 1 in 1,000,000, also expressed as 1×10^{-5} or 1×10^{-6}, respectively).

DPR set a regulatory cancer risk goal for 1,3-D of 1 in 100,000 (1×10^{-5}) in the 2016 Risk Management Directive (DPR 2016). Cancer risk can be estimated using air monitoring results and evaluated against the cancer risk goal using equation 1:

$$\text{Risk} = \text{CPF}_H * \text{LAC} * \text{nBR} \qquad\qquad (1)$$

where:

Risk = probability of an additional case of cancer over a 70-year period.
CPF_H = estimated cancer potency factor in humans $(\text{mg/kg/day})^{-1}$.
LAC = mean lifetime (70-year) air concentration (mg m^{-3}).
nBR = normalized breathing rate of a human adult ($\text{m}^3 \text{ kg}^{-1} \text{ day}^{-1}$).

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The DPR-estimated value of CPF_H based on a portal-of-entry effect, is 0.014 $(mg/kg/day)^{-1}$ (DPR 2015). DPR assumes nBR to be 0.28 $m^3 kg^{-1} day^{-1}$ (DPR 2015). For this study and based on the available monitoring data, LAC is taken as the mean annual concentration of total 1,3-D at either Parlier or Delhi locations for all available monitoring years, with non-detection samples assigned a value of ½ RL. The value of LAC assumes continuous exposure at this concentration over a 70-year period.

Table 4 summarizes the annual mean concentration of 1,3-D and lifetime cancer risk estimates based on 2017 mean annual concentrations at Delhi and Parlier. In 2017, the resulting cancer risk estimates in Delhi fall below the 1.0×10^{-5} cancer risk goal. However, cancer risk estimates for Parlier exceeded the 0.56 ppb regulatory target for 70-year inhalation exposure, with an estimated cancer risk of 1.1×10^{-5} (Table 4).

Table 4. Summary of annual air concentrations and cancer risk estimates for measured air concentrations of 1,3-D at Delhi and Parlier across all monitoring studies.

Site	Year	Mean annual concentration [ppb]	Regulatory target concentration [ppb]	Cancer risk estimate	Cancer risk target
Delhi	2017	0.13	0.56	2.3×10^{-6}	1.0×10^{-5}
Parlier	2017	0.62	0.56	1.1×10^{-5}	1.0×10^{-5}

6.4 December Air Concentrations

In Delhi, monitoring data indicated a large (53%) reduction in mean December 1,3-D air concentrations between 2016 and 2017 following the ban on December applications (Table 6). December 2017 air concentrations were characterized by much lower ambient concentrations of 1,3-D in the first week as compared to December 2016, and December 2017 concentrations were comparable or slightly lower than December 2016 through the end of the month (Figure 3). December 2017 air concentrations were consistently above the RL throughout the 1-month period with the latter half of December 2017 characterized by relatively low but stable 1,3-D concentrations.

In Parlier, mean December 2017 air concentrations were effectively unchanged from December 2016 air concentrations following the ban on December applications (Table 6). Ambient 1,3-D concentrations measured in the first week of December 2017 were approximately double those recorded in the same time period of the previous year (Figure 3). December 2017 concentrations dropped sharply near the end of week 1 and declined to levels far below December 2016 concentrations during weeks 2 and 3. Ambient air concentrations during the last two weeks of December were comparable between years.
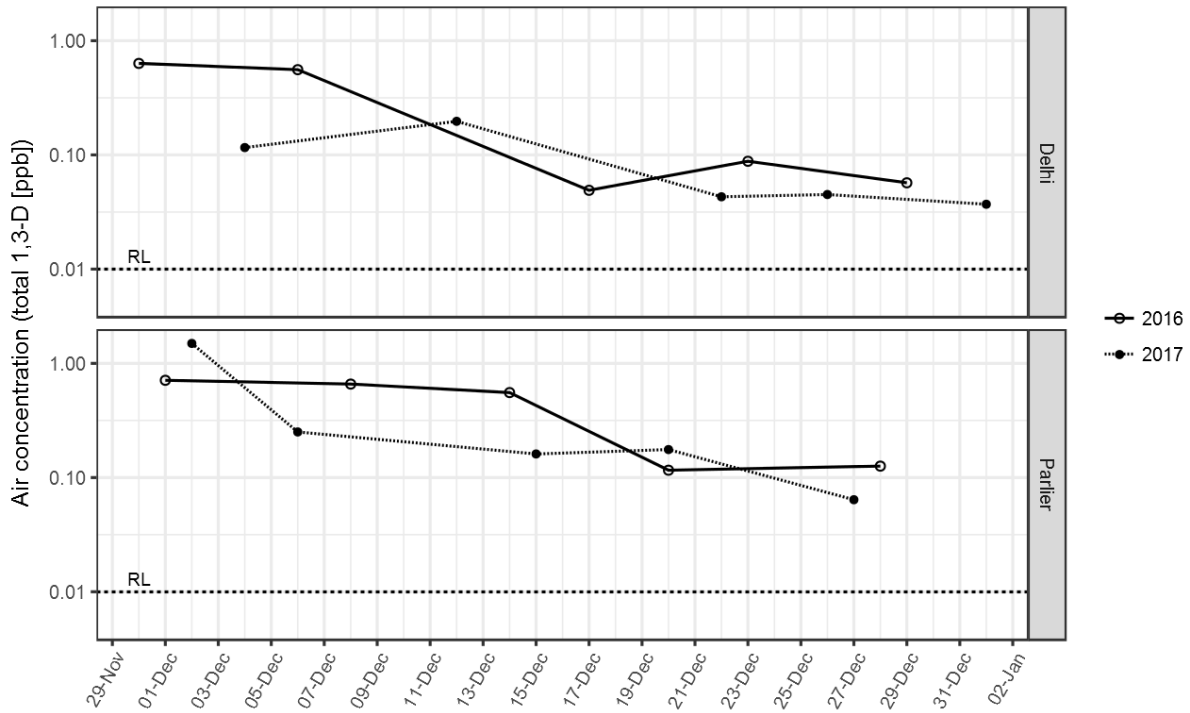
Figure 3. Overlay of December 2016 (pre-revision of permit conditions) and December 2017 (post-revision) concentrations by monitoring location.

Table 6. Comparison of mean December 2016 and December 2017 ambient air concentrations.

Site	Dec 2016 (ppb)	Dec 2017 (ppb)	Reduction (%)
Delhi	0.19	0.09	-53%
Parlier	0.43	0.43	<-1%

6.5 Data Validation/Quality Assurance Results

A total of 18 pairs of co-located samples were collected over the 13-month course of the study. Each pair consisted of a 'primary' and 'duplicate' sample. Prior to installation of Xonteck 901 canister samplers in January 2017, both primary and duplicate samples were collected with passive flow regulators; two such co-located pairs were collected. Following installation of the Xonteck 901 canister samplers, primary samples were collected on the Xonteck 901 while duplicate samples were collected with a passive flow regulator; 16 such co-located pairs were collected.

Of the 18 total pairs collected, 12 pairs (67%) measured above the RL. A paired t-test revealed no significant difference between co-located pairs on the basis of total 1,3-D (mean difference = 0.012 ppb, standard deviation (SD)=0.063 ppb, *p*=0.55). Of the 16 co-located pairs collected on different sampling equipment, 11 (69%) measured above the RL; a paired two-tailed t-test revealed no significant systematic difference between the 11 co-located pairs (mean difference = 0.013 ppb, SD=0.066 ppb, *p*=0.54). Mean percent difference between individual co-located pairs exceeded 50% on two occasions (Table A-3,

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appendix). In one case, a large percent difference resulted from a small absolute difference between sample concentrations near the RL. The second case of large percent difference (81%) resulted from relatively large differences in absolute measured concentrations, whereby the quality control sample indicated less than half the concentration of the primary sample (0.323 ppb primary vs 0.137 ppb duplicate); both samples were determined to be valid based on flow rate and ending sample pressure; the reason for the large observed difference could not be determined.

Laboratory spike recovery rates reported by CDFA CAC laboratory averaged 97.5% for cis-1,3-D (SD = 4.1%) and 96.8% for trans-1,3-D (SD = 6.0%) between December 2016 and December 2017. Laboratory spike and laboratory blank results are included in Table A-4 (appendix).

7. Discussion

7.1 December air concentrations

Mean air concentrations in Parlier during December 2017 were nearly identical to those of the prior December despite a ban on December applications in 2017. Preliminary 2017 pesticide use reporting (PUR) data suggests that the elevated concentration near the beginning of December 2017 was due to a large amount (80,000 lbs+) of use occurring within 10 miles of the Parlier monitoring location in the two weeks prior to the December 1 cutoff (DPR 2018), approximately 20,000 lbs of which was applied in the two days prior to the cutoff. Those applications consisted uniformly of untarped, deep shank injection applications. Field studies have demonstrated that untarped methods typically produce peak emissions within 48-h post-application and cumulative emissions typically stabilize within two weeks post-application, with small amounts of residual fumigant in the soil column suggesting the potential for continued low-level volatilization past two weeks (Gao et al. 2008, Gao and Trout 2007). The effect of soil temperatures on long-term cumulative volatilization has not been measured in any controlled fashion (Spurlock 2016), and field flux studies of untarped soils rarely continue beyond two weeks post-application. It is possible that slowed diffusion and degradation may result in a longer volatilization period under cool conditions in certain soils. Therefore, continued volatilization of 1,3-D from the soil surface in the weeks following the cessation of fumigation activities may have been the driving force behind the elevated concentrations observed throughout December. Additional factors arising from winter meteorological conditions (e.g., low mixing heights, attenuated sunlight) may have further contributed to the elevated December concentrations.

Mean December 2017 concentrations in Delhi were 53% lower than the prior year and did not show the same sharp decline from November concentrations as was observed in Parlier, with concentrations being relatively stable throughout the month. Preliminary 2017 PUR data indicates approximately 13,000 lbs of use within 10 miles of the Delhi monitoring location in the two weeks prior to the December 1, 2017 cutoff, approximately a third of which (3,900 lbs) occurred in the two days prior to the cutoff. As was the case in Parlier, applications surrounding Delhi consisted of untarped, deep-shank applications that are expected to complete a majority of emissions within 2 weeks post-application, but which may continue to emit at lower levels past that time. As was also the case in Parlier, the continued volatilization of 1,3-D

from November applications and winter meteorological factors may have influenced December air concentrations near Delhi.

7.2 Elevated detection in Parlier

Monitoring results at Parlier indicated annual concentrations exceeding the 0.56 ppb regulatory target for lifetime (70-year) cancer risk on an annual basis. The average annual concentration for 2017 was strongly influenced by a single detection retrieved in September 2017, which ranks among the highest 24-h concentration of 1,3-D observed as part of any DPR or ARB ambient air monitoring study. Possible sources contributing to this elevated concentration were examined based on preliminary PUR data.

An evaluation of pesticide use records in the surrounding region was performed based on preliminary PUR data for 2017. That evaluation indicated only three 1,3-D applications within 5 miles of the monitoring location in the days prior to sample collection. Two of those applications were considered as unlikely to have been a major contributor to measured concentrations because of:

1. A location of approximately 5 miles from the monitoring site.
2. Completion of application 6 to 7 days prior to the beginning of the air sample, during a period when emissions from the soil surface are estimated to be relatively low based on past observations from field flux studies and fumigant flux models.
3. Relatively small application amounts (less than 1,000 lbs) per application.
4. In the case of one application, the use of a totally impermeable film tarpaulin over the field to mitigate emissions.

The remaining application was considered as the likely primary source of the elevated concentration. This was due to factors including:

1. A location of less than 1 mile from the monitoring site in a Public Land Survey System (PLSS) section adjacent to the monitoring site.
2. Completion of application approximately 12-h prior to the beginning of air sampling, resulting in air sampling during a period of high field emissions.
3. Relatively large application amount (approximately 3,000 lbs).
4. Untarped application method which may emit a large proportion of applied material over the first 24-48 h following application.

The precise location of the fumigated field within the reported PLSS section could not be immediately identified based on the reported field ID. A search by permit ID indicated a single 40 ac block historically fumigated by the permittee in the reported PLSS section. The precise location of the field could not be confirmed with the Fresno County Agricultural Commissioner. Depending on the location of the fumigated field within the 40 ac block, geospatial data suggests that the fumigant was applied at a distance of 0.25 to 0.50 miles (1320-2640 ft) southeast of the monitoring site.

On-site meteorological data from the California Irrigation Management Information System (CIMIS) station #39 indicates that the fumigation fell upwind of the monitoring location for a period of several

hours during the second day of monitoring (CIMIS 2018). However, low wind speeds and low mast height of the on-site data invalidated much of the CIMIS dataset for air dispersion modeling purposes. Subsequent efforts to model the detection using computer simulations based on the nearest available valid meteorological dataset (Fresno Yosemite International Airport) were not able to reproduce the observed detection (see Tao 2018). Sources of uncertainty in the model include location and shape of the fumigated field, meteorological data, and flux profile estimates.

8.   Future monitoring activity

Monitoring activities as part of the present study will continue at least to the end of 2018 with minor changes to the study protocol. In 2018, at least 6 fortified field spikes will be retrieved from the Delhi monitoring site for analysis by CDFA CAC laboratory. In mid-2018, a second Xonteck 901 replaced the passive regulator previously used to collect co-located duplicate samples and will additionally be used for the collection of fortified field spikes.

Data collected as part of the ongoing study will contribute to a growing dataset of ambient 1,3-D measurements collected throughout the state as part of CDPR and ARB monitoring programs. Such data facilitates the continuous evaluation of 1,3-D regulatory efforts and the development of models to estimate ambient air 1,3-D concentrations based on use.

9.   Acknowledgements

10.   References

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Appendix A – Raw results for Delhi and Parlier

Table A-1. Summary of primary air sample results from Delhi.

Date Start	Sample No.	RL (ppb)	total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
11/29/2016	A001	0.01	0.633	0.319	0.314
12/5/2016	A002	0.01	0.558	0.274	0.284
12/16/2016	A003	0.01	0.049	0.025	0.024
12/22/2016	A004	0.01	0.088	0.044	0.044
12/28/2016	A006	0.01	0.057	0.027	0.030
1/5/2017	A009	0.01	0.005	0.005	0.005
1/11/2017	A010	0.01	0.005	0.005	0.005
1/17/2017	A012	0.01	0.005	0.005	0.005
1/25/2017	A013	0.01	0.005	0.005	0.005
1/30/2017	A014	0.01	0.005	0.005	0.005
2/8/2017	A016	0.01	0.066	0.037	0.029
2/13/2017	A018	0.01	0.042	0.022	0.020
2/25/2017	A019	0.01	0.021	0.010	0.011
3/2/2017	A020	0.01	0.466	0.282	0.184
3/8/2017	A021	0.01	0.783	0.432	0.351
3/16/2017	A022	0.01	0.161	0.091	0.070
3/22/2017	A025	0.01	0.053	0.028	0.025
3/26/2017	A026	0.01	0.395	0.216	0.179
4/5/2017	A027	0.01	1.064	0.532	0.532
4/14/2017	A028	0.01	0.202	0.100	0.102
4/20/2017	A029	0.01	0.278	0.155	0.123
4/24/2017	A031	0.01	0.072	0.038	0.034
5/4/2017	A033	0.01	0.113	0.056	0.057
5/12/2017	A034	0.01	0.024	0.013	0.011
5/17/2017	A035	0.01	0.149	0.104	0.045
5/22/2017	A037	0.01	0.050	0.026	0.024
5/30/2017	A039	0.01	0.005	0.005	0.005
6/8/2017	A040	0.01	0.052	0.027	0.025
6/12/2017	A043	0.01	0.034	0.023	0.011
6/22/2017	A044	0.01	0.005	0.005	0.005
6/28/2017	A045	0.01	0.005	0.005	0.005
7/6/2017	A046	0.01	0.039	0.024	0.015
7/10/2017	A049	0.01	0.005	0.005	0.005
7/21/2017	A050	0.01	0.034	0.021	0.013
7/25/2017	A051	0.01	0.031	0.014	0.017
8/3/2017	A053	0.01	0.022	0.011	0.011
8/7/2017	A054	0.01	0.005	0.005	0.005

Date Start	Sample No.	RL (ppb)	total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
8/18/2017	A056	0.01	0.005	0.005	0.005
8/22/2017	A057	0.01	0.005	0.005	0.005
8/31/2017	A059	0.01	0.058	0.034	0.024
9/7/2017	A061	0.01	0.092	0.045	0.047
9/15/2017	A062	0.01	0.228	0.122	0.106
9/18/2017	A063	0.01	0.066	0.037	0.029
9/27/2017	A065	0.01	0.192	0.084	0.108
10/2/2017	A066	0.01	0.005	0.005	0.005
10/13/2017	A068	0.01	0.024	0.013	0.011
10/17/2017	A069	0.01	0.098	0.058	0.040
10/25/2017	A072	0.01	0.078	0.046	0.032
10/29/2017	A073	0.01	0.082	0.042	0.04
11/8/2017	A074	0.01	0.515	0.292	0.223
11/13/2017	A076	0.01	0.087	0.048	0.039
11/17/2017	A077	0.01	0.132	0.080	0.052
11/20/2017	A078	0.01	0.323	0.180	0.143
11/26/2017	A080	0.01	0.516	0.239	0.277
12/3/2017	A081	0.01	0.116	0.062	0.054
12/11/2017	A082	0.01	0.197	0.090	0.107
12/21/2017	A084	0.01	0.043	0.020	0.023
12/25/2017	A086	0.01	0.045	0.019	0.026
12/31/2017	A087	0.01	0.037	0.017	0.020

Table A-2. Summary of primary air sample results from Parlier.

Date Start	Sample No.	RL (ppb)	total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
11/30/2016	B001	0.01	0.711	0.344	0.367
12/7/2016	B002	0.01	0.659	0.32	0.339
12/13/2016	B003	0.01	0.555	0.254	0.301
12/19/2016	B005	0.01	0.116	0.054	0.062
12/27/2016	B006	0.01	0.126	0.066	0.06
1/5/2017	B007	0.01	0.005	0.005	0.005
1/10/2017	B008	0.01	0.005	0.005	0.005
1/20/2017	B010	0.01	0.005	0.005	0.005
1/24/2017	B012	0.01	0.005	0.005	0.005
2/2/2017	B014	0.01	0.406	0.285	0.121
2/11/2017	B016	0.01	0.172	0.094	0.078
2/16/2017	B017	0.01	0.139	0.079	0.06

Date Start	Sample No.	RL (ppb)	total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
2/23/2017	B018	0.01	0.103	0.064	0.039
2/27/2017	B019	0.01	0.125	0.069	0.056
3/6/2017	B020	0.01	0.782	0.442	0.34
3/15/2017	B021	0.01	0.432	0.221	0.211
3/24/2017	B022	0.01	0.122	0.071	0.051
3/27/2017	B023	0.01	0.119	0.061	0.058
4/2/2017	B024	0.01	0.937	0.545	0.392
4/11/2017	B025	0.01	0.725	0.395	0.33
4/18/2017	B026	0.01	0.981	0.546	0.435
4/28/2017	B027	0.01	0.544	0.271	0.273
5/3/2017	B028	0.01	0.457	0.229	0.228
5/8/2017	B029	0.01	0.066	0.032	0.034
5/19/2017	B30	0.01	0.156	0.072	0.084
5/25/2017	B031	0.01	0.005	0.005	0.005
5/30/2017	B032	0.01	0.005	0.005	0.005
6/8/2017	B033	0.01	0.005	0.005	0.005
6/13/2017	B034	0.01	0.005	0.005	0.005
6/20/2017	B035	0.01	0.005	0.005	0.005
6/30/2017	B036	0.01	0.005	0.005	0.005
7/2/2017	B037	0.01	0.005	0.005	0.005
7/11/2017	B038	0.01	0.005	0.005	0.005
7/16/2017	B039	0.01	0.163	0.083	0.08
7/26/2017	B040	0.01	0.005	0.005	0.005
7/31/2017	B041	0.01	0.005	0.005	0.005
8/8/2017	B042	0.01	0.005	0.005	0.005
8/13/2017	B043	0.01	0.005	0.005	0.005
8/24/2017	B044	0.01	0.05	0.026	0.024
8/28/2017	B045	0.01	1.298	0.824	0.474
9/7/2017	B046	0.01	0.005	0.005	0.005
9/10/2017	B049	0.01	0.107	0.048	0.059
9/19/2017	B048	0.01	15.96	9.23	6.73
9/25/2017	B049	0.01	1.496	0.657	0.839
10/3/2017	B050	0.01	0.217	0.113	0.104
10/11/2017	B051	0.01	0.128	0.065	0.063
10/16/2017	B052	0.01	0.149	0.083	0.066
10/24/2017	B053	0.01	0.307	0.178	0.129
10/30/2017	B054	0.01	0.167	0.092	0.075
11/6/2017	B055	0.01	0.057	0.031	0.026
11/16/2017	B056	0.01	0.334	0.216	0.118
11/19/2017	B057	0.01	3.09	1.78	1.31

Date Start	Sample No.	RL (ppb)	total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)
12/1/2017	B058	0.01	1.496	0.900	0.596
12/5/2017	B059	0.01	0.251	0.132	0.119
12/14/2017	B060	0.01	0.161	0.078	0.083
12/19/2017	B061	0.01	0.176	0.08	0.096
12/26/2017	B062	0.01	0.064	0.031	0.033

Table A-3. Summary of co-located sample results.

Site	Date Start	Sample No.	Sample Type	RL (ppb)	total 1,3-D (ppb)	cis-1,3-D (ppb)	trans-1,3-D (ppb)	Mean Difference (%)
Delhi	12/28/2016	A006	Primary - Regulator	0.01	0.057	0.027	0.03	6.90%
Delhi	12/28/2016	A008	Duplicate - Regulator	0.01	0.056	0.028	0.028	
Parlier	1/10/2017	B008	Primary - Regulator	0.01	0.005	0.005	0.005	N/A[#]
Parlier	1/10/2017	B009	Duplicate - Regulator	0.01	0.005	0.005	0.005	
Parlier	1/24/2017	B012	Primary - Xonteck	0.01	0.005	0.005	0.005	N/A[#]
Parlier	1/24/2017	B011	Duplicate - Regulator	0.01	0.005	0.005	0.005	
Delhi	1/30/2017	A014	Primary - Xonteck	0.01	0.005	0.005	0.005	N/A[#]
Delhi	1/30/2017	A015	Duplicate - Regulator	0.01	0.005	0.005	0.005	
Parlier	2/2/2017	B014	Primary - Xonteck	0.01	0.406	0.285	0.121	10.91%
Parlier	2/2/2017	B013	Duplicate - Regulator	0.01	0.364	0.259	0.105	
Delhi	2/8/2017	A016	Primary - Xonteck	0.01	0.066	0.037	0.029	6.25%
Delhi	2/8/2017	A017	Duplicate - Regulator	0.01	0.062	0.034	0.028	
Parlier	2/11/2017	B016	Primary - Xonteck	0.01	0.172	0.094	0.078	7.23%
Parlier	2/11/2017	B015	Duplicate - Regulator	0.01	0.160	0.087	0.073	
Delhi	3/22/2017	A025	Primary - Xonteck	0.01	0.053	0.028	0.025	9.01%
Delhi	3/22/2017	A024	Duplicate - Regulator	0.01	0.058	0.024	0.034	
Delhi	4/14/2017	A028	Primary - Xonteck	0.01	0.202	0.1	0.102	34.09%
Delhi	4/14/2017	A029	Duplicate - Regulator	0.01	0.285	0.122	0.163	
Delhi	4/24/2017	A031	Primary - Xonteck	0.01	0.072	0.038	0.034	28.57%
Delhi	4/24/2017	A032	Duplicate - Regulator	0.01	0.096	0.047	0.049	
Delhi	5/22/2017	A037	Primary - Xonteck	0.01	0.050	0.026	0.024	53.16%
Delhi	5/22/2017	A038	Duplicate - Regulator	0.01	0.029	0.013	0.016	
Delhi	8/3/2017	A052	Primary - Xonteck	0.01	0.005	0.005	0.005	N/A[#]
Delhi	8/3/2017	A053	Duplicate - Regulator	0.01	0.022	0.011	0.011	
Delhi	8/22/2017	A057	Primary - Xonteck	0.01	0.005	0.005	0.005	N/A[#]
Delhi	8/22/2017	A058	Duplicate - Regulator	0.01	0.005	0.005	0.005	
Delhi	10/2/2017	A066	Primary - Xonteck	0.01	0.005	0.005	0.005	N/A[#]
Delhi	10/2/2017	A067	Duplicate - Regulator	0.01	0.005	0.005	0.005	
Delhi	10/17/2017	A069	Primary - Xonteck	0.01	0.098	0.058	0.04	9.63%

Delhi	10/17/2017	A070	Duplicate - Regulator	0.01	0.089	0.055	0.034	
Delhi	11/8/2017	A074	Primary - Xonteck	0.01	0.515	0.292	0.223	2.49%
Delhi	11/8/2017	A075	Duplicate - Regulator	0.01	0.528	0.298	0.23	
Delhi	11/20/2017	A078	Primary - Xonteck	0.01	0.323	0.18	0.143	80.87%
Delhi	11/20/2017	A079	Duplicate - Regulator	0.01	0.137	0.074	0.063	
Delhi	12/11/2017	A082	Primary - Xonteck	0.01	0.197	0.09	0.107	5.43%
Delhi	12/11/2017	A083	Duplicate - Regulator	0.01	0.208	0.092	0.116	

[#] Co-located pairs measuring below RL are not used in quantifiable comparisons.

Table A-4. Recovery rates from laboratory quality control samples.

Analysis date	cis-1,3-D recovery (%)	trans-1,3-D recovery (%)	Sample type
12/5/2016	ND	ND	lab blank
12/28/2016	ND	ND	lab blank
1/6/2017	ND	ND	lab blank
1/24/2017	ND	ND	lab blank
2/3/2017	ND	ND	lab blank
2/16/2017	ND	ND	lab blank
2/17/2017	ND	ND	lab blank
3/2/2017	ND	ND	lab blank
3/14/2017	ND	ND	lab blank
4/3/2017	ND	ND	lab blank
4/11/2017	ND	ND	lab blank
6/2/2017	ND	ND	lab blank
6/8/2017	ND	ND	lab blank
6/22/2017	ND	ND	lab blank
6/27/2017	ND	ND	lab blank
7/17/2017	ND	ND	lab blank
7/27/2017	ND	ND	lab blank
8/9/2017	ND	ND	lab blank
8/28/2017	ND	ND	lab blank
9/8/2017	ND	ND	lab blank
9/27/2017	ND	ND	lab blank
10/5/2017	ND	ND	lab blank
10/19/2017	ND	ND	lab blank
11/9/2017	ND	ND	lab blank
11/13/2017	ND	ND	lab blank
12/4/2017	ND	ND	lab blank
12/15/2017	ND	ND	lab blank
12/29/2017	ND	ND	lab blank
1/11/2018	ND	ND	lab blank
12/5/2016	101.0%	105.0%	lab spike
12/28/2016	99.3%	103.0%	lab spike
1/6/2017	91.3%	97.3%	lab spike
1/24/2017	91.3%	102.7%	lab spike
2/3/2017	101.0%	101.0%	lab spike
2/16/2017	100.0%	99.3%	lab spike
2/17/2017	99.3%	97.3%	lab spike
3/2/2017	90.0%	82.7%	lab spike
3/14/2017	98.7%	101.0%	lab spike
4/3/2017	97.3%	90.0%	lab spike

4/11/2017	94.7%	91.3%	lab spike
4/28/2017	101.0%	111.0%	lab spike
5/8/2017	103.0%	94.0%	lab spike
6/2/2017	99.3%	98.7%	lab spike
6/8/2017	99.3%	101.0%	lab spike
6/22/2017	101.0%	96.7%	lab spike
6/27/2017	88.7%	85.3%	lab spike
7/17/2017	91.3%	90.7%	lab spike
7/27/2017	100.0%	94.0%	lab spike
8/9/2017	96.0%	93.3%	lab spike
8/28/2017	100.0%	98.7%	lab spike
9/8/2017	100.0%	102.0%	lab spike
9/27/2017	96.7%	98.7%	lab spike
10/5/2017	89.3%	84.7%	lab spike
10/19/2017	97.3%	97.3%	lab spike
11/10/2017	101.0%	99.3%	lab spike
11/13/2017	98.0%	98.7%	lab spike
12/4/2017	101.0%	98.7%	lab spike
12/15/2017	98.7%	97.3%	lab spike
12/29/2017	94.7%	95.3%	lab spike
1/11/2018	101.3%	94.7%	lab spike