



2017 Seasonal Ambient Air Monitoring of Methyl Isothiocyanate (MITC) in Kern County

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By

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Monitoring Report Approval

Report Title: 2017 Seasonal Ambient Air Monitoring of Methyl Isothiocyanate (MITC) in Kern County

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Summary

Department of Pesticide Regulation (DPR) staff collected four consecutive 24 h air samples per week to measure for ambient air concentrations of methyl isothiocyanate (MITC) in four Kern County high-use communities over a 12-week period from June 5, 2017 to August 23, 2017. The four selected communities were all characterized by relatively high levels of MITC use. The selected communities were: Arvin, Bakersfield, Edmundson Acres, and Rosedale.

A total of 242 samples, consisting of 194 primary samples and 48 quality control (QC) samples were collected by DPR personnel over the 12 week period. Of the 48 QC samples, there were 24 samples that tested for breakthrough, 8 co-located samples, 8 field spikes, and 8 field blanks. A total of three samples were invalidated during the study: one sample was invalidated due to a flow restriction and two samples were invalidated due to an ending flow rate outside of the acceptable range. Additionally, two QC samples (breakthrough) were not analyzed due to improper reporting of their primary sample status during sample check-in. These samples are not included in this report.

MITC concentrations ranging from below the reporting limit to a maximum concentration of 4.01 ppb (Arvin) were measured in the study. Maximum 24 h concentrations at the other sampling sites were: 0.17 ppb at Bakersfield, 0.95 ppb at Edmundson Acres, 0.11 ppb at Rosedale. Maximum 4-week rolling average concentrations at Arvin 1.03 ppb is just slightly above DPR's subchronic screening level of 1.0 ppb for MITC (based on a 4-week rolling average). Exceedance a screening level does not necessarily indicate adverse health effects occurred, however, it does indicate the need for DPR to conduct a detailed evaluation to determine if any restrictions on the pesticide use may be needed

1.0 Introduction

MITC is the byproduct of the soil fumigants metam-sodium, metam-potassium, and dazomet. On contact with water or warm, moist soil, metam-sodium, dazomet, and metam-potassium quickly decompose to create MITC, which is used in pre-plant fumigations for the control of weeds, fungi and nematodes. MITC is used heavily in Kern County, with over 3 million pounds of active ingredient applied each year for 2015 and 2016 (DPR 2017). Peak use of MITC in Kern County occurs during the summer months of July and August (DPR 2017).

DPR currently monitors for MITC and other fumigants as part of its Air Monitoring Network (AMN); however, AMN sampling site locations were selected to capture a broad selection of pesticides and were not chosen specifically for MITC. As a result, monitoring in the highest use locations of MITC does not always occur. Intensive monitoring in high-use communities allows DPR to assess the maximum seasonal exposures to MITC in these communities and to assess if any measures are needed to mitigate unacceptable air concentrations.

In June 2017, the United States Environmental Protection Agency (US EPA) approved a Quality Assurance Project Plan (QAPP) for DPR to monitor for MITC in various high use communities during the high use season (DPR, 2017). Here we report ambient air monitoring results for MITC in four Kern County communities from June 5, 2017 to August 23, 2017. Sampling involved the collection of four consecutive 24 h air samples from each monitoring location per week during a 12-week period. The objectives of the study were to: [1] collect monitoring data to assess maximum subchronic MITC concentrations in regions of high use; and [2] to compare those measured air concentrations to subchronic human health screening levels.

2.0 Sampling Sites

Four communities located within the high MITC-use region of Kern County were selected for inclusion in the monitoring study. The selected communities were: Arvin, Bakersfield, Edmundson Acres, and Rosedale. Location coordinates for each sampling site location are included in Table 1.

Table 1: Sampler Waypoints

Community	Sampler Location	Site Coordinates
Arvin	Arvin High School	35°13'02.2"N 118°50'14.1"W
Bakersfield	Bakersfield's ARB Office Building	35°21'23.9"N 119°03'45.1"W
Edmundson Acres	Di Giorgio Elementary	35°14'21.1"N 118°47'19.1"W
Rosedale	Water Well Site	35°23'36.5"N 119°08'12.0"W

2.1 Arvin

The Arvin sampling site was located at Arvin High School (900 Varsity Road, Arvin, CA 93203). Sampling equipment was placed on the rooftop of a building located at the western half of campus (35°13'02.2"N 118°50'14.1"W). The sampling equipment was approximately at a total height of 8 meters (5 meters above the ground with the air sampling media height adding another 3 meters above the rooftop). Figure 1 displays an aerial view of the sampling site with the sampler location marked. Application of MITC generators from 2015-2016 have largely occurred to the southeast and north of Arvin. Figure 2 displays the cumulative total pounds of MITC-generator active ingredient from 2015 and 2016 near the study area.

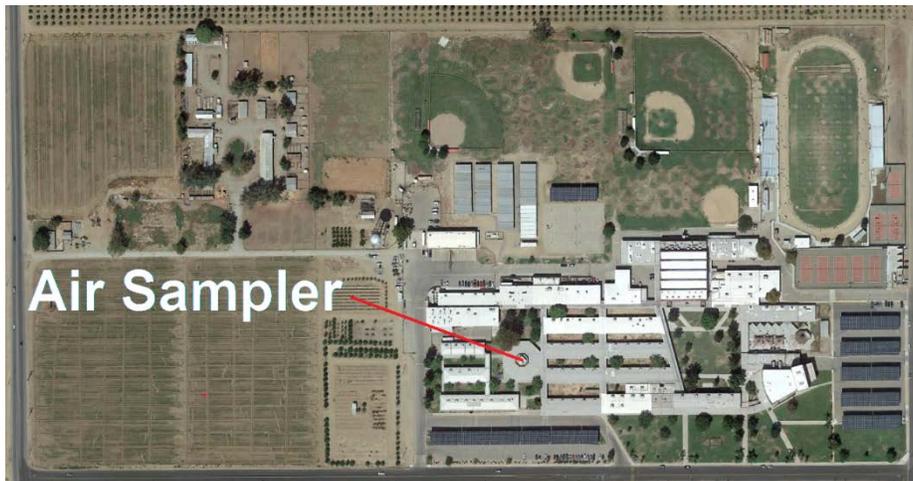


Figure 1. Aerial view of monitoring site in Arvin.

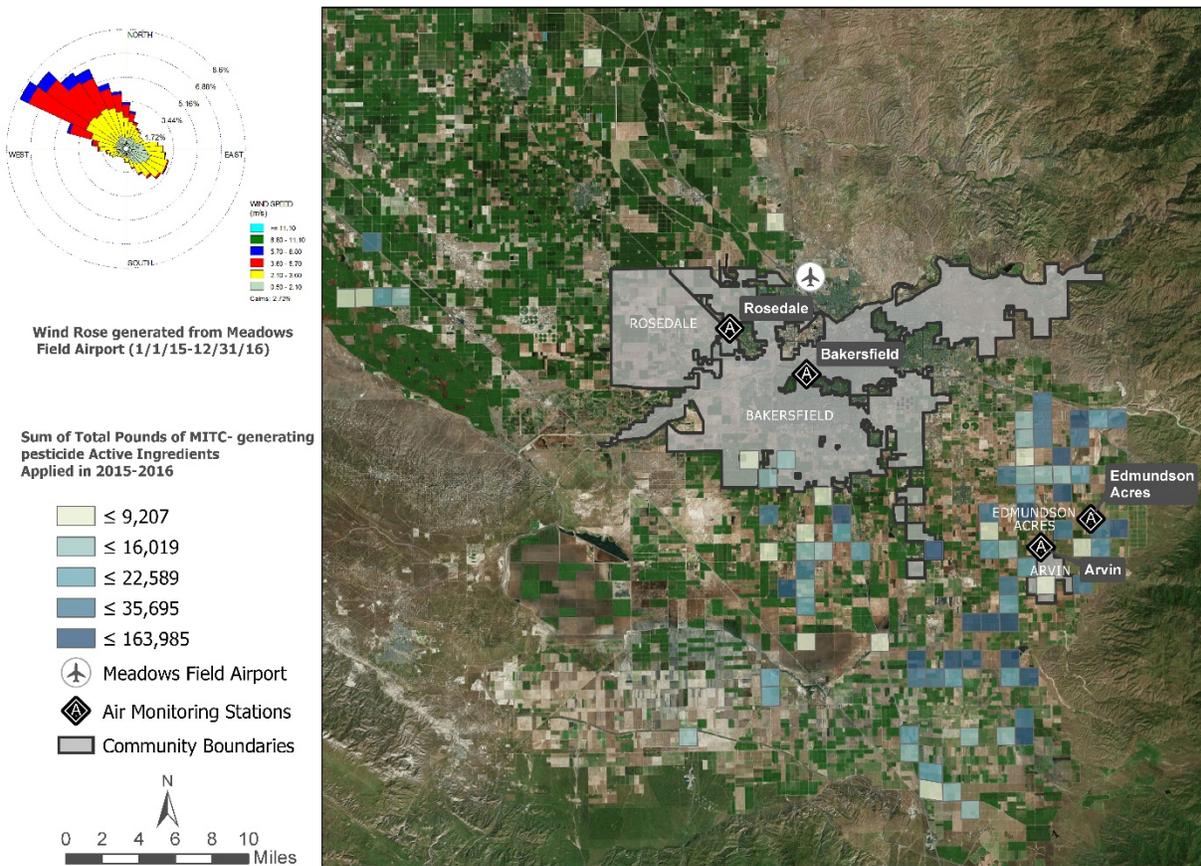


Figure 2. Cumulative total pounds of MITC-generator active ingredient from January 1, 2015 to December 31, 2016 with wind rose from Meadows Field Airport to the north of Bakersfield.

2.2 Bakersfield

The Bakersfield sampling site was located at the ARB office building on 5558 California Avenue, Bakersfield, CA 93309. The sampling equipment was placed indoors while the inlet tubing was routed to the rooftop where sorbent tubes were approximately 6 meters above the ground (35°21'23.9"N 119°03'45.1"W). As shown in Figure 2, there was little to no reported use of MITC-generators during 2015 – 2016 near the monitoring site, with most reported use occurring greater than six miles to the south and south-east of the sampling site. Therefore, this sampling site was selected as a background location due to its lower reported use totals and to the site’s position within the developed, urban surroundings. Figure 3 shows an aerial view of the Bakersfield sampling site with the sampler location marked.



Figure 3. Aerial view of monitoring site in Bakersfield.

2.3 Edmundson Acres

The Edmundson Acres sampling site was located at Di Giorgio Elementary School (19405 Buena Vista Boulevard, Arvin, CA 93203). Sampling equipment was placed inside a temperature-controlled trailer with tubing routed to the rooftop where sorbent tubes were approximately 4 meters above the ground ($35^{\circ}14'21.1''\text{N}$ $118^{\circ}47'19.1''\text{W}$). The Di Giorgio site served as the designated quality control (QC) location where all QC samples were collected. Figure 4 shows an aerial view of the sampling site with the sampler location marked.



Figure 4. Aerial view of monitoring site in Di Giorgio.

2.4 Rosedale

The sampling site in Rosedale was located at a water well located on 3605 Old Farm Road, Bakersfield, CA 93312. The sampling equipment was located within an enclosure with tubing routed to a mast supporting the sorbent tube approximately 2 meters above the ground ($35^{\circ}23'36.5''\text{N}$ $119^{\circ}08'12.0''\text{W}$). Figure 5 shows an aerial view of the sampling site with the sampler location marked.



Figure 5. Aerial view of monitoring site in Rosedale CDP.

3.0 Methods

3.1 Sampling Equipment

MITC in ambient air was collected by passing ambient air through manufactured pre-packed 200/1800 mg coconut charcoal sorbent tubes (SKC Inc.® # 226-16-02) using an attached SKC® personal sample pump set at a flow rate of 1.5 liters per minute (LPM) \pm 10% for 24 h. The sampling inlet height varied at each site but conformed to US EPA ambient air siting requirements (40 CFR Part 58). Actual sampling protocol was adapted from DPR’s SOP “Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps” (DPR, 2001).

3.2 Sampling Procedures

Sampling began at all sites on the morning of June 5, 2017, and each sample was collected for a 24 h period. Air flow through the sorbent tubes was recorded from the pump at the start and stop of the sampling event. Collection of each 24 h sample typically took place between the hours of 0700 and 1100.

As the air sampling commenced at each monitoring site, the study number, site location code, sample tracking number, sampling date, sampling time, flow rates, weather conditions, and staff signatures were documented on the Chain of Custody form (COC). DPR personnel previously calibrated all pumps used for air sampling to a flow rate of 1.5 LPM as required in this study. Air sampler flow rates were measured using Bios Defender 510® flow standard at the beginning and the end of sampling period.

At the end of each sampling period, sampled sorbent tubes were tightly capped at each end with manufacturer supplied end caps, placed in insulated transport containers on dry ice (-78.5 °C) for storage and transport. Samples were transported to DPR’s West Sacramento warehouse, where they were logged and placed in a freezer at approximately -20°C until delivered to the Department of Food and Agriculture Center for Analytical Chemistry (CDFA CAC) laboratory for analysis. Samples were typically analyzed within 1 to 2 weeks after collection from the field.

3.3 Sample Analysis

Collected air samples were analyzed for residues of MITC by CDFA CAC laboratory using laboratory method EMON-SM-41.9-MSD "Determination of MITC in Air by GC-MS" (CDFA, 2018a). As part of this analytical method, samples are extracted with 10 mL of 0.1% CS₂ in ethyl acetate with agitation for 30 minutes. The extract is then analyzed by gas chromatography. All results are reported as micrograms (µg) of MITC per sample.

4.0 Results

4.1 Samples That Did Not Meet Quality Control Criteria

- A total of two samples collected at the Arvin sampling site did not meet sampling quality control criteria:
 - Sample A005 was lost when the air sampler experienced flow restriction issues that caused it to prematurely stop after only two hours (sample duration < 24 hours), and
 - Sample A022 had an ending flow rate outside of the acceptable range (flow rate ≠ 1.5 LPM).
- A total of one sample collected at the Rosedale sampling site did not meet sampling quality control criteria:
 - Sample C028 had an ending flow rate outside of the acceptable range (flow rate ≠ 1.5 LPM).
- A total of two samples collected at the Edmundson Acres sampling site were not analyzed due to improper reporting during sample check-in:
 - Samples D078 and D082 were not analyzed due to an error in labeling during sample check in. The samples were mistakenly labeled as "backup" samples and were not routed for analysis. This error was not discovered until the storage stability period of 28 days had passed and the samples were no longer valid.

4.2 Arvin

Table 2 summarizes the results of all samples collected at the Arvin sampling site. Figure 6 displays the results over the course of the study. Low detections of MITC in ambient air were observed in June, with the highest concentration determined to be 0.01 ppb on June 29. All collected samples with concentrations below the method detection limit (MDL) referred as "non-detects" (ND) were given a concentration value of ½ MDL (ND = 0.001 ppb) for the purposes of determining average concentrations. Similarly, all collected samples with concentrations above the MDL but below the Limit of Quantification (LOQ) referred as "Trace" were given a value equal to the midpoint between the LOQ and MDL (Trace = 0.0025 ppb) for the purposes of determining average concentrations.

Maximum 24 h concentrations at this sampling site were measured during the month of July, with the highest concentration measured at 4.01 ppb on July 10, 2017 (Table 2). Although, the July 10th sample ended with a measured flow rate outside of the acceptable criteria (1,778 mL/min) which should have invalidated the sample, due to the high concentration measured, this sample was included in all average concentrations for this sampling site. A valid sample collected on July 11, 2017 had the second highest concentration measured at this site (3.55 ppb) indicating the concentration measured the preceding day

was accurate and should be retained for further consideration. Additionally, every sample collected in July had a quantifiable concentration of MITC, correlating with the historical high use season of the fumigant in the surrounding area.

As a result of high 24 h concentrations measured in the month of July, and with inclusion of the July 10th sample, the maximum 4-week rolling average concentration of 1.03 ppb is just slightly above the established MITC subchronic screening level of 1.0 ppb (Table 2 and Figure 7). Exceedance of a screening level does not necessarily indicate adverse health effects occurred, however, it does indicate the need for DPR to conduct a detailed evaluation to determine if any restrictions on the pesticide use may be needed.

Table 2. Summary of results from samples collected at Arvin.

Sample Number	Location Code	Start Date	End Date	MITC Conc. (ppb)	Adj. Conc. (ppb)	4-week Rolling Average
A001	A	6/5/17	6/6/17	ND	0.00	--
A002	A	6/6/17	6/7/17	ND	0.00	--
A003	A	6/7/17	6/8/17	ND	0.00	--
A004	A	6/8/17	6/9/17	ND	0.00	--
A006	A	6/14/17	6/15/17	Trace	0.00	--
A007	A	6/15/17	6/16/17	Trace	0.00	--
A008	A	6/16/17	6/17/17	Trace	0.00	--
A009	A	6/21/17	6/22/17	Trace	0.00	--
A010	A	6/22/17	6/23/17	Trace	0.00	--
A011	A	6/23/17	6/24/17	Trace	0.00	--
A012	A	6/24/17	6/25/17	Trace	0.00	--
A013	A	6/26/17	6/27/17	0.01	0.01	--
A014	A	6/27/17	6/28/17	Trace	0.00	--
A015	A	6/28/17	6/29/17	ND	0.00	--
A016	A	6/29/17	6/30/17	0.01	0.01	--
A017	A	7/2/17	7/3/17	0.70	0.70	--
A018	A	7/3/17	7/4/17	0.09	0.09	0.05
A019	A	7/4/17	7/5/17	0.13	0.13	0.06
A020	A	7/5/17	7/6/17	0.07	0.07	0.06
A021	A	7/9/17	7/10/17	3.28	3.28	0.27
A022	A	7/10/17	7/11/17	4.01 [†]	4.01 [†]	0.49
A023	A	7/11/17	7/12/17	3.55	3.55	0.66
A024	A	7/12/17	7/13/17	0.31	0.31	0.64
A025	A	7/20/17	7/21/17	0.21	0.21	0.77
A026	A	7/21/17	7/22/17	0.41	0.41	0.80
A027	A	7/22/17	7/23/17	0.13	0.13	0.81
A028	A	7/23/17	7/24/17	0.05	0.05	0.81
A029	A	7/26/17	7/27/17	0.47	0.47	0.90
A030	A	7/27/17	7/28/17	0.66	0.66	0.94
A031	A	07/28/17	07/29/17	1.36	1.36	1.03
A032	A	7/29/17	7/30/17	0.16	0.16	0.97
A033	A	7/30/17	7/31/17	0.32	0.32	0.94
A034	A	7/31/17	8/1/17	0.23	0.23	0.91
A035	A	8/1/17	8/2/17	1.28	1.28	0.98
A036	A	8/2/17	8/3/17	0.26	0.26	0.99
A037	A	8/9/17	8/10/17	0.28	0.28	0.44
A038	A	8/10/17	8/11/17	0.39	0.39	0.44
A039	A	8/11/17	8/12/17	0.43	0.43	0.44
A040	A	8/12/17	8/13/17	0.08	0.08	0.42
A041	A	8/14/17	8/15/17	0.04	0.04	0.40
A042	A	8/15/17	8/16/17	0.01	0.01	0.38

Sample Number	Location Code	Start Date	End Date	MITC Conc. (ppb)	Adj. Conc. (ppb)	4-week Rolling Average
A043	A	8/16/17	8/17/17	0.01	0.01	0.36
A044	A	8/17/17	8/18/17	Trace	0.00	0.34
A045	A	8/19/17	8/20/17	Trace	0.00	0.32
A046	A	8/20/17	8/21/17	ND	0.00	0.32
A047	A	8/21/17	8/22/17	Trace	0.00	0.31
A048	A	8/22/17	8/23/17	0.10	0.10	0.30

ND = samples with no detectable amount (measured concentration is below MDL), considered to be 0.001ppb.

Trace = Samples with measured amounts less than the limit of quantitation, but greater than method detection limit, considered to be 0.003 ppb.

†Sample had an ending flow rate that was outside of the acceptable criteria (>10% of target flow rate of 1.5 LPM).

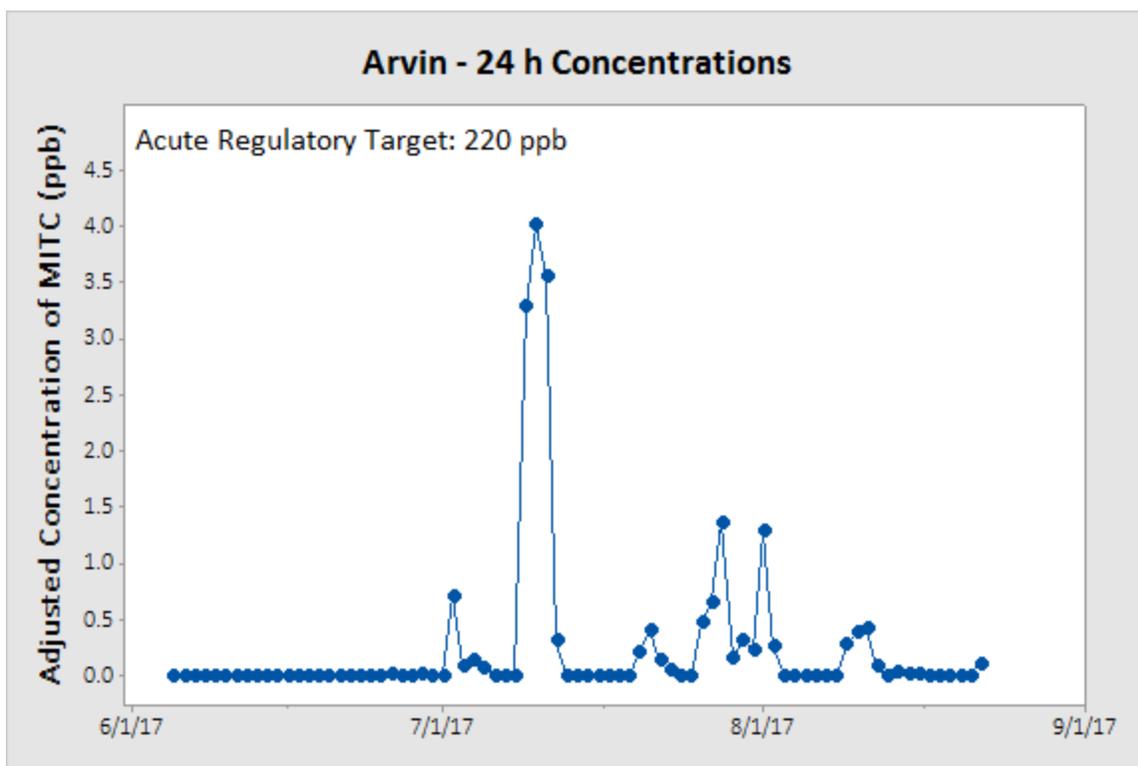


Figure 6. Measured 24 h concentrations of MITC collected at the Arvin sampling site.

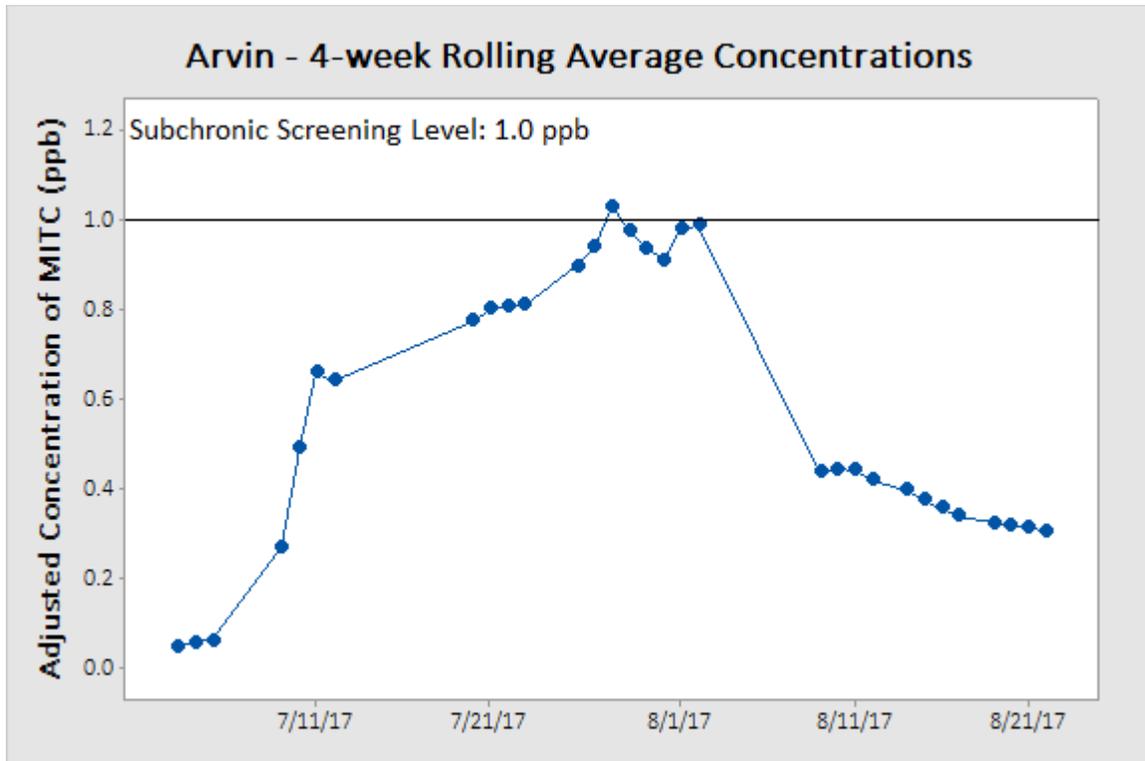


Figure 7. Calculated 4-week rolling average concentrations of MITC at the Arvin sampling site. Dotted line represents the subchronic screening level of 1.0 ppb.

4.3 Bakersfield

Table 3 summarizes the results at the Bakersfield sampling site and Figure 8 displays 24 h concentrations of MITC measured over the study period. The maximum 24 h concentration measured at this sampling site took place on July 28, 2017 (0.17 ppb) and the second highest concentration was detected on August 2, 2017 with a measured concentration of 0.17 ppb as well. A maximum 4-week rolling average concentration of 0.08 ppb was measured during the month of August (Table 3 and Figure 9).

Table 3. Summary of results from samples collected at Bakersfield.

Sample Number	Location Code	Start Date	End Date	MITC Conc. (ppb)	Adj. Conc. (ppb)	4-week Rolling Average
B001	B	6/5/17	6/6/17	ND	0.00	--
B002	B	6/6/17	6/7/17	ND	0.00	--
B003	B	6/7/17	6/8/17	ND	0.00	--
B004	B	6/8/17	6/9/17	ND	0.00	--
B005	B	6/13/17	6/14/17	0.01	0.01	--
B006	B	6/14/17	6/15/17	0.03	0.03	--
B007	B	6/15/17	6/16/17	0.01	0.01	--
B008	B	6/16/17	6/17/17	Trace	0.00	--
B009	B	6/21/17	6/22/17	0.01	0.01	--
B010	B	6/22/17	6/23/17	ND	0.00	--
B011	B	6/23/17	6/24/17	Trace	0.00	--
B012	B	6/24/17	6/25/17	Trace	0.00	--
B013	B	6/26/17	6/27/17	ND	0.00	--
B014	B	6/27/17	6/28/17	ND	0.00	--
B015	B	6/28/17	6/29/17	0.04	0.04	--
B016	B	6/29/17	6/30/17	0.03	0.03	--
B017	B	7/2/17	7/3/17	Trace	0.00	--
B018	B	7/3/17	7/4/17	Trace	0.00	0.01
B019	B	7/4/17	7/5/17	Trace	0.00	0.01
B020	B	7/5/17	7/6/17	0.04	0.04	0.01
B021	B	7/9/17	7/10/17	0.02	0.02	0.01
B022	B	7/10/17	7/11/17	0.01	0.01	0.01
B023	B	7/11/17	7/12/17	0.01	0.01	0.01
B024	B	7/12/17	7/13/17	0.06	0.06	0.01
B025	B	7/20/17	7/21/17	0.12	0.12	0.02
B026	B	7/21/17	7/22/17	0.13	0.13	0.03
B027	B	7/22/17	7/23/17	0.06	0.06	0.03
B028	B	7/23/17	07/24/17	0.01	0.01	0.03
B029	B	7/26/17	7/27/17	0.07	0.07	0.04
B030	B	7/27/17	7/28/17	0.07	0.07	0.04
B031	B	07/28/17	07/29/17	0.17	0.17	0.05
B032	B	7/29/17	7/30/17	0.13	0.13	0.06
B033	B	7/30/17	7/31/17	0.05	0.05	0.06
B034	B	7/31/17	8/1/17	0.08	0.08	0.06
B035	B	8/1/17	8/2/17	0.05	0.05	0.06
B036	B	8/2/17	8/3/17	0.17	0.17	0.07
B037	B	8/9/17	8/10/17	0.05	0.05	0.07
B038	B	8/10/17	8/11/17	0.02	0.02	0.08
B039	B	8/11/17	8/12/17	0.04	0.04	0.08
B040	B	8/12/17	8/13/17	0.09	0.09	0.08
B041	B	8/14/17	8/15/17	Trace	0.00	0.08
B042	B	8/15/17	8/16/17	ND	0.00	0.07
B043	B	8/16/17	8/17/17	Trace	0.00	0.07
B044	B	8/17/17	8/18/17	Trace	0.00	0.07
B045	B	8/19/17	8/20/17	Trace	0.00	0.06
B046	B	8/20/17	8/21/17	ND	0.00	0.06
B047	B	8/21/17	8/22/17	Trace	0.00	0.05
B048	B	8/22/17	8/23/17	0.01	0.01	0.05

ND = samples with no detectable amount (measured concentration is below MDL), considered to be 0.001 ppb.

Trace = Samples with measured amounts less than the limit of quantitation, but greater than method detection limit, considered to be 0.003 ppb.

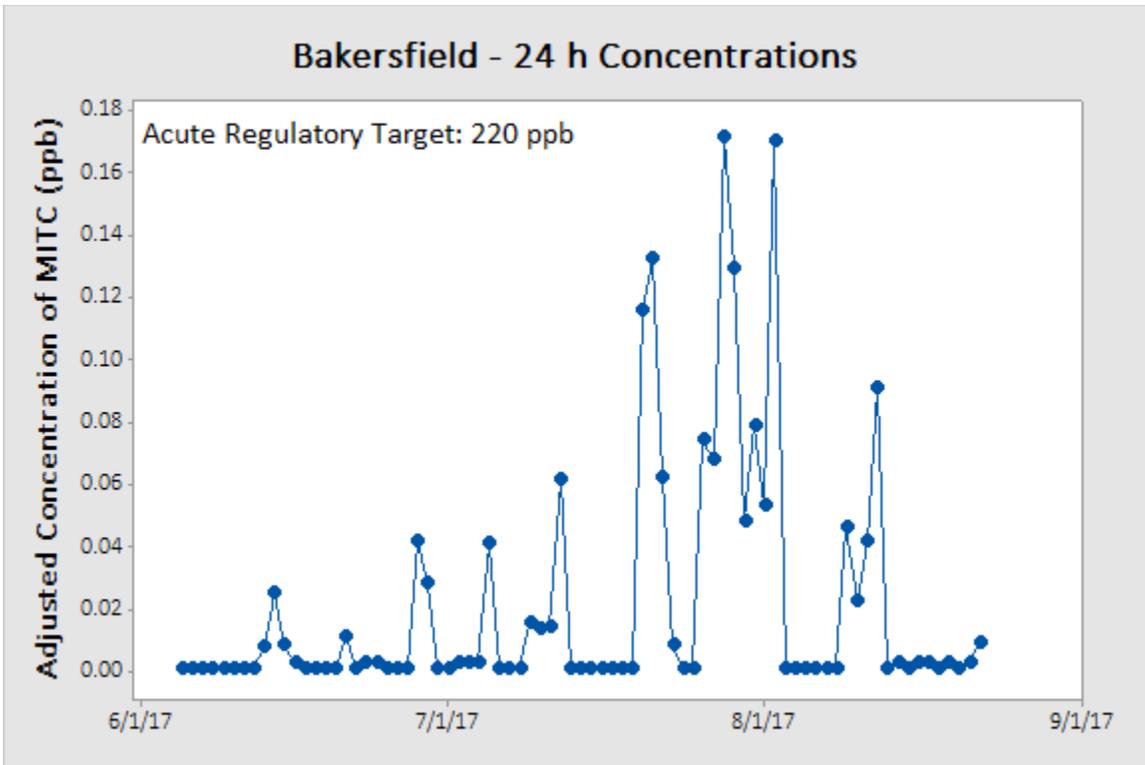


Figure 8. Measured 24 h MITC concentrations for samples collected at Bakersfield.

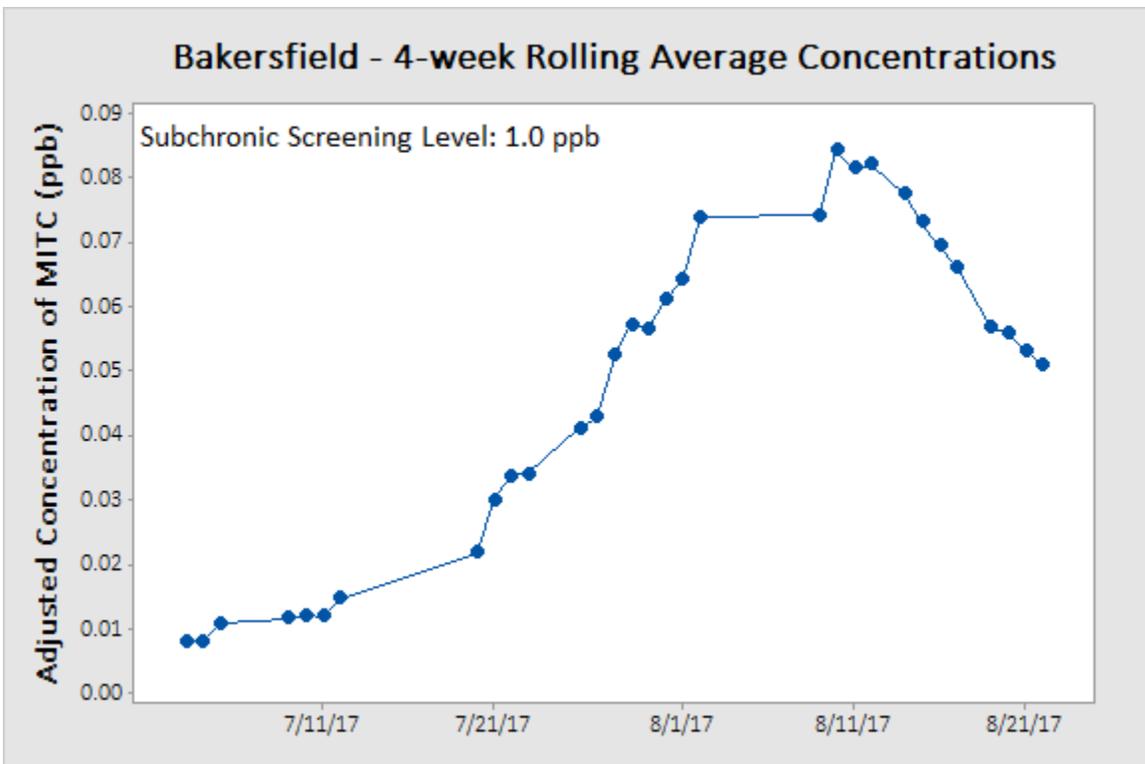


Figure 9. Calculated 4-week rolling average concentrations of MITC at the Bakersfield sampling site.

4.4 Rosedale

Of the four sites, samples at Rosedale consistently had the lowest concentrations of MITC. Table 4 summarizes the results at Rosedale and Figure 10 displays the 24 h concentrations of MITC over the study period. The maximum 24 h concentration at this sampling site occurred on August 2, 2017 with a concentration of 0.11 ppb; the second highest concentration was detected on July 21, 2017 with a measured concentration of 0.08 ppb (Figure 10). A sample collected on July 23, 2017 was determined to be invalid as the ending flow of 1.68 LPM was outside of the acceptable criteria (1.5 LPM \pm 10%). While its ending flow was higher than the acceptable value, the determined concentration of MITC for this sample was measured at trace level. Figure 11 displays the 4-week rolling average concentrations of MITC.

Table 4. Summary of results from samples collected at Rosedale.

Sample Number	Location Code	Start Date	End Date	MITC Conc. (ppb)	Adj. Conc. (ppb)	4-week Rolling Average
C001	C	6/5/17	6/6/17	ND	0.00	--
C002	C	6/6/17	6/7/17	ND	0.00	--
C003	C	6/7/17	6/8/17	ND	0.00	--
C004	C	6/8/17	6/9/17	ND	0.00	--
C005	C	6/13/17	6/14/17	Trace	0.00	--
C006	C	6/14/17	6/15/17	0.01	0.01	--
C007	C	6/15/17	6/16/17	0.01	0.01	--
C008	C	6/16/17	6/17/17	Trace	0.00	--
C009	C	6/21/17	6/22/17	0.01	0.01	--
C010	C	6/22/17	6/23/17	Trace	0.00	--
C011	C	6/23/17	6/24/17	Trace	0.00	--
C012	C	6/24/17	6/25/17	Trace	0.00	--
C013	C	6/26/17	6/27/17	Trace	0.00	--
C014	C	6/27/17	6/28/17	ND	0.00	--
C015	C	6/28/17	6/29/17	0.01	0.01	--
C016	C	6/29/17	6/30/17	0.01	0.01	--
C017	C	7/2/17	7/3/17	Trace	0.00	--
C018	C	7/3/17	7/4/17	ND	0.00	0.00
C019	C	7/4/17	7/5/17	Trace	0.00	0.00
C020	C	7/5/17	7/6/17	Trace	0.00	0.00
C021	C	7/9/17	7/10/17	ND	0.00	0.00
C022	C	7/10/17	7/11/17	Trace	0.00	0.00
C023	C	7/11/17	7/12/17	Trace	0.00	0.00
C024	C	7/12/17	7/13/17	Trace	0.00	0.00
C025	C	7/20/17	7/21/17	0.05	0.05	0.01
C026	C	7/21/17	7/22/17	0.08	0.08	0.01
C027	C	7/22/17	7/23/17	0.03	0.03	0.01
C028	C	7/23/17	07/24/17	Trace [†]	0.00 [†]	0.01
C029	C	7/26/17	7/27/17	0.02	0.02	0.01
C030	C	7/27/17	7/28/17	0.02	0.02	0.02
C031	C	07/28/17	07/29/17	0.02	0.02	0.02
C032	C	7/29/17	7/30/17	0.05	0.05	0.02
C033	C	7/30/17	7/31/17	0.02	0.02	0.02
C034	C	7/31/17	8/1/17	0.02	0.02	0.02
C035	C	8/1/17	8/2/17	0.05	0.05	0.02
C036	C	8/2/17	8/3/17	0.11	0.11	0.03
C037	C	8/9/17	8/10/17	0.01	0.01	0.03
C038	C	8/10/17	8/11/17	0.01	0.01	0.03
C039	C	8/11/17	8/12/17	0.01	0.01	0.03
C040	C	8/12/17	8/13/17	0.04	0.04	0.03

Sample Number	Location Code	Start Date	End Date	MITC Conc. (ppb)	Adj. Conc. (ppb)	4-week Rolling Average
C041	C	8/14/17	8/15/17	ND	0.00	0.03
C042	C	8/15/17	8/16/17	ND	0.00	0.03
C043	C	8/16/17	8/17/17	Trace	0.00	0.03
C044	C	8/17/17	8/18/17	Trace	0.00	0.03
C045	C	8/19/17	8/20/17	Trace	0.00	0.02
C046	C	8/20/17	8/21/17	Trace	0.00	0.02
C047	C	8/21/17	8/22/17	Trace	0.00	0.02
C048	C	8/22/17	8/23/17	Trace	0.00	0.02

ND = samples with no detectable amount (measured concentration is below MDL), considered to be 0.001 ppb.

Trace = Samples with measured amounts less than the limit of quantitation, but greater than method detection limit, considered to be 0.003 ppb.

†Sample had an ending flow rate that was outside of the acceptable criteria (>10% of target flow rate of 1.5 LPM).

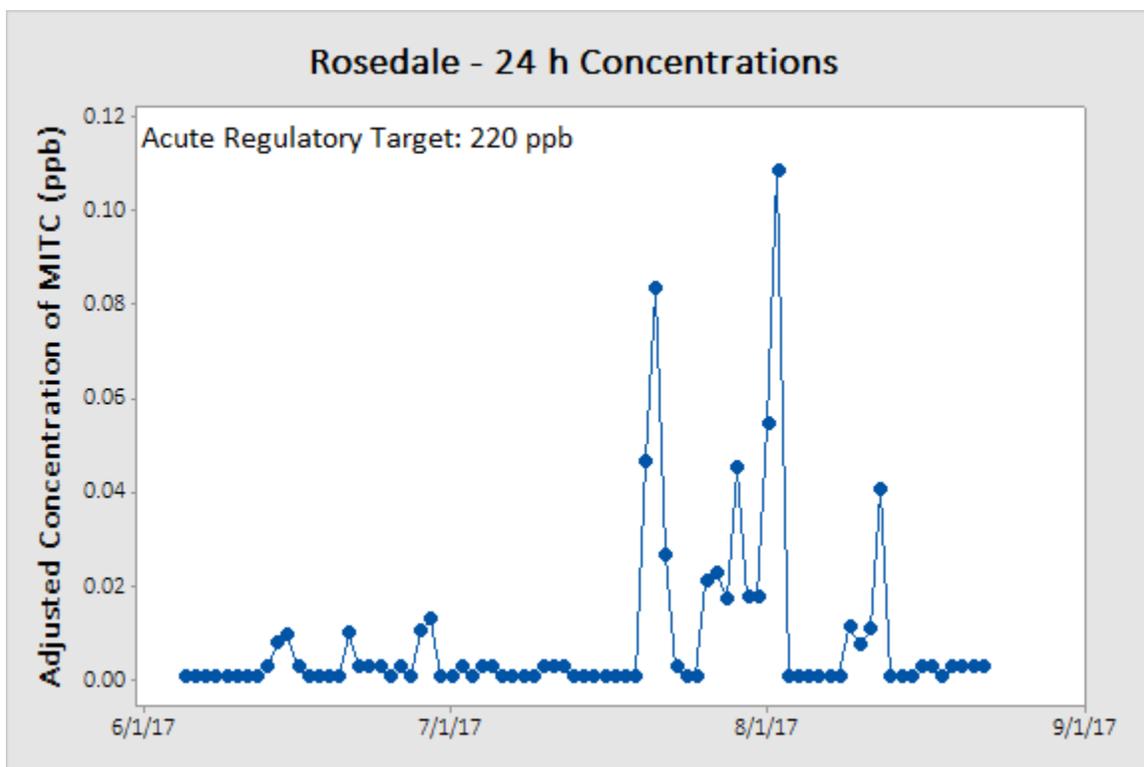


Figure 10. Measured 24 h MITC concentrations for samples collected at Rosedale.

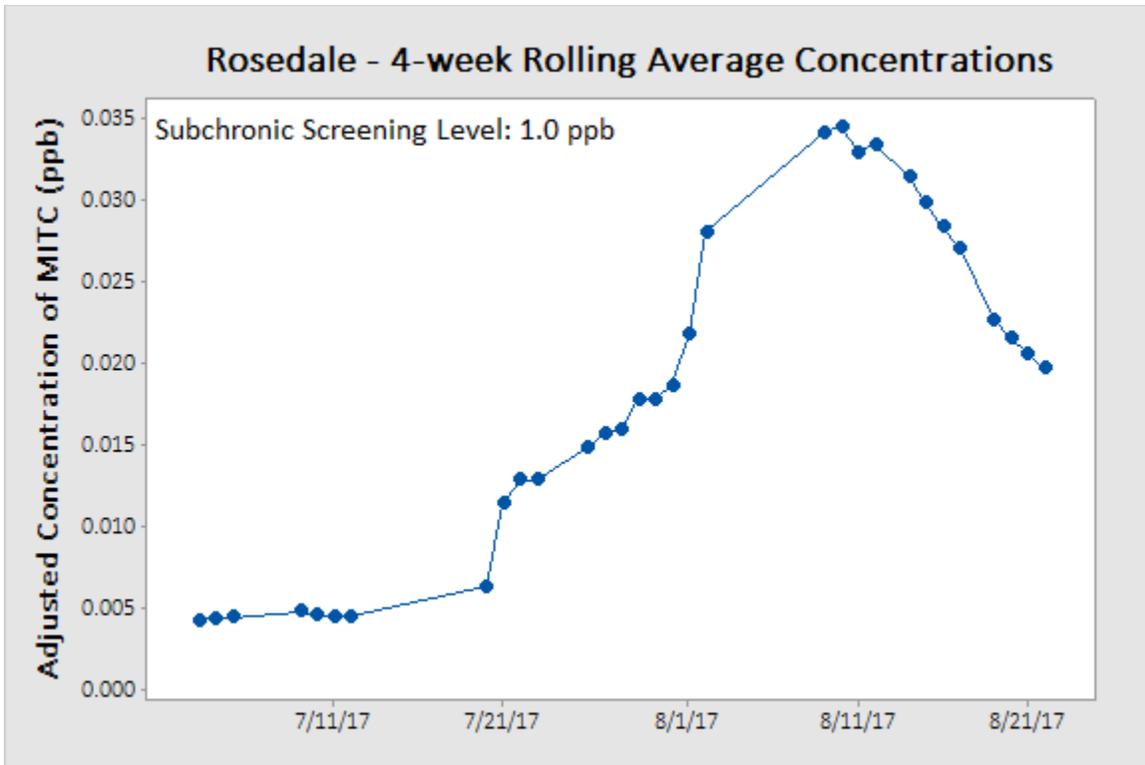


Figure 11. Calculated 4-week rolling average concentrations of MITC at the Rosedale sampling site.

4.5 Edmundson Acres

Samples collected at the Edmundson Acres sampling site were found, on average, to have the second highest measured concentrations and the greatest number of quantifiable detections during the study (Table 5). During the month of June, only two samples (D025 and D031) were found to have quantifiable amounts of MITC. These two samples were collected during the same 24 hour period as the two quantifiable samples collected at the Arvin site (A013 – June 26 to 27 and A016 – 29 to 30). Given the close proximity of the sampling site in Edmundson Acres to that in Arvin (approximately 3.1 miles) these samples may have represented the same nearby MITC applications as the measured concentrations between the two sites were identical (0.01 ppb).

Detections increased during the month of July, with a peak concentration of 0.95 ppb measured on July 9 (Table 5 and Figure 12). The second highest concentration was detected on August 9 with a measured concentration of 0.94 ppb. Similarly to Arvin, every sample collected in Edmundson Acres during July was determined to have quantifiable concentrations of MITC.

Table 5. Summary of results from samples collected at Edmundson Acres.

Sample Number	Location Code	Start Date	End Date	MITC Conc. (PPB)	Adj. Conc. (PPB)	4-week Rolling Average
D001	D	6/5/17	6/6/17	ND	0.00	--
D003	D	6/6/17	6/7/17	ND	0.00	--
D005	D	6/7/17	6/8/17	ND	0.00	--
D006	D	6/8/17	6/9/17	ND	0.00	--
D009	D	6/13/17	6/14/17	Trace	0.00	--
D013	D	6/14/17	6/15/17	Trace	0.00	--
D014	D	6/15/17	6/16/17	Trace	0.00	--
D016	D	6/16/17	6/17/17	Trace	0.00	--
D017	D	6/21/17	6/22/17	Trace	0.00	--
D020	D	6/22/17	6/23/17	ND	0.00	--
D022	D	6/23/17	6/24/17	Trace	0.00	--
D024	D	6/24/17	6/25/17	Trace	0.00	--
D025	D	6/26/17	6/27/17	0.01	0.01	--
D028	D	6/27/17	6/28/17	Trace	0.00	--
D029	D	6/28/17	6/29/17	ND	0.00	--
D031	D	6/29/17	6/30/17	0.01	0.01	--
D032	D	7/2/17	7/3/17	0.09	0.09	--
D034	D	7/3/17	7/4/17	0.02	0.02	0.01
D036	D	7/4/17	7/5/17	0.03	0.03	0.01
D038	D	7/5/17	7/6/17	0.04	0.04	0.01
D042	D	7/9/17	7/10/17	0.95	0.95	0.07
D043	D	7/10/17	7/11/17	0.46	0.46	0.09
D045	D	7/11/17	7/12/17	0.19	0.19	0.10
D047	D	7/12/17	7/13/17	0.12	0.12	0.10
D049	D	7/20/17	7/21/17	0.11	0.11	0.13
D053	D	7/21/17	7/22/17	0.05	0.05	0.13
D054	D	7/22/17	7/23/17	0.06	0.06	0.13
D056	D	7/23/17	7/24/17	0.03	0.03	0.14
D060	D	7/26/17	7/27/17	0.51	0.51	0.18
D062	D	7/27/17	7/28/17	0.13	0.13	0.19
D063	D	7/28/17	7/29/17	0.08	0.08	0.19
D064	D	7/29/17	7/30/17	0.27	0.27	0.20
D065	D	7/30/17	7/31/17	0.05	0.05	0.19
D067	D	7/31/17	8/1/17	0.03	0.03	0.19
D070	D	8/1/17	8/2/17	0.16	0.16	0.19
D073	D	8/2/17	8/3/17	0.14	0.14	0.20
D075	D	8/9/17	8/10/17	0.94	0.94	0.19
D077	D	8/10/17	8/11/17	0.13	0.13	0.19
D080	D	8/11/17	8/12/17	0.19	0.19	0.19
D081	D	8/12/17	8/13/17	0.06	0.06	0.18
D083	D	8/14/17	8/15/17	0.02	0.02	0.18
D086	D	8/15/17	8/16/17	0.01	0.01	0.17
D087	D	8/16/17	8/17/17	0.01	0.01	0.16
D090	D	8/17/17	8/18/17	Trace	0.00	0.15
D093	D	8/19/17	8/20/17	Trace	0.00	0.15
D094	D	8/20/17	8/21/17	Trace	0.00	0.15
D097	D	8/21/17	8/22/17	0.01	0.01	0.15
D099	D	8/22/17	8/23/17	0.01	0.01	0.14

ND = samples with no detectable amount (measured concentration is below MDL), considered to be 0.001 ppb.

Trace = Samples with measured amounts less than the limit of quantitation, but greater than method detection limit, considered to be 0.003 ppb.

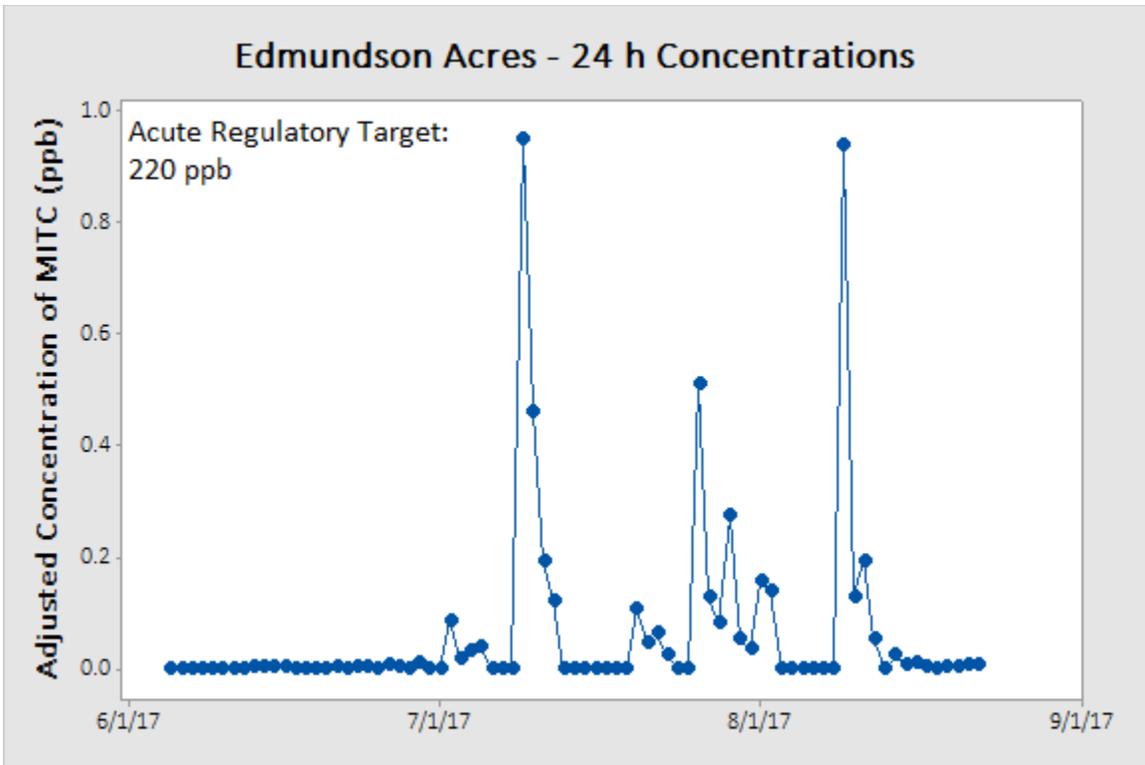


Figure 12. Measured 24 h MITC concentrations for samples collected at Edmundson Acres.

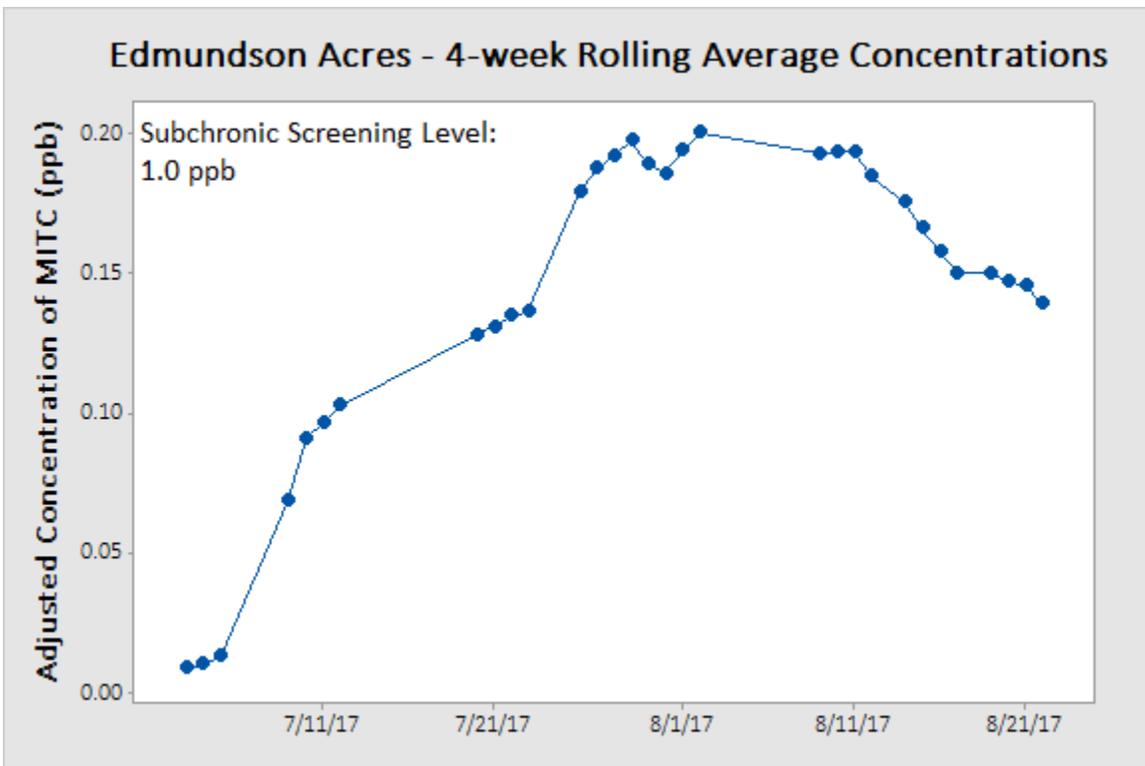


Figure 13. Calculated 4-week rolling average concentrations of MITC at the Edmundson Acres sampling site.

4.6 Quality Assurance | Quality Control

As previously mentioned, the sampling site at Edmundson Acres served as the dedicated QA/QC site for the duration of the study. All breakthrough samples, co-located samples, field blanks, and field spikes were collected at this sampling location. Tables 6 – 9 summarize the results of all QA/QC samples.

None of the breakthrough samples had quantifiable amounts of MITC. A total of three breakthrough sample contained trace levels of MITC (samples: D041, D048, and D091), indicating possible low breakthrough potential of MITC through the sorbent material for these samples (Table 6). Breakthrough sample D041 was collected on July 9, the same day with the highest 24 h concentration for the primary sample at Edmundson Acres.

Table 7 list MITC concentrations determined for both primary and co-located samples collected at Edmundson Acres. The recovery of collocated (duplicated) samples had good agreement, with less than 25% difference.

Table 8 list field blanks results. All eight field blanks were found to have no detectable amounts of MITC (Table 8).

Eight field spikes were collected and the results are summarized in Table 9. Percent recovery of field spikes varied greatly with a wide range of 0 - 150%. Coincidentally, field spikes D040, D069, D072, and D076 were collected on days with significant amounts of MITC measured in ambient air. Overall, for all samples, it appeared that for most of the field spikes, the amount spiked was too low compared to the ambient concentration detected in the collected samples. The low spike amounts and measured ambient concentrations made it difficult to accurately calculate a recovery percentage.

Table 9 also compares the amount of MITC determined for field spikes compared to primary samples. The difference between the field spike and primary samples' amount of MITC was used to determine the percent recovery. Equation 1 details how the recovery from field spikes were calculated.

Table 6. Summary of results from breakthrough QA/QC samples collected at Edmundson Acres.

Location Code	Start Date	End Date	Primary		Breakthrough	
			Sample Number	MITC Conc. (ppb)	Sample Number	MITC Conc. (ppb)
D	6/5/17	6/6/17	D001	ND	D002	ND
D	6/8/17	6/9/17	D006	ND	D007	ND
D	6/14/17	6/15/17	D013	Trace	D012	ND
D	6/16/17	6/17/17	D016	Trace	D015	ND
D	6/21/17	6/22/17	D017	Trace	D018	ND
D	6/22/17	6/23/17	D020	ND	D021	ND
D	6/27/17	6/28/17	D028	Trace	D027	ND
D	6/29/17	6/30/17	D031	0.01	D030	ND
D	7/3/17	7/4/17	D034	0.02	D035	ND
D	7/4/17	7/5/17	D036	0.03	D037	ND
D	7/5/17	7/6/17	D038	0.04	D039	ND
D	7/9/17	7/10/17	D042	0.95	D041	Trace
D	7/11/17	7/12/17	D045	0.19	D044	ND
D	7/20/17	7/21/17	D049	0.11	D048	Trace
D	7/21/17	7/22/17	D053	0.05	D052	ND
D	7/31/17	8/1/17	D067	0.04	D068	ND
D	8/2/17	8/3/17	D073	0.14	D074	ND
D	8/14/17	8/15/17	D083	0.02	D084	ND
D	8/16/17	8/17/17	D087	0.01	D088	ND
D	8/17/17	8/18/17	D090	Trace	D091	Trace
D	8/21/17	8/22/17	D097	0.01	D098	ND
D	8/22/17	8/23/17	D099	0.01	D100	ND

Table 7. Summary of results from co-located QA/QC samples collected at Edmundson Acres.

Duplicate Sample Number	Start Date	End Date	MITC Conc. (ppb)	Primary Sample Number	MITC Conc. (ppb)	Absolute Percent Difference
D010	6/13/17	6/14/17	Trace	D009	Trace	NA
D026	6/26/17	6/27/17	Trace	D025	0.01	N/A*
D046	7/12/17	7/13/17	0.16	D047	0.12	25
D050	7/20/17	7/21/17	0.10	D049	0.11	10
D057	7/23/17	07/24/17	0.03	D056	0.03	1.5 [†]
D079	8/10/17	8/11/17	0.13	D077	0.13	1.3 [†]
D089	8/16/17	8/17/17	0.01	D087	0.01	13 [†]
D095	8/20/17	8/21/17	Trace	D094	Trace	NA

* Due to Trace level concentration in co-located sample, the % change could not be calculated for this sample pair.

[†] Results reported to one-one hundredth of ppb, difference calculated with complete values.

Table 8. Summary of results from field blank QA/QC samples collected at Edmundson Acres.

Sample Number	Location Code	Start Date	End Date	MITC Conc. (ppb)
D008	D	6/8/17	6/8/17	ND
D011	D	6/13/17	6/13/17	ND
D023	D	6/23/17	6/23/17	ND
D033	D	7/2/17	7/2/17	ND
D051	D	7/20/17	07/20/17	ND
D058	D	7/23/17	7/24/17	ND
D071	D	8/1/17	8/1/17	ND
D085	D	8/14/17	8/14/17	ND

Table 9. Summary of results from field spike QA/QC and primary samples collected at Edmundson Acres.

Location Code	Start Date	End Date	Primary Sample		Field Spike Sample			
			Sample Number	MITC Amount (µg)	Sample Number	MITC Amount (µg)	Spiked Amount (µg)	Percent Recovery
D	6/6/17	6/7/17	D005	ND	D004	0.13	0.2	65
D	6/21/17	6/22/17	D017	Trace	D019	Trace	0.15	0
D	7/5/17	7/6/17	D038	0.26	D040	0.47	0.1	NA*
D	7/31/17	8/1/17	D067	0.22	D069	0.34	0.08	150
D	8/1/17	8/2/17	D073	0.99	D072	1.08	0.06	NA*
D	8/9/17	8/10/17	D075	6.23	D076	7.13	0.08	NA*
D	8/17/17	8/18/17	D090	Trace	D092	ND	0.25	0
D	8/20/17	8/21/17	D094	Trace	D096	0.13	0.15	87

* Spike levels were too low compared to ambient air concentrations measured to be able to make a valid recovery calculation. Sample recovery not calculated.

$$\frac{[\text{Measured Amount of MITC from Spike}] - [\text{Measured Amount of MITC from Primary}]}{[\text{Initial Amount of MITC from Spike}]} \times 100\% = \text{Spike Recovery}$$

Equation 1. Calculation of spike recoveries.

4.7 Laboratory QA/QC

As part of CDFA CAC laboratory’s QA/QC protocols, laboratory blanks and spikes are analyzed with each field sample set. In total, the lab prepared ten laboratory spikes and ten laboratory blanks. Tables 10 and 11 list the results of these laboratory samples. The average recovery of all laboratory spikes was 72.5% and all laboratory blanks were determined to have no detectable levels of MITC.

Table 10. Results of laboratory spike analysis.

Analysis Date	Spike Level (µg/sample)	Result (µg/sample)	Percent Recovery
6/5/2017	0.5	0.388	77.6
6/30/2017	0.5	0.374	74.8
7/13/2017	0.5	0.346	69.2
7/18/2017	0.5	0.398	79.6
7/26/2017	0.5	0.338	67.6
8/7/2017	0.5	0.365	73.0
8/16/2017	0.5	0.342	68.4
8/17/2017	0.5	0.370	74.0
8/24/2017	0.5	0.345	69.0
8/30/2017	0.5	0.361	72.2

Table 11. Results of laboratory blank analysis.

Analysis Date	Result (µg/sample)	Reporting Limit (µg/sample)
6/5/2017	ND	0.05
6/30/2017	ND	0.05
7/13/2017	ND	0.05
7/18/2017	ND	0.05
7/26/2017	ND	0.05
8/7/2017	ND	0.05
8/16/2017	ND	0.05
8/17/2017	ND	0.05
8/24/2017	ND	0.05
8/30/2017	ND	0.05

5.0 Discussion

5.1 Recovery of MITC from Sorbent Tubes

Recovery of MITC from laboratory spikes was within tolerance set by CDFA CAC laboratory. However, percent recovery for most of the field MITC spike samples showed that the spike levels were too low compared to ambient air concentrations measured to be able to make a valid recovery calculation (Table 9). For example, on 08/09/2017, 0.08 micrograms of MITC were added to the field fortified spike sample, but the co-located field sample collected during sampling contained 6.23 micrograms, this meant that the spiked amount was only 1.3% of the ambient air concentration collected. For these extremely low spike levels, normal variations in ambient sampling will cause unacceptable spike recoveries. Specifying the appropriate spike amount is problematic since the ambient pesticide concentration is unknown until after the sample is collected and analyzed.

Additionally, at DPR's request, CDFA's CAC laboratory investigated the spike recovery levels and issued a total of three memorandums addressing the MITC recovery issues and modifications to improve future spikes (CDFA, 2018b). CAC laboratory modified their solvent extraction procedure to improve the overall extraction efficiency. Additionally, the CAC laboratory theorized that MITC in ambient air may trap (adsorb) differently to the charcoal matrix than MITC from a standard spiking solution. Thus, the amount of ambient MITC may not be biased low when compared to the recovery of field spike samples.

5.2 Study Summary

DPR collected a total of 242 ambient air samples during the peak application period of MITC in Kern County from June 5th to August 23rd, 2017. Monitoring was conducted at one location in the four communities of: Arvin, Bakersfield, Edmundson Acres, and Rosedale. 24 h samples were collected on a consecutive four-day period every week for 12 weeks. Analysis of the samples determined 24-hour ambient air concentrations of MITC ranging from ND to a maximum concentration of 4.01 ppb at the sampling site in Arvin, located approximately 15 miles to the southeast of Bakersfield. Maximum 24 h concentrations of MITC at the other three sites were: 0.17 ppb at Bakersfield, 0.95 ppb at Edmundson Acres, and 0.11 ppb at Rosedale. Table 12 summarizes the sampling height, peak concentration and date of peak concentration for each site.

Table 12. Summary of study sites.

Site Name	Approx. Sampler Height (meters)	Maximum Measured 24-hr Concentration (ppb)	Date of Maximum Concentration	Maximum Measured Rolling 4-week Average Concentration (ppb)	Date of Maximum Rolling Average Concentration
Arvin	8	4.01	7/10/2017	1.03	7/28/2017
Bakersfield	6	0.17	7/28/2017	0.08	8/10/2017
Rosedale	2	0.11	8/2/2017	0.03	8/10/2017
Edmundson Acres	4	0.95	7/9/2017	0.20	8/2/2017

6.0 References

CDFA (2018a). Determination of MITC in Air by GC-MS, EMON-SM-41.9-MSD. California Department of Food and Agriculture. Sacramento, CA.

https://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/emon-sm-05-041_rev2.pdf

CDFA (2018b). Memoranda Addressing MITC Field Spike Recoveries. California Department of Food and Agriculture. Sacramento CA.

DPR (2001). Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps. California Department of Pesticide Regulation. Sacramento, CA.

<https://www.cdpr.ca.gov/docs/emon/pubs/sops/eqai001.pdf>

DPR (2017). Quality Assurance Project Plan for Monitoring of Seasonal Concentrations of Methyl Isothiocyanate (MITC) in Ambient Air in Communities of High-Use Regions. FY 2016/2017. California Department of Food and Agriculture, Center for Analytical Chemistry. Sacramento, CA

https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study311_final_approved_qapp_with_appendices_06122017.pdf

Appendix

Comments from United States Environmental Protection Agency, Region 9, on the Draft 2017 Seasonal Ambient Air Monitoring of Methyl Isothiocyanate (MITC) in Kern County

Study Design

Number	Comment	Response	Action
1.	The QAPP indicated that the study would include 4 sites in high MITC-use areas in Kern and Santa Barbara Counties, and one background site in an area of lower use. The study includes 4 sites, 3 of which are on the list of high-use sites in Table 4 of the QAPP. One of the sites in the study is Bakersfield, which is not on the ranked list in Table 4. Please clarify how the final sampling sites were selected.	<p>Although it was the intent to include a total of five sampling sites (4 sites + 1 background site) as part of this study, due to site availability and permission issues, we were only able to secure a total of four sampling sites as part of this study (3 sites + 1 background site).</p> <p>Table 4 in the QAPP lists the top 10 communities in the state. The City of Bakersfield ranked 23rd statewide in our analysis (data not shown). Therefore, the Bakersfield sampling site has been designated as our background site in the revised report.</p>	Changes to report were made.
2.	The report identifies Rosedale as the background site, but it is ranked higher than Arvin in Table 4 of the QAPP, and is often discussed in the report as one of the high-use sites. Please clarify.	The sampling site of Bakersfield has been designated as the background site since it ranks lower in use than the other selected communities. Report language has been updated to reflect this change.	Changes to report were made.
3.	Table 5 of the QAPP projects collection of 290 total samples, but the report indicates that 242 were collected. Presumably, some of that is due to having 4 sites instead of 5, but please clarify.	The initial number of 290 samples was assuming a total of 5 sampling locations (48 samples x 5 sites). Since only four locations were included in the monitoring, a total of 242 samples was obtained (48 samples x 4 sites + QC Samples)	No changes to report are needed.
4.	The description of the sampling media height at Arvin is not completely clear. Is the total height 8 meters?	The sampling media height was approximately 8 meters above the ground as it was placed on mast situated above a rooftop of one of Arvin High School's buildings.	No changes to report are needed.
5.	It would be helpful to include a bit more description of each sampling site in terms of location compared to nearby agricultural fields that my use MITC generators.	<p style="text-align: center;">Comment acknowledged by DPR.</p> <p>Greater sampling sites details were included in the report</p>	Changes to report were made.
6.	Sample siting conformed to US EPA ambient air siting requirements (40 CFR Part 58) assuming a regional scale. If micro scale were assumed, the Arvin siting (at 8m) is above the requirements. For future studies, since quantifiable levels of MITC were found, please consider the micro scale evaluation for the high school in Arvin and the elementary school in Edmundson. It is recommended that sampling media in these locations be placed within the breathing zone, not to exceed 2m above ground.	The purpose of the monitoring in this study was to assess representative MITC air concentrations in each community (large spatial area) and not necessarily concentrations in the immediate sampling location (high school, water well, etc.) and as such it would be inappropriate to place the sampler inlet at heights less than 2 m. The Department currently conducts other types of air monitoring studies, some of which do target breathing zone air concentrations of pesticides.	No changes to report are needed.

Appendix

Comments from United States Environmental Protection Agency, Region 9, on the Draft 2017 Seasonal Ambient Air Monitoring of Methyl Isothiocyanate (MITC) in Kern County

QA/QC

Number	Comment	Response	Action
1.	It appears that one of the problems was the level of spike added to each sample. The level for the field spikes ranged from 0.08 – 0.25 ug/sample (compared to 0.5 ug/sample for laboratory spikes). For samples D040, D072, and D076, in particular, the spike levels were too low compared to the sample concentration to be able to make a valid recovery calculation. We recommend not calculating the recovery for those samples and entering “NA” in the percentage recovery column in Table 9. The effect of spike-to-background ratio on expected recovery is illustrated in Table 1 of the ASTM Standard D5788-95.	Comment acknowledged by DPR. Table 9 calculations have been adjusted to reflect USEPA’s recommendations.	Changes to report were made.
2	We cannot reproduce most of the calculations in Table 9. If the sample level was ND or Trace, how was recovery calculated? Please clarify.	The report was updated to include a spike recovery equation on page 32. Equation 1 provides greater details on the determination of the spike recoveries.	Changes to report were made.
3.	Samples D019 and D092 with 0% recovery indicate a problem with preparation and/or handling. We suggest a literature search for information on typical/acceptable field recovery rates for this kind of sampling.	Comment acknowledged by DPR.	No changes to report are needed.
4.	Given the field spike results, it is not appropriate to suggest that actual concentrations in ambient air might have been either higher or lower than measured.	Comment acknowledged by DPR. The report was updated to remove this language.	Changes to report were made.
5.	Blanks were all good. Agreement between co-located samples was good. Acceptable QC results should be highlighted as reasons to accept the field results.	Comment acknowledged by DPR.	No changes to report are needed.
6.	We are glad to see that CDFA is exploring the question of the stability of MITC on the sampling medium at ambient temperatures (i.e., under transport to the site and sampling conditions). We were not understanding whether or not the field spike sampling tubes were stored and transported on dry ice prior to being placed in a sampler; it sounds like not.	As part of DPR’s air sampling procedures, all field spikes are stored in a freezer prior to transport. During transport, spike samples are placed under dry ice until sample set-up. After collection, spike samples are removed from the air sampler and are immediately placed under dry ice during transport back to DPR’s warehouse where they are placed in a freezer prior to sample analysis.	No changes to report are needed.
7.	Please explain why D078 and D082 were not analyzed. The reason given is that, “...the error was not detected until after the 28-day storage stability period had elapsed.” According to Table 6 in the QAPP, samples would have been stable for 60 days. Also, please review Chain of Custody procedures to prevent this kind of error.	Samples D078 and D082 were not analyzed due to an error in labeling during sample check in. The samples were mistakenly labeled as “backup” samples and were not routed for analysis. This error was not discovered until the storage stability period of 28 days had passed and the samples were no longer valid.	No changes to report are needed.

Appendix

Comments from United States Environmental Protection Agency, Region 9, on the Draft 2017 Seasonal Ambient Air Monitoring of Methyl Isothiocyanate (MITC) in Kern County

Presentation of Results

Number	Comment	Response	Action
1.	In the summary section, consider including a table site name, sorbent height above ground, maximum concentration, date max concentration was measured. This would allow easy comparison between sites.	<p style="text-align: center;">Comment acknowledged by DPR.</p> <p>Table 12 was added to the updated report (page 34).</p>	Changes to report were made.
2.	Figures 5, 7, 9 and 11 include data points for days that no samples were collected. Please correct.	<p style="text-align: center;">Comment acknowledged by DPR.</p> <p>All data has been plotted in a time series line plot with time on the x-axis and air concentrations on the y-axis.</p> <p>In the figures included in the report, the lines were added to make it easier for the reader to see the time-series pattern. We included bolded points to highlight and differentiate the actual sample data from the lines that simply connect a data point to the next data point.</p>	No changes to report are needed.
3.	The term "subchronic" is not specific. For this study, it is being defined as a 4-week exposure period, thus the 4-week rolling averages. We suggest that you edit the third paragraph of the Summary to clarify: "Concentrations at Arvin exceeded DPR's subchronic human health screening level of 3,000 ng/m ³ for MITC (based on a 4-week rolling average)	<p style="text-align: center;">Comment acknowledged by DPR.</p> <p>Report was edited as suggested to emphasize the 4-week time period.</p>	Changes to report were made.