



**2017 Seasonal Ambient Monitoring for the Pesticide Active Ingredients  
Methyl Bromide and Chloropicrin in Siskiyou County**

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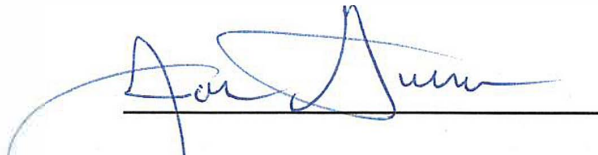
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## Monitoring Report Approval

**Report Title:** 2017 Seasonal Ambient Monitoring for the Pesticide Active Ingredients Methyl Bromide and Chloropicrin in Siskiyou County

**Project Lead:** Pheng Lee, Air Pollution Specialist

**Approval:** The following monitoring report has been reviewed and approved by the Community Air Monitoring Branch.



Joe Guerrero, Manager  
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3-8-19

Date



Kenneth R. Stroud, Chief  
Community Air Monitoring Branch

3-13-19

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## Executive Summary

### 2017 Seasonal Ambient Monitoring for the Pesticide Active Ingredients Methyl Bromide and Chloropicrin in Siskiyou County

At the request of the Department of Pesticide Regulation (DPR), the California Air Resources Board (CARB) conducted an air monitoring study for the pesticide active ingredients methyl bromide and chloropicrin in Siskiyou County from July 9 through September 7, 2017. The monitoring was conducted in communities near historical high-use areas. There were four sampling locations throughout the county. A total of 161 methyl bromide and 171 chloropicrin, including both primary and quality control (QC) samples, were collected by the Community Air Monitoring Branch (CAMB) staff over the nine-week sampling period. The four monitoring sites were set up around Siskiyou County in the cities of Dorris, Tulelake, Weed, and the census-designated place Macdoel. An additional QC site was set up at the Macdoel site due to it being the expected high-use site, based on historical-use data. Methyl bromide samples were collected in Summa canisters using a Tisch Environmental 3-channel canister sampler while the chloropicrin samples were collected on XAD-4 sorbent tubes using a vacuum pump air sampling set up. The sampling flow rate for methyl bromide was between 7 and 8 standard cubic centimeters per minute (SCCM) and 100 SCCM for chloropicrin. Both canister and XAD-4 sorbent tube samples were analyzed by gas chromatography/mass spectrometry (GS/MS) by CARB's Northern Laboratory Branch (NLB) in Sacramento.

#### **Methyl Bromide Results**

Nine out of the 161 total analyzed samples, including QC samples (i.e., collocated and spike), were invalidated due to various sampling issues such as machine malfunction or sample line leak. Two samples (8/2/2017 and 8/7/2017) could not be collected because the sampler malfunctioned and there were no equipment available for replacement. Of the 142 analyzed primary samples, 41 had quantifiable methyl bromide concentrations, which ranged from 0.03 to 4.50 parts per billion (ppb). The three samples with the highest concentrations were from the Macdoel site on 7/25/2017 (1.90 ppb) and 8/30/2017 (4.50 ppb), as well as from the Dorris site on 8/7/17 (2.50 ppb). Blank and trip spike samples were not collected for methyl bromide because the sample media used were evacuated canisters, so contamination during transit or passive contamination out in the field was a non-issue. The QC results for methyl bromide are provided in more detail in the Quality Control Results section on page 16.

#### **Chloropicrin Sorbent Tube Results**

A total of 171 samples, including primaries, field spikes, collocated and blanks were collected of which 19 samples were invalidated. Of the 144 analyzed primary samples, 59 had quantifiable chloropicrin concentrations. The quantifiable chloropicrin concentrations ranged from 0.160 to 44.313 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). The three samples with the highest chloropicrin concentrations were collected at the Macdoel site on 8/21/17 ( $44.313 \mu\text{g}/\text{m}^3$ ) and 8/29/17 ( $22.263 \mu\text{g}/\text{m}^3$ ) as well as at the Dorris site on 8/7/17 ( $12.258 \mu\text{g}/\text{m}^3$ ). The QC results for chloropicrin are provided in more detail in the Quality Control Results section on page 16.

The methyl bromide and chloropicrin results are summarized in the table below.

Site	Compound	Invalid	Non-Detect Count	Trace Level Count	Quantifiable Count	Total
Dorris	Methyl Bromide	1	17	0	18	36
	Chloropicrin	7	7	2	20	36
Macdoel	Methyl Bromide	4	10	0	22	36
	Chloropicrin	6	5	0	25	36
Tulelake	Methyl Bromide	3 (2)*	31	0	0	34
	Chloropicrin	1	19	2	14	36
Weed	Methyl Bromide	1	34	0	1	36
	Chloropicrin	5	31	0	0	36
Total	Methyl Bromide	9	92	0	41	142
	Chloropicrin	19	62	4	59	144

\*Two scheduled run samples, on 8/2/2017 and 8/7/2017, were not collected because equipment malfunctioned.

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Appendix VI: Monitoring Field Log Sheets for Methyl Bromide and Chloropicrin

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Appendix X: 2017 Air Monitoring Network Matrix Spike Results and Matrix Spike Experimental Results (memo. dated October 8, 2018)

## 1.0 Background

At the request of the Department of Pesticide Regulation (DPR) and as part of the proposed monitoring requests included in the 2016 Budget Act, the California Air Resources Board (CARB) conducted air monitoring for the pesticide active ingredients methyl bromide and chloropicrin in Siskiyou County in the summer of 2017. Methyl bromide is a colorless, non-flammable fumigant that is odorless and is used to control fungi, weeds, insects, arachnids, microbes, nematodes, and vertebrates. Similarly, chloropicrin is also an odorless fumigant that is generally used for pre-plant soil preparation. Historically, both pesticides have been used in agriculture activities in California.

DPR's 2016 Use Information and Air Monitoring Recommendation Report (included in Appendix I), showed that Siskiyou County had the highest and fifth highest methyl bromide and chloropicrin usage for years 2012 – 2014 in the State, respectively. The report also showed that for those years, the total reported usage for both pesticides in Siskiyou County was over 4 million pounds. Based on these numbers, DPR requested pesticide sampling in Siskiyou County in 2017.

A total of 161 methyl bromide and 171 chloropicrin samples, including both primary and quality control (QC), were collected by the Community Air Monitoring Branch (CAMB) staff in Siskiyou County from July 9 through September 7, 2017. Throughout the study, monitoring occurred continuously for 24-hour periods, four consecutive days per week with random sampling each week. . The "Sampling Protocol for Methyl Bromide and Chloropicrin Monitoring in Siskiyou County" is included in Appendix II.

## 2.0 Sampling Sites

The locations for air monitoring were guided by DPR's recommendations which specifically stated that sampling sites should be located on school grounds or other public places, near the edge of the recommended communities and downwind of the pesticide high-use areas. While Siskiyou County is large in land area, populous cities were limited to the one major highway corridor (I-5). This made site selection a challenge because most of the agriculture land and activities were north and northeast of I-5, away from the populated areas of the County. For this reason, the monitoring sites for the study were limited to three smaller cities and a census designated place (CDP). The four monitoring sites, which included a collocated and a background site for the study, were as follows:

- Dorris City – Butte Valley Elementary School
- Macdoel CDP – Butte Valley Middle School (collocated site)
- Tulelake City – Tulelake Elementary School
- Weed City – Weed Elementary School (background site)

The geographic latitude and longitude coordinates of the monitoring sites were obtained from Google Earth and are included in Table 1. Also included in Table 1 are the addresses of the schools where the monitoring sites were located. Figure 1 shows an aerial view of the monitoring sites in Siskiyou County with the site locations marked in yellow pins. The samplers were placed either on top of school buildings or on school grounds with a fence enclosure. As an example, Figure 2 shows the collocated



samplers at the Macdoel site. Photographs of the samplers at each monitoring site can be seen in Appendix III.

Table 1: Sampler Locations

City or CDP	School Address	Lat/Long Coordinates (WGS84)	Probe Height from Ground
Dorris City	615 W 3 <sup>rd</sup> St., Dorris, CA 96023	41.9628 / -121.9244	4.2 meter
Macdoel CDP	13001 Old State Hwy, Macdoel, CA 96058	41.8176 / -122.0058	4.5 meter
Tulelake City	461 2 <sup>nd</sup> St., Tulelake, CA 96134	41.9557 / -121.4788	4.5 meter
Weed City	575 White Ave., Weed, CA 96094	41.4267 / -122.3811	1.5 meter

Figure 1: Aerial Overview of Monitored Area



Figure 2: Methyl Bromide and Chloropicrin Samplers at the Macdoel Site



### 3.0 Methods

At each monitoring site, a Tisch TE-323 sampler was used for methyl bromide sampling. Sample flow was controlled by adjusting the flow knob on the sampler. Flow was verified with an Alicat mass flow meter before and after each sample run. The flow rate was set between 7 and 8 sccm to achieve a finalized target pressure canister of 10 psig +/- 5 psig. The goal was to have a constant flow rate throughout the entire 24-hour sampling period. The canister was collected and sent to CARB's laboratory in Sacramento for analysis.

For chloropicrin sampling, the air sampler was a vacuum pump capable of drawing air at least 1 liter per minute. Sample flow was controlled by an in-line rotameter, and flow was verified with an Alicat mass flow meter before and after each run. The flow rate was set to 100 sccm. Intake air was drawn continuously through an XAD-4 sorbent tube during the entire 24-hour sampling period. Samples were collected, stored with dry ice, and sent to CARB's laboratory for analysis.

At the end of each sampling day, the sampled canisters and sorbent tubes were documented in field logs. At the end of each sampling week, the collected samples

were transported back to CARB's MLD Northern Laboratory Branch (NLB) and stored in a freezer or were given to laboratory staff for analysis.

The NLB analyzed all samples from this pesticide study. The collected methyl bromide and chloropicrin samples were analyzed following the "MLD 058 Standard Operating Procedure for the Determination of Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" and "Standard Operating Procedure for the Analysis of Trichloronitromethane (Chloropicrin) in Ambient Air Using Gas Chromatography/Mass Spectrometry," respectively. These SOPs are included in Appendices IV and V.

The detailed field logs and the certification of the mass flow meters are located in Appendices VI and VII.

#### **4.0 Deviations from Protocol**

This study included five deviations from the study protocol.

- The DPR protocol required that at least 10% of the total number of collected samples be QC samples (i.e., collocated, blank and spike), however, an agreement between DPR and CARB allowed for one QC sample per week, and the study was run as such. Nine weekly QC samples were collected at the Macdoel site over the nine-week study.
- The monitoring recommendation for the study was 12 weeks. However, CARB and DPR collectively agreed that the study could be shortened to nine weeks. There were two reasons for this agreement: 1) pesticide-use permits from the Siskiyou County Agriculture Commissioner showed a decrease in applications and, 2) there was a concurrent chloropicrin study in Santa Maria that overlapped this study.
- Typically, sorbent tubes used for sampling should only be opened just prior to utilization and then collected right after sampling stops. This ensures no passive contamination and/or degradation of the sorbent materials in the tubes due to humidity or temperature fluctuations. During the study, the first sample tube of each week was opened and the pump programmed to begin to run between 3 to 5 days later, depending on the sampling schedule for the week; for this reason, the first sample of each week may have been compromised. However, for weeks which had quantifiable concentrations, the data showed that the concentration of the first sample of each week was consistent with samples collected during the rest of the week, suggesting that the first samples of each week experienced minimal impact from this monitoring practice. This sampling issue did not impact methyl bromide data because the media used for sampling was an evacuated canister.
- While the focus of this study was on the pesticide active ingredients methyl bromide and chloropicrin, cis- and trans- 1,3 dichloropropene were also analyzed from the canister samples. Cis- and trans- 1,3 dichloropropene concentrations were below the detection limit at all of the four sites in this study. These data are included in Appendix VIII.
- The inlet probe height at the Weed site is 1.5 meters above the ground. Typically, the inlet probe height should be at a minimum of 2 meters above the ground. Due to rooftop access and power restrictions at the Weed Elementary School, this site was set

on the ground in a parking lot near the school at a power pole owned and operated by the Siskiyou County Air Pollution Control District.

## 5.0 Results

Many of the collected methyl bromide samples had concentrations below the method detection limit (<0.03 ppb). Of the 142 analyzed primary samples, 41 samples had quantifiable methyl bromide concentrations, which ranged from 0.03 ppb to 4.50 ppb. The three samples with the highest concentrations were from the Macdoel site on 7/25/2017 (1.90 ppb) and 8/30/2017 (4.50 ppb) as well as from the Dorris site on 8/7/17 (2.50 ppb).

Similarly, most of the collected chloropicrin samples also had concentrations below the method detection limit (<0.004 ug/sample). Of the 144 analyzed primary samples, 59 had quantifiable chloropicrin concentrations. The quantifiable chloropicrin concentrations ranged from 0.157 µg/m<sup>3</sup> to 44.313 µg/m<sup>3</sup>. The three samples with the highest chloropicrin concentrations were collected at the Macdoel site on 8/21/17 (44.313 µg/m<sup>3</sup>) and 8/29/17 (22.263 µg/m<sup>3</sup>) as well as at the Dorris site on 8/7/17 (12.258 µg/m<sup>3</sup>).

Table 2 summarizes the individual site results of the study. The summary results of each site are included in Tables 3 through 10. The full analytical laboratory reports are included in Appendices VIII and IX.

Table 2: Sampling Results Summary

Site	Compound	Invalid	Non-Detect Count	Trace Level Count	Quantifiable Count	Total
Dorris	Methyl Bromide	1	17	0	18	36
	Chloropicrin	7	7	2	20	36
Macdoel	Methyl Bromide	4	10	0	22	36
	Chloropicrin	6	5	0	25	36
Tulelake	Methyl Bromide	3 (2)*	31	0	0	34
	Chloropicrin	1	19	2	14	36
Weed	Methyl Bromide	1	34	0	1	36
	Chloropicrin	5	31	0	0	36
Total	Methyl Bromide	9	92	0	41	142
	Chloropicrin	19	62	4	59	144

\*Two scheduled run samples, on 8/2/2017 and 8/7/2017, were not collected because the equipment malfunctioned.

## 5.1 Invalidations

Methyl bromide samples were invalidated for one of four reasons:

1. The Tisch sampler malfunctioned.
2. There was a leak in the sample line.
3. The end pressure of the canister was below 6 psig.
4. There was a collection error.

There were 11 invalidated methyl bromide samples during the study.

Dorris

- 7/19/2017

Macdoel

- 7/10/2017, 7/16/2017 (collocate), 8/13/2017, 8/20/2017, 8/27/2017 and 9/5/2017 (spike)

Tulelake

- 7/16/2017, 8/6/2017 and 8/29/2017

Weed

- 8/21/2017

Chloropicrin samples were invalidated primarily due to end flow failing flow criteria of 100 sccm +/- 20%.

There were 19 invalidated chloropicrin samples during the study.

Dorris

- 8/13/2017, 8/14/2017, 8/19/2017, 8/27/2017, 9/4/2017, 9/6/2017 and 9/7/2017

Macdoel

- 7/17/2017, 7/18/2017, 7/19/2017, 8/8/2017, 9/5/2017 and 9/6/2017

Tulelake

- 8/19/2017

Weed

- 8/8/2017, 8/14/2017, 8/19/2017, 9/4/2017 and 9/5/2017

Table 3: Dorris Methyl Bromide Results

Sample ID	Sample Name	Sample Date	Sample Time (min.)	Start Flow (sccm)	End Flow (sccm)	Avg. Flow (sccm)	Canister Vol. (psig)	Methyl Bromide (ppb)*
200508851	DR-1	7/9/2017	1456	7.61	8.09	7.85	15	ND
200508861	DR-2	7/10/2017	1427	8.09	7.72	7.91	15	ND
200508837	DR-3	7/11/2017	1414	7.72	7.8	7.76	13	ND
200508815	DR-4	7/12/2017	1420	7.80	7.83	7.82	13	ND
200509233	DR-5	7/16/2017	1430	7.83	7.85	7.84	15	ND
200509262	DR-6	7/17/2017	1430	7.85	7.75	7.80	15	ND
200509287	DR-7	7/18/2017	1426	7.75	7.52	7.64	15	ND
200509299	DR-8	7/19/2017	1440	7.52	7.82	7.67	3	Invalidated**
200509867	DR-9	7/24/2017	1415	7.82	7.71	7.77	15	0.05
200509888	DR-10	7/25/2017	1429	7.71	7.92	7.82	15	0.18
200509971	DR-11	7/26/2017	1428	7.92	8.12	8.02	13	ND
200509975	DR-12	7/27/2017	1415	8.12	8.27	8.20	13	ND
200510494	DR-13	7/31/2017	1420	8.27	7.72	8.00	12	ND
200510538	DR-14	8/1/2017	1440	7.72	7.85	7.79	11	0.43
200510542	DR-15	8/2/2017	1400	7.85	7.9	7.88	13	1.40
200510545	DR-16	8/3/2017	1417	7.90	7.88	7.89	15	1.20
200510587	DR-17	8/6/2017	1422	7.88	8.31	8.10	14	0.30
200510685	DR-18	8/7/2017	1410	8.31	8.29	8.30	14	2.50
200510904	DR-19	8/8/2017	1414	8.29	8.32	8.31	15	0.21
200510908	DR-20	8/9/2017	1423	8.32	8.41	8.37	14	0.07
200511251	DR-21	8/12/2017	1427	8.41	8.44	8.43	15	ND
200511299	DR-22	8/13/2017	1430	8.44	8.35	8.40	15	ND
200511315	DR-23	8/14/2017	1415	8.35	8.15	8.25	15	0.10
200511330	DR-24	8/15/2017	1413	8.15	8.10	8.13	15	0.22
200511530	DR-25	8/19/2017	1405	8.10	8.16	8.13	12	0.11
200511803	DR-26	8/20/2017	1456	8.16	7.83	8.00	14	ND
200511828	DR-27	8/21/2017	1426	7.79	7.5	7.65	11	0.11
200511850	DR-28	8/22/2017	1430	7.50	7.71	7.61	14	ND
200512537	DR-29	8/27/2017	1427	7.71	7.88	7.80	15	0.04
200512542	DR-30	8/28/2017	1413	7.88	8.25	8.07	14	0.07
200512547	DR-31	8/29/2017	1408	7.82	7.88	7.85	13	0.07
200512551	DR-32	8/30/2017	1400	7.88	8.01	7.95	13	0.06
200513050	DR-33	9/4/2017	1435	7.98	7.88	7.93	14	0.06
200513055	DR-34	9/5/2017	1426	7.88	7.72	7.80	13	ND
200513060	DR-35	9/6/2017	1430	7.72	7.92	7.82	12	ND
200513064	DR-36	9/7/2017	1390	7.92	8.15	8.04	13	ND

Note: While the target finalized canister pressure was 10 psig +/- 5 psig, a final canister pressure of 5 psig or greater is considered valid.

\*ND (non-detect) < 0.03 ppb.

\*\*One (1) sample was invalidated because there was a collection error. Eighteen (18) samples had quantifiable methyl bromide concentrations. Seventeen (17) samples were non-detectable.

Table 4: Dorris Chloropicrin Results

Barcode	Sample Name	Start Date	Sampling Time (hour)	Start Flow (sccm)	End Flow (sccm)	Avg Flow (sccm)	volume (m3)	Chloropicrin (ug/sample)*	Chloropicrin (ug/m3)		
DPR00723	DR-1	7/9/2017	24.3	99.6	97.2	98.4	0.143	ND	ND		
DPR00729	DR-2	7/10/2017	23.9	99.7	101	100.4	0.144	ND	ND		
DPR00735	DR-3	7/11/2017	23.6	101.7	101.9	101.8	0.144	ND	ND		
DPR00741	DR-4	7/12/2017	23.9	100.9	100.5	100.7	0.144	ND	ND		
DPR00747	DR-5	7/16/2017	23.8	99.7	97.2	98.5	0.141	ND	ND		
DPR00753	DR-6	7/17/2017	23.8	100.8	101.2	101.0	0.144	ND	ND		
DPR00759	DR-7	7/18/2017	23.8	100.1	102	101.1	0.144	ND	ND		
DPR00765	DR-8	7/19/2017	23.8	100.1	96.2	98.2	0.140	0.047	0.333		
DPR00771	DR-9	7/24/2017	23.5	100.5	100.8	100.7	0.142	0.031	0.218		
DPR00777	DR-10	7/25/2017	23.9	100.1	100.7	100.4	0.144	0.162	1.124		
DPR00783	DR-11	7/26/2017	23.8	100.3	99.8	100.1	0.143	Trace	Trace		
DPR00789	DR-12	7/27/2017	23.6	100.2	99.1	99.7	0.141	Trace	Trace		
DPR00795	DR-13	7/31/2017	23.8	100.9	89	95.0	0.136	0.025	0.182		
DPR00801	DR-14	8/1/2017	23.7	97.5	86.3	91.9	0.131	0.332	2.542		
DPR00807	DR-15	8/2/2017	23.8	98.6	90.3	94.5	0.135	1.170	8.675		
DPR00813	DR-16	8/3/2017	23.8	101	83.6	92.3	0.132	0.988	7.495		
DPR00819	DR-17	8/6/2017	23.5	99.7	92.1	95.9	0.135	0.279	2.063		
DPR00825	DR-18	8/7/2017	23.7	101	99.8	100.4	0.143	1.750	12.258		
DPR00831	DR-19	8/8/2017	23.6	100.9	95.9	98.4	0.139	0.610	4.379		
DPR00837	DR-20	8/9/2017	23.7	100.5	90.4	95.5	0.136	0.471	3.468		
DPR00843	DR-21	8/12/2017	23.8	101.4	80.8	91.1	0.130	0.142	1.095		
DPR00848	DR-22	8/13/2017	Invalidated**								
DPR00853	DR-23	8/14/2017	Invalidated**								
DPR00858	DR-24	8/15/2017	23.7	104.2	92.8	98.5	0.140	1.110	7.921		
DPR00863	DR-25	8/19/2017	Invalidated**								
DPR00868	DR-26	8/20/2017	24.3	101.5	89.5	95.5	0.139	0.044	0.315		
DPR00873	DR-27	8/21/2017	23.6	101.9	90.7	96.3	0.136	0.609	4.466		
DPR00878	DR-28	8/22/2017	23.1	101.5	90.7	96.1	0.133	0.060	0.447		
DPR00883	DR-29	8/27/2017	Invalidated**								
DPR00888	DR-30	8/28/2017	23.7	102.8	80.1	91.5	0.130	0.295	2.267		
DPR00893	DR-31	8/29/2017	23.3	101.7	84.5	93.1	0.130	0.205	1.578		
DPR00898	DR-32	8/30/2017	23.2	102.5	83.3	92.9	0.129	0.283	2.189		
DPR00903	DR-33	9/4/2017	Invalidated**								
DPR00908	DR-34	9/5/2017	23.2	105	94.5	99.8	0.139	0.113	0.814		
DPR00913	DR-35	9/6/2017	Invalidated**								
DPR00918	DR-36	9/7/2017	Invalidated**								

\*ND (non-detect) < 0.004 ug/sample; Trace < 0.021 ug/sample.

\*\*Seven (7) samples were invalidated because the end flows did not meet flow criteria of 100 sccm +/-20%. Twenty (20) samples had quantifiable chloropicrin concentrations. Seven (7) samples were non-detectable, and two (2) samples had trace amounts.

Table 5: Macdoel Methyl Bromide Results

Sample ID	Sample Name	Sample Date	Sample Time (min.)	Start Flow (sccm)	End Flow (sccm)	Avg. Flow (sccm)	Canister Vol. (psig)	Methyl Bromide (ppb)*
200508850	MD-1	7/9/2017	1439	7.94	8.12	8.03	11	ND
200508859	MD-2	7/10/2017	1424	8.12	7.51	7.82	0	Invalidated**
200508835	MD-3	7/11/2017	1419	7.51	7.66	7.59	14	ND
200508814	MD-4	7/12/2017	1420	7.66	7.81	7.74	15	ND
200509228	MD-5	7/16/2017	1442	7.81	7.89	7.85	15	ND
200509258	MD-6	7/17/2017	1430	7.91	8.05	7.98	15	ND
200509285	MD-7	7/18/2017	1430	8.05	8.02	8.04	14	0.04
200509290	MD-8	7/19/2017	1420	8.02	8.05	8.04	14	ND
200509865	MD-9	7/24/2017	1419	8.05	7.62	7.84	16	1.50
200509886	MD-10	7/25/2017	1427	7.62	8.21	7.92	12	1.90
200509970	MD-11	7/26/2017	1428	8.21	7.60	7.91	13	1.10
200509974	MD-12	7/27/2017	1420	7.60	7.89	7.75	15	1.10
200510492	MD-13	7/31/2017	1421	7.89	7.85	7.87	14	0.58
200510536	MD-14	8/1/2017	1410	7.85	8.12	7.99	15	0.13
200510541	MD-15	8/2/2017	1409	8.12	7.6	7.86	15	0.15
200510544	MD-16	8/3/2017	1408	7.60	7.70	7.65	14	0.08
200510584	MD-17	8/6/2017	1426	7.70	8.10	7.90	14	0.08
200510683	MD-18	8/7/2017	1416	8.10	8.08	8.09	12	0.09
200510903	MD-19	8/8/2017	1415	8.08	8.15	8.12	13	ND
200510907	MD-20	8/9/2017	1431	8.15	8.12	8.14	13	ND
200511249	MD-21	8/12/2017	1430	8.12	7.75	7.94	14	0.04
200511286	MD-22	8/13/2017	1440	7.75	0.00	3.88	-6	Invalidated**
200511313	MD-23	8/14/2017	1430	7.85	7.80	7.83	12	ND
200511329	MD-24	8/15/2017	1410	7.80	7.98	7.89	14	ND
200511529	MD-25	8/19/2017	1416	7.98	8.37	8.18	12	0.08
200511801	MD-26	8/20/2017	82	7.90	0.00	3.95	-24	Invalidated**
200511826	MD-27	8/21/2017	1422	7.90	7.91	7.91	15	1.30
200511849	MD-28	8/22/2017	1420	7.91	8.10	8.01	14	0.39
200512536	MD-29	8/27/2017	1439	8.17	4.10	6.14	1	Invalidated**
200512540	MD-30	8/28/2017	1412	7.50	7.80	7.65	15	0.03
200512545	MD-31	8/29/2017	1410	7.50	7.49	7.50	15	0.23
200512550	MD-32	8/30/2017	1404	7.92	8.17	8.05	13	4.50
200513049	MD-33	9/4/2017	1429	8.23	7.72	7.98	14	0.08
200513053	MD-34	9/5/2017	1430	7.72	8.20	7.96	12	0.03
200513058	MD-35	9/6/2017	1409	8.20	8.10	8.15	14	0.17
200513063	MD-36	9/7/2017	1407	8.10	8.28	8.19	13	0.91

Note: While the target finalized canister pressure was 10 psig +/- 5 psig, a final canister pressure of 5 psig or greater is considered valid.

\*ND (non-detect) < 0.03 ppb.

\*\*Four (4) samples were invalidated because the sampler malfunctioned. Twenty-two (22) samples had quantifiable methyl bromide concentrations. Ten (10) samples were non-detectable.



Table 6: Macdoel Chloropicrin Results

Barcode	Sample Name	Start Date	Sampling Time (hour)	Start Flow (sccm)	End Flow (sccm)	Avg Flow (sccm)	volume (m3)	Chloropicrin (ug/sample)*	Chloropicrin (ug/m3)
DPR00721	MD-1	7/9/2017	23.9	99.2	107.4	103.3	0.148	ND	ND
DPR00727	MD-2	7/10/2017	23.9	99.4	114.1	106.8	0.153	ND	ND
DPR00733	MD-3	7/11/2017	23.7	100.3	94.6	97.5	0.139	ND	ND
DPR00739	MD-4	7/12/2017	24	100.8	105	102.9	0.148	ND	ND
DPR00745	MD-5	7/16/2017	23.8	100	101.1	100.6	0.144	ND	ND
DPR00751	MD-6	7/17/2017	Invalidated**						
DPR00757	MD-7	7/18/2017	Invalidated**						
DPR00763	MD-8	7/19/2017	Invalidated**						
DPR00769	MD-9	7/24/2017	23.2	100.7	97.1	98.9	0.138	0.384	2.793
DPR00775	MD-10	7/25/2017	23.9	99.9	99.1	99.5	0.143	0.300	2.105
DPR00781	MD-11	7/26/2017	23.9	99.2	99.9	99.6	0.143	0.100	0.699
DPR00787	MD-12	7/27/2017	23.7	100.6	99.7	100.2	0.142	0.230	1.617
DPR00793	MD-13	7/31/2017	23.8	100.2	105.1	102.7	0.147	0.309	2.107
DPR00799	MD-14	8/1/2017	23.9	100.5	98.4	99.5	0.143	0.077	0.539
DPR00805	MD-15	8/2/2017	23.8	100.3	96.2	98.3	0.140	0.084	0.600
DPR00811	MD-16	8/3/2017	23.8	101.3	101.7	101.5	0.145	0.040	0.275
DPR00817	MD-17	8/6/2017	23.7	99	103.9	101.5	0.144	0.035	0.244
DPR00823	MD-18	8/7/2017	23.6	100.5	100.6	100.6	0.142	0.065	0.460
DPR00829	MD-19	8/8/2017	Invalidated**						
DPR00835	MD-20	8/9/2017	24.1	99.9	98.6	99.3	0.144	0.026	0.179
DPR00841	MD-21	8/12/2017	23.7	100.8	107.5	104.2	0.148	0.307	2.075
DPR00846	MD-22	8/13/2017	23.8	101.1	107.8	104.5	0.149	0.056	0.373
DPR00851	MD-23	8/14/2017	23.8	100.3	99.9	100.1	0.143	0.024	0.171
DPR00856	MD-24	8/15/2017	23.8	100.4	101.6	101.0	0.144	0.036	0.246
DPR00861	MD-25	8/19/2017	23.5	103.1	100.1	101.6	0.143	0.182	1.268
DPR00866	MD-26	8/20/2017	24.4	100.9	110.5	105.7	0.155	0.311	2.010
DPR00871	MD-27	8/21/2017	23.5	101.4	94.5	98.0	0.138	6.120	44.313
DPR00876	MD-28	8/22/2017	23.1	102	95.2	98.6	0.137	1.380	10.098
DPR00881	MD-29	8/27/2017	23.9	101.8	89.7	95.8	0.137	0.122	0.891
DPR00886	MD-30	8/28/2017	23.4	101.9	81.9	91.9	0.129	0.081	0.631
DPR00891	MD-31	8/29/2017	23.5	100	90.5	95.3	0.134	2.990	22.263
DPR00896	MD-32	8/30/2017	23.3	99.8	83.5	91.7	0.128	0.148	1.153
DPR00901	MD-33	9/4/2017	23.9	102	114.2	108.1	0.155	0.119	0.770
DPR00906	MD-34	9/5/2017	Invalidated**						
DPR00911	MD-35	9/6/2017	Invalidated**						
DPR00916	MD-36	9/7/2017	23.7	108.7	113.1	110.9	0.158	1.260	7.990

\*ND (non-detect) < 0.004 ug/sample.

\*\*Six (6) samples were invalidated because the end flows did not meet flow criteria of 100 sccm +/-20%. Twenty-five (25) samples had quantifiable chloropicrin concentrations. Five (5) samples were non-detectable.

Table 7: Tulelake Methyl Bromide Results

Sample ID	Sample Name	Sample Date	Sample Time (min.)	Start Flow (sccm)	End Flow (sccm)	Avg. Flow (sccm)	Canister Vol. (psig)	Methyl Bromide (ppb)*
200508852	TL-1	7/9/2017	1457	7.69	24	15.85	26	ND
200508862	TL-2	7/10/2017	1420	7.22	7.15	7.19	12	ND
200508839	TL-3	7/11/2017	1417	7.15	8.02	7.59	12	ND
200508812	TL-4	7/12/2017	1421	8.02	7.99	8.01	15	ND
200509235	TL-5	7/16/2017	67	7.99	0.00	4.00	-20	Invalidated**
200509264	TL-6	7/17/2017	1430	7.86	7.85	7.86	13	ND
200509288	TL-7	7/18/2017	1430	7.85	7.81	7.83	14	ND
200509301	TL-8	7/19/2017	1431	7.81	7.80	7.81	14	ND
200509870	TL-9	7/24/2017	1515	7.8	7.95	7.88	21	ND
200509889	TL-10	7/25/2017	1426	7.95	7.84	7.90	12	ND
200509972	TL-11	7/26/2017	1426	7.84	7.93	7.89	11	ND
200509976	TL-12	7/27/2017	1416	7.93	7.86	7.90	14	ND
200510495	TL-13	7/31/2017	1493	7.86	8.16	8.01	15	ND
200510539	TL-14	8/1/2017	1416	8.16	0.00	4.08	17	ND
XXXX	TL-15	8/2/2017	0	0.00	0.00	0.00	n/a	Did not sample***
200510546	TL-16	8/3/2017	1402	7.95	7.90	7.93	15	ND
200510588	TL-17	8/6/2017	162	7.90	0.00	3.95	-10	Invalidated**
XXXX	TL-18	8/7/2017	0	0.00	0.00	0.00	n/a	Did not sample***
200510905	TL-19	8/8/2017	1411	8.24	8.14	8.19	14	ND
200510909	TL-20	8/9/2017	1436	8.14	8.05	8.10	15	ND
200511252	TL-21	8/12/2017	1426	8.05	8.08	8.07	16	ND
200511301	TL-22	8/13/2017	1433	8.08	8.08	8.08	15	ND
200511316	TL-23	8/14/2017	1430	8.08	8.15	8.12	12	ND
200511332	TL-24	8/15/2017	1410	8.15	8.17	8.16	15	ND
200511531	TL-25	8/19/2017	1413	8.17	8.19	8.18	16	ND
200511804	TL-26	8/20/2017	1484	8.19	8.47	8.33	18	ND
200511830	TL-27	8/21/2017	1412	8.47	8.6	8.54	17	ND
200511851	TL-28	8/22/2017	1439	8.50	8.46	8.48	15	ND
200512538	TL-29	8/27/2017	1420	8.46	8.42	8.44	20	ND
200512543	TL-30	8/28/2017	1424	8.42	8.53	8.48	18	ND
200512548	TL-31	8/29/2017	1409	8.53	8.41	8.47	1	Invalidated**
200512552	TL-32	8/30/2017	1402	8.39	8.59	8.49	16	ND
200513051	TL-33	9/4/2017	1432	8.51	8.45	8.48	18	ND
200513056	TL-34	9/5/2017	1428	8.45	8.10	8.28	15	ND
200513061	TL-35	9/6/2017	1430	8.10	7.75	7.93	12	ND
200513065	TL-36	9/7/2017	1380	7.75	7.65	7.70	12	ND

Note: While the target finalized canister pressure was 10 psig +/- 5 psig, a final canister pressure of 5 psig or greater is considered valid.

\*ND (non-detect) < 0.03 ppb.

\*\*Three (3) samples were invalidated because the sampler malfunctioned. Thirty-one (31) samples were non-detectable.

\*\*\*Two samples (8/2/17 and 8/7/17) could not be collected because the sampler malfunctioned and there was no spare equipment available to collect the samples.

Table 8: Tulelake Chloropicrin Results

Barcode	Sample Name	Start Date	Sampling Time (hour)	Start Flow (sccm)	End Flow (sccm)	Avg Flow (sccm)	volume (m3)	Chloropicrin (ug/sample)*	Chloropicrin (ug/m3)		
DPR00724	TL-1	7/9/2017	24.3	99.3	101.1	100.2	0.146	ND	ND		
DPR00730	TL-2	7/10/2017	23.9	99.6	98.5	99.1	0.142	ND	ND		
DPR00736	TL-3	7/11/2017	23.6	101	104.7	102.9	0.146	ND	ND		
DPR00742	TL-4	7/12/2017	23.9	99.9	102.3	101.1	0.145	ND	ND		
DPR00748	TL-5	7/16/2017	23.8	99.5	101.8	100.7	0.144	ND	ND		
DPR00754	TL-6	7/17/2017	23.8	100.4	97.2	98.8	0.141	ND	ND		
DPR00760	TL-7	7/18/2017	23.9	99.7	101.2	100.5	0.144	ND	ND		
DPR00766	TL-8	7/19/2017	23.9	99.8	105.1	102.5	0.147	ND	ND		
DPR00772	TL-9	7/20/2017	23.5	99.8	100.3	100.1	0.141	ND	ND		
DPR00778	TL-10	7/25/2017	23.8	100.5	98.7	99.6	0.142	ND	ND		
DPR00784	TL-11	7/26/2017	23.8	99.8	100.9	100.4	0.143	ND	ND		
DPR00790	TL-12	7/27/2017	23.7	100.3	99.2	99.8	0.142	ND	ND		
DPR00796	TL-13	7/31/2017	23.8	100.3	96.1	98.2	0.140	ND	ND		
DPR00802	TL-14	8/1/2017	23.8	100.5	97.6	99.1	0.141	ND	ND		
DPR00808	TL-15	8/2/2017	23.8	99.7	89.5	94.6	0.135	ND	ND		
DPR00814	TL-16	8/3/2017	23.8	100.2	118.5	109.4	0.156	ND	ND		
DPR00820	TL-17	8/6/2017	23.7	98.4	110.2	104.3	0.148	ND	ND		
DPR00826	TL-18	8/7/2017	23.5	100.4	99.1	99.8	0.141	ND	ND		
DPR00832	TL-19	8/8/2017	23.4	100.8	102.6	101.7	0.143	ND	ND		
DPR00838	TL-20	8/9/2017	24	99.7	99.2	99.5	0.143	0.142	0.993		
DPR00844	TL-21	8/12/2017	23.7	100.2	101.4	100.8	0.143	0.107	0.746		
DPR00849	TL-22	8/13/2017	23.9	99.9	87.3	93.6	0.134	0.021	0.157		
DPR00854	TL-23	8/14/2017	23.8	99.3	91.8	95.6	0.136	0.096	0.706		
DPR00859	TL-24	8/15/2017	24.7	102.1	84.1	93.1	0.138	0.087	0.629		
DPR00864	TL-25	8/19/2017	Invalidated**								
DPR00869	TL-26	8/20/2017	24.8	100.4	85.7	93.1	0.138	0.036	0.258		
DPR00874	TL-27	8/21/2017	23.8	99.1	95.7	97.4	0.139	0.185	1.328		
DPR00879	TL-28	8/22/2017	24.1	99.2	97.1	98.2	0.142	Trace	Trace		
DPR00884	TL-29	8/27/2017	23.7	101.9	98.9	100.4	0.143	0.367	2.569		
DPR00889	TL-30	8/28/2017	23.9	101.2	101.7	101.5	0.145	0.183	1.261		
DPR00894	TL-31	8/29/2017	23.5	100.9	88.5	94.7	0.134	0.085	0.634		
DPR00899	TL-32	8/30/2017	23.2	101.9	87.7	94.8	0.132	0.574	4.349		
DPR00904	TL-33	9/4/2017	24	102.1	85.8	94.0	0.135	0.050	0.369		
DPR00909	TL-34	9/5/2017	23.9	99.8	95	97.4	0.140	Trace	Trace		
DPR00914	TL-35	9/6/2017	23.7	104.8	90.2	97.5	0.139	0.045	0.322		
DPR00919	TL-36	9/7/2017	23.4	103.1	87.3	95.2	0.134	0.058	0.431		

\*ND (non-detect) < 0.004 ug/sample; Trace < 0.021 ug/sample.

\*\*One (1) sample was invalidated due to an end flow issue. Fourteen (14) samples had quantifiable chloropicrin concentrations. Two (2) samples had trace amounts. Nineteen (19) samples were non-detectable.

Table 9: Weed Methyl Bromide Results

Sample ID	Sample Name	Sample Date	Sample Time (min.)	Start Flow (sccm)	End Flow (sccm)	Avg. Flow (sccm)	Canister Vol. (psig)	Methyl Bromide (ppb)*
200508849	WD-1	7/9/2017	1437	7.95	7.90	7.93	14	ND
200508858	WD-2	7/10/2017	1430	7.91	7.63	7.77	13	ND
200508833	WD-3	7/11/2017	1421	7.63	7.56	7.60	14	ND
200508813	WD-4	7/12/2017	1423	7.51	7.81	7.66	13	ND
200509227	WD-5	7/16/2017	1433	7.81	7.92	7.87	14	ND
200509256	WD-6	7/17/2017	1430	7.92	8.05	7.99	15	ND
200509284	WD-7	7/18/2017	1430	8.05	8.10	8.08	13	ND
200509289	WD-8	7/19/2017	1422	8.10	7.97	8.04	12	ND
200509864	WD-9	7/24/2017	1421	7.97	8.04	8.01	11	ND
200509885	WD-10	7/25/2017	1436	8.04	8.66	8.35	15	ND
200509969	WD-11	7/26/2017	1434	8.66	8.79	8.73	16	ND
200509973	WD-12	7/27/2017	1418	8.79	8.56	8.68	14	ND
200510491	WD-13	7/31/2017	1410	8.56	7.98	8.27	16	ND
200510535	WD-14	8/1/2017	1445	7.98	7.92	7.95	7	ND
200510540	WD-15	8/2/2017	1420	7.92	7.96	7.94	13	ND
200510543	WD-16	8/3/2017	1410	7.96	7.75	7.86	13	ND
200510582	WD-17	8/6/2017	1415	7.75	7.88	7.82	11	ND
200510682	WD-18	8/7/2017	1416	7.88	7.86	7.87	12	ND
200510902	WD-19	8/8/2017	1429	7.86	7.86	7.86	11	ND
200510906	WD-20	8/9/2017	1416	7.86	7.91	7.89	12	ND
200511248	WD-21	8/12/2017	1427	7.91	7.84	7.88	12	ND
200511284	WD-22	8/13/2017	1430	7.84	7.85	7.85	13	ND
200511311	WD-23	8/14/2017	1430	7.85	8.01	7.93	10	ND
200511327	WD-24	8/15/2017	1420	8.01	8.01	8.01	13	ND
200511528	WD-25	8/19/2017	1411	8.01	8.02	8.02	11	ND
200511800	WD-26	8/20/2017	1442	8.02	7.50	7.76	13	ND
200511825	WD-27	8/21/2017	1369	7.50	7.35	7.43	-2	Invalidated**
200511848	WD-28	8/22/2017	1410	7.35	7.05	7.20	14	ND
200512535	WD-29	8/27/2017	1436	7.66	6.85	7.26	11	ND
200512539	WD-30	8/28/2017	1404	6.84	6.90	6.87	9	ND
200512544	WD-31	8/29/2017	1412	6.90	7.09	7.00	8	ND
200512549	WD-32	8/30/2017	1410	7.09	7.25	7.17	10	0.04
200513048	WD-33	9/4/2017	1430	7.28	7.62	7.45	11	ND
200513052	WD-34	9/5/2017	1430	7.62	7.75	7.69	12	ND
200513057	WD-35	9/6/2017	1430	7.75	7.65	7.70	12	ND
200513062	WD-36	9/7/2017	1430	7.65	7.75	7.70	12	ND

Note: While the target finalized canister pressure was 10 psig +/- 5 psig, a final canister pressure of 5 psig or greater is considered valid.

\*ND (non-detect) < 0.03 ppb.

\*\*One (1) sample was invalidated because the sampler malfunctioned. One (1) sample had quantifiable concentration. Thirty-four (34) samples were non-detectable.

Table 10: Weed Chloropicrin Results

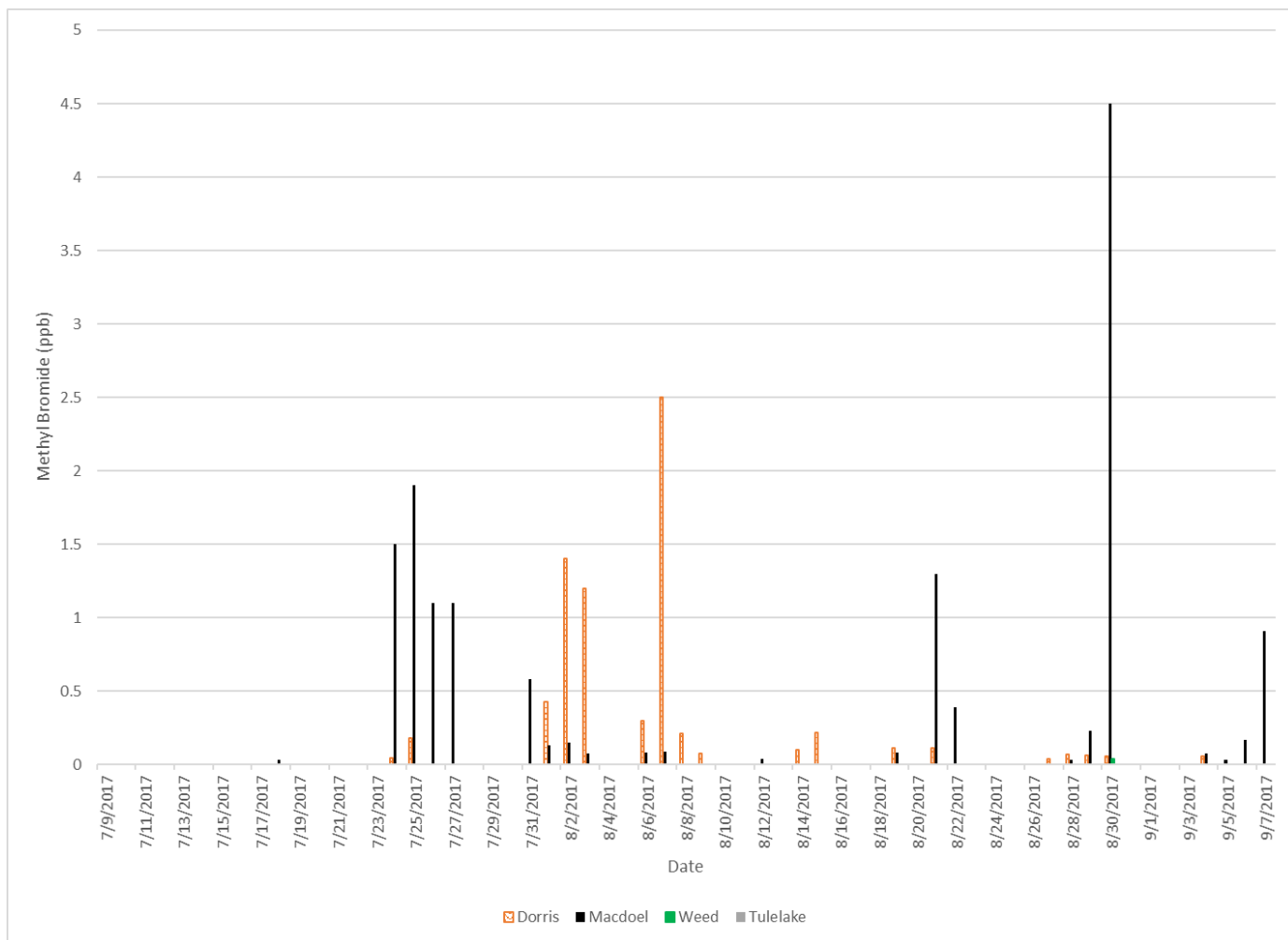
Barcode	Sample Name	Start Date	Sampling Time (hour)	Start Flow (sccm)	End Flow (sccm)	Avg Flow (sccm)	volume (m3)	Chloropicrin (ug/sample)*	Chloropicrin (ug/m3)
DPR00720	WD-1	7/9/2017	23.9	101.1	103	102.1	0.146	ND	ND
DPR00726	WD-2	7/10/2017	23.9	100.1	102.3	101.2	0.145	ND	ND
DPR00732	WD-3	7/11/2017	23.8	101.3	102.9	102.1	0.146	ND	ND
DPR00738	WD-4	7/12/2017	23.9	100.3	103.1	101.7	0.146	ND	ND
DPR00744	WD-5	7/16/2017	23.8	101.1	106.2	103.7	0.148	ND	ND
DPR00750	WD-6	7/17/2017	23.9	101.2	102.6	101.9	0.146	ND	ND
DPR00756	WD-7	7/18/2017	23.8	101.3	104.1	102.7	0.147	ND	ND
DPR00762	WD-8	7/19/2017	23.8	98.9	102.8	100.9	0.144	ND	ND
DPR00768	WD-9	7/20/2017	23.7	99.5	99.9	99.7	0.142	ND	ND
DPR00774	WD-10	7/25/2017	23.9	100.2	99.3	99.8	0.143	ND	ND
DPR00780	WD-11	7/26/2017	24	99.6	99.7	99.7	0.143	ND	ND
DPR00786	WD-12	7/27/2017	23.6	100	99.5	99.8	0.141	ND	ND
DPR00792	WD-13	7/31/2017	23.8	99.8	93	96.4	0.138	ND	ND
DPR00798	WD-14	8/1/2017	23.8	98.8	93.8	96.3	0.138	ND	ND
DPR00804	WD-15	8/2/2017	23.7	99.2	92.7	96.0	0.136	ND	ND
DPR00810	WD-16	8/3/2017	23.8	100.5	89.8	95.2	0.136	ND	ND
DPR00816	WD-17	8/6/2017	23.5	100.6	98.1	99.4	0.140	ND	ND
DPR00822	WD-18	8/7/2017	24.2	100.2	99.3	99.8	0.145	ND	ND
DPR00828	WD-19	8/8/2017	Invalidated**						
DPR00834	WD-20	8/9/2017	23.6	99.6	87.1	93.4	0.132	ND	ND
DPR00840	WD-21	8/12/2017	23.7	101	88.5	94.8	0.135	ND	ND
DPR00845	WD-22	8/13/2017	23.9	101.2	84.1	92.7	0.133	ND	ND
DPR00850	WD-23	8/14/2017	Invalidated**						
DPR00855	WD-24	8/15/2017	23.7	103.2	96	99.6	0.142	ND	ND
DPR00860	WD-25	8/19/2017	Invalidated**						
DPR00865	WD-26	8/20/2017	24	101.3	102.5	101.9	0.147	ND	ND
DPR00870	WD-27	8/21/2017	23.4	100.2	91.7	96.0	0.135	ND	ND
DPR00875	WD-28	8/22/2017	23.1	101.5	85.7	93.6	0.130	ND	ND
DPR00880	WD-29	8/27/2017	23.8	101.3	85.3	93.3	0.133	ND	ND
DPR00885	WD-30	8/28/2017	23.3	102.5	81.7	92.1	0.129	ND	ND
DPR00890	WD-31	8/29/2017	23.5	102.1	100.1	101.1	0.143	ND	ND
DPR00895	WD-32	8/30/2017	23.3	100.8	81.5	91.2	0.127	ND	ND
DPR00900	WD-33	9/4/2017	Invalidated**						
DPR00905	WD-34	9/5/2017	Invalidated**						
DPR00910	WD-35	9/6/2017	23.9	105.3	102.6	104.0	0.149	ND	ND
DPR00915	WD-36	9/7/2017	23.7	102.6	119.5	111.1	0.158	ND	ND

\*ND (non-detect) < 0.004 ug/sample.

\*\*Five (5) samples were invalidated because the end flows did not meet flow criteria of 100 sccm +/-20%. Thirty-one (31) samples had no quantifiable chloropicrin concentrations.

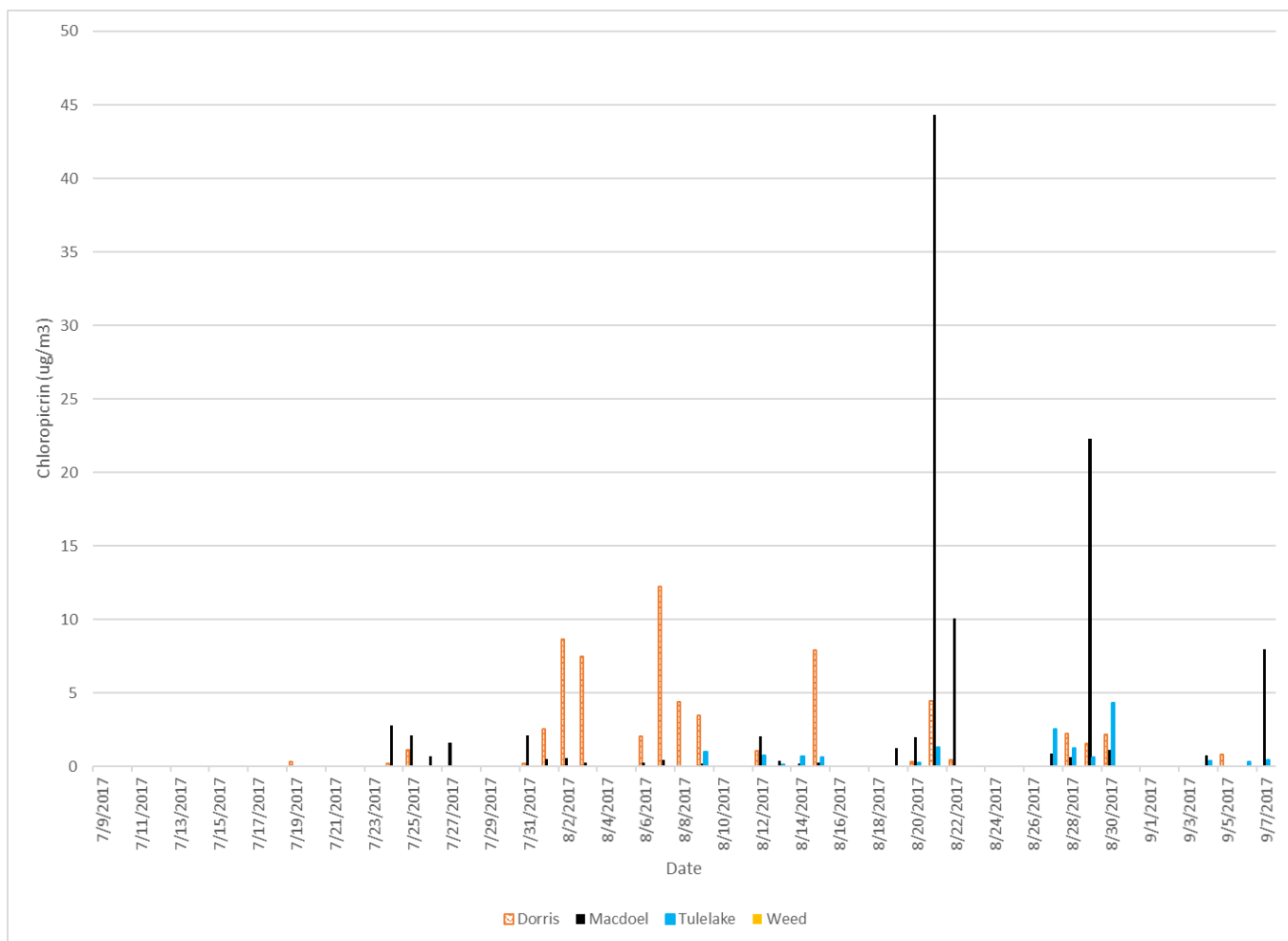
Time-series graphs for methyl bromide and chloropicrin are included in Graphs 1 and 2.

Graph 1: Methyl Bromide Concentrations Throughout the Study



Note: There were no quantifiable methyl bromide concentrations at the Tulelake site.

Graph 2: Chloropicrin Concentrations Throughout the Study



Note: There were no quantifiable chloropicrin concentrations at the Weed site.

## 6.0 Quality Control Results

This section summarizes the quality control (QC) samples collected at the Macdoel site. The Macdoel site was chosen as the QC site due to its location in a historically high-use pesticide area. An additional Tisch sampler and a vacuum pump sampling setup were added to this site to collect QC samples. In total, 9 field spikes and 10 collocated samples were collected for methyl bromide, and 9 field spikes, 9 field blanks and 9 collocated samples were collected for chloropicrin. Field blanks and trip spikes were not collected for methyl bromide because the sample media was an evacuated canister, so passive contamination was not a concern. In addition, trip spikes were not collected for chloropicrin; only collocated, field spikes, and field blanks were collected in the study as recommended.

## Methyl Bromide

The formula for calculating the Relative Percent Difference (RPD) for methyl bromide is as follows:

$$RPD = (\text{Collocate result, ppb} - \text{Primary result, ppb}) \div (\text{Average, ppb of Collocate and Primary}) \times 100$$

There were ten (10) collocated methyl bromide samples collected in the study. However, one collocated sample (7/16/2017) was invalidated due to the finalized or end canister pressure (<6 PSI) being too low for analysis. Lab results were not provided for the collocated sample on 8/20/2017 in week 7 of the study because the sampler malfunctioned. Of the remaining eight (8) analyzed collocated canister samples, one had a non-detectable concentration while seven collocated samples met the RPD criteria of +/- 25%. Table 11 summarizes the RPD for methyl bromide at the Macdoel site.

Table 11: Collocated Relative Percent Difference for Methyl Bromide

Compound	Sample ID	Sample Date	Primary Result (ppb)	Collocated Result (ppb)	Relative % Difference
Methyl Bromide	200508850	7/9/2017	<MDL	<MDL	N/A*
	200509285	7/18/2017	0.04	0.03	-12.1%
	200509865	7/24/2017	1.50	1.70	12.5%
	200510492	7/31/2017	0.58	0.60	3.4%
	200510584	8/6/2017	0.08	0.07	-7.9%
	200511249	8/12/2017	0.04	0.03	-16.2%
	200512545	8/29/2017	0.23	0.25	8.3%
	200513058	9/6/2017	0.17	0.16	-6.1%

\*N/A = Not applicable because primary and collocate results were below the minimum detection limit.

The formula for calculating the Spike Percent Recovery (SPR) for methyl bromide is as follows:

$$\begin{aligned} \text{Vol. in canister, L} &= (\text{Can Pressure, psi} + 14.7, \text{ psi}) \times 1 \text{ atm} \div 14.7, \text{ psi} \times 6 \text{ L/atm} \\ \text{Spike Amount, ppb} &= (\text{Std Conc., ppb} \times \text{Amount Spike, L}) \div \text{Vol. in canister, L} \\ \text{SPR} &= (\text{Spiked result, ppb} - \text{Primary result, ppb}) \div \text{Spike Amount, ppb} \times 100 \end{aligned}$$

Nine canisters were spiked with 0.2 L of a known concentration of the target compound in this study; of these, three (8/3/2017, 8/27/2017 and 9/5/2017) were invalidated due to sampler malfunction. The remaining six spiked canisters were analyzed, and the SPR for all six samples did not meet criteria (70% – 130%). For this reason, CARB conducted some experimental tests, and after further evaluation of the test results, CARB recommended to invalidate the spike data from this study. The experimental test



results and CARB's recommendation could be found in Appendix X. Table 12 summarizes the SPR for methyl bromide at the Macdoel site.

Table 12: Spike Percent Recovery for Methyl Bromide

Sample ID	Sample Date	Primary Result (ppb)	Spiked Result (ppb)	Amount Spike (L)	Std. Conc. (ppb)	Sample Canister Pressure (psig)	Percent Recovery
200509258	7/17/2017	ND	0.19	0.2	77	14.40	13.5%
200509886	7/25/2017	1.90	2.30	0.2	77	12.20	28.5%
200510536	8/1/2017	0.13	0.30	0.2	77	21.60	16.4%
200510683	8/7/2017	0.09	0.29	0.2	77	13.90	15.5%
200511826	8/21/2017	1.30	1.20	0.2	77	12.00	-7.1%
200512540	8/28/2017	0.03	0.04	0.2	77	11.90	0.4%

### **Chloropicrin**

The formula for calculating the RPD for chloropicrin is as follows:

$$RPD = 2 \times (\text{Collocated result, ug/m}^3 - \text{Primary result, ug/m}^3) \div (\text{Collocated result, ug/m}^3 + \text{Primary result, ug/m}^3) \times 100$$

There were nine collocated chloropicrin samples collected in the study. Two collocated samples were non-detectable. Six collocated samples' RPD were within the +/- 25% criteria while one collocated sample (i.e., 7/31/2017) fell outside of this criteria. Table 13 summarizes the RPD for chloropicrin at the Macdoel site.

Table 13: Collocated Relative Percent Difference for Chloropicrin

Barcode	Sample Name	Start Date	Sampling Time (hour)	Avg Flow (sccm)	volume (m3)	Chloropicrin (ug/sample)*	Chloropicrin (ug/m3)	Percent Relative Difference
DPR00721	MD-1	7/9/2017	23.9	103.3	0.148	ND		
DPR00722	MD-1-CO	7/9/2017	24.7	103.1	0.153	ND		
DPR00745	MD-5	7/16/2017	23.8	100.6	0.144	ND		
DPR00746	MD-5-CO	7/16/2017	23.8	101.4	0.145	ND		
DPR00775	MD-10	7/25/2017	23.9	99.5	0.143	0.300	2.105	-1.00%
DPR00776	MD-10-CO	7/25/2017	23.9	99.5	0.143	0.298	2.084	
DPR00793	MD-13	7/31/2017	23.8	102.7	0.147	0.309	2.107	-145.98%
DPR00794	MD-13-CO	7/31/2017	23.8	99.8	0.143	0.047	0.329	
DPR00817	MD-17	8/6/2017	23.7	101.5	0.144	0.035	0.244	-2.07%
DPR00818	MD-17-CO	8/6/2017	23.7	97.2	0.138	0.033	0.239	
DPR00841	MD-21	8/12/2017	23.7	104.2	0.148	0.307	2.075	-9.38%
DPR00842	MD-21-CO	8/12/2017	23.7	101.0	0.144	0.272	1.889	
DPR00861	MD-25	8/19/2017	23.5	101.6	0.143	0.182	1.268	2.72%
DPR00862	MD-25-CO	8/19/2017	23.4	103.8	0.145	0.189	1.303	
DPR00881	MD-29	8/27/2017	23.9	95.8	0.137	0.122	0.891	-7.33%
DPR00882	MD-29-CO	8/27/2017	23.9	93.5	0.134	0.111	0.828	
DPR00901	MD-33	9/4/2017	23.9	108.1	0.155	0.119	0.770	-22.86%
DPR00902	MD-33-CO	9/4/2017	23.9	96.7	0.139	0.085	0.612	

\*ND (non-detect) < 0.004 ug/sample. The RPD criteria is +/- 25% of the expected value.

Note: The computed RPD in the above table is slightly different compared to the RPD in the lab report in Appendix IX. The reason for this difference is because the RPD above is computed for the entire sample which takes into account the sampling time and average flow of each sample. The lab's RPD is computed using just the extracted amount which is only 1 mL of the entire sample. Also note that the lab's unit is ng/mL compared to the unit above used in the computation, which is ug/m3.

The formula for calculating the SPR for chloropicrin is as follows:

$$SPR = (Net\ Spike, ug/sample \div Spike\ Amount, ug/sample) \times 100$$

There were nine field spike samples collected in the study. The SPR for two samples (MD-2-FS and MD-6-FS) could not be computed because the primary samples were not quantifiable. Four field spike recoveries fell outside the spike recovery criteria (70 – 130% of expected value). Three field spike samples (i.e., MD-22-FS, MD-30-FS and MD-34-FS) were within recovery criteria. Table 14 summarizes the SPR for chloropicrin at the Macdoel site.

Table 14: Spike Percent Recovery for Chloropicrin

Barcode	Sample Name	Start Date	Sampling Time (hour)	Avg Flow (sccm)	volume (m3)	Chloropicrin (ug/sample)*	Chloropicrin (ug/m3)	Spike Amount (ug/sample)	Primary Sample Result (ug/m3)	Field Spike Result (ug/m3)	Net Spike (ug/m3)	Net Spike (ug/sample)	Spike % Recovery
DPR00727	MD-2	7/10/2017	23.9	106.8	0.153	ND	ND		ND				
DPR00728	MD-2-FS	7/10/2017	23.9	101.4	0.145	0.059	0.406	0.06		0.406	--	--	--
DPR00751	MD-6	7/17/2017	23.8	80.1	0.114	Trace	Trace		Trace				
DPR00752	MD-6-FS	7/17/2017	23.7	105.4	0.149	0.06	0.402	0.06		0.402	--	--	--
DPR00781	MD-11	7/26/2017	23.9	99.6	0.143	0.100	0.699		0.699				
DPR00782	MD-11-FS	7/26/2017	23.9	99.5	0.142	0.141	0.992	0.06		0.992	0.293	0.041	68.33%
DPR00799	MD-14	8/1/2017	23.9	99.5	0.143	0.077	0.539		0.539				
DPR00800	MD-14-FS	8/1/2017	23.8	99.4	0.141	0.106	0.751	0.06		0.751	0.212	0.029	48.33%
DPR00823	MD-18	8/7/2017	23.6	100.6	0.142	0.065	0.460		0.460				
DPR00824	MD-18-FS	8/7/2017	23.6	99.95	0.141	0.106	0.751	0.06		0.751	0.291	0.041	68.33%
DPR00846	MD-22	8/13/2017	23.8	104.5	0.149	0.056	0.373		0.373				
DPR00847	MD-22-FS	8/13/2017	23.8	97.45	0.139	0.101	0.726	0.06		0.726	0.353	0.049	81.66%
DPR00866	MD-26	8/20/2017	24.4	105.7	0.155	0.311	2.010		2.010				
DPR00867	MD-26-FS	8/20/2017	24.5	100.0	0.147	0.414	2.810	0.06		2.810	0.800	0.117	195.00%
DPR00886	MD-30	8/28/2017	23.4	91.9	0.129	0.081	0.631		0.631				
DPR00887	MD-30-FS	8/28/2017	23.5	96.25	0.135	0.156	1.155	0.06		1.155	0.524	0.070	116.66%
DPR00906	MD-34	9/5/2017	23.8	116.0	0.166	0.041	0.246		0.246				
DPR00907	MD-34-FS	9/5/2017	23.8	86.6	0.123	0.081	0.658	0.06		0.658	0.412	0.050	83.33%

\*ND (non-detect) < 0.004 ug/sample; Trace < 0.021 ug/sample.

SPR criteria is 70 – 130% of the expected value. SPR ranges from 48% to 195%.

Note: The computed SPR in the above table is slightly different compared to the SPR in the lab report in Appendix IX. The reason for this difference is because the SPR above is computed for the entire sample which takes into account the sampling time and average flow of each sample. The lab's SPR is computed using just the extracted amount which is only 1 mL of the entire sample. Also note that the lab's unit is ng/mL compared to the unit above used in the computation, which is ug/m3.

In addition to field spikes and collocated samples, field blanks were also collected for chloropicrin at the Macdoel site. As expected, all field blanks were non-detectable. Table 15 summarizes the blank results at this site.

Table 15: Field Blank Results for Chloropicrin

Barcode	Sample Name	Start Date	Extr. Vol. (mL)	Chloropicrin (ug/mL)	Chloropicrin (ug/sample)*
DPR00734	MD-3-FB	7/11/2017	3.0	ND	ND
DPR00758	MD-7-FB	7/18/2017	3.0	ND	ND
DPR00788	MD-12-FB	7/27/2017	3.0	ND	ND
DPR00806	MD-15-FB	8/2/2017	3.0	ND	ND
DPR00830	MD-19-FB	8/8/2017	3.0	ND	ND
DPR00852	MD-23-FB	8/14/2017	3.0	ND	ND
DPR00872	MD-27-FB	8/21/2017	3.0	ND	ND
DPR00892	MD-31-FB	8/29/2017	3.0	ND	ND
DPR00912	MD-35-FB	9/6/2017	3.0	ND	ND

\*ND (non-detect) < 0.004 ug/sample.

Note: No field blanks were collected for methyl bromide because the sample media is an evacuated canister.

## 7.0 Breakthrough Results

Breakthrough analysis refers to analyzing the secondary sorbent bed of the XAD-4 resin tube to determine if any amount of sample was not retained in the primary sorbent bed. For this reason, breakthrough analyses were only performed on the collected

chloropicrin samples in the study. Breakthrough was detected in nine field spikes, ten primary and four collocated samples. The breakthrough sample results are summarized in Table 16.

Table 16: Breakthrough Sampling Results for Chloropicrin

Barcode	Sample Name	Start Date/Time	Front Half Chloropicrin (ng/mL)	Back Half Chloropicrin (ng/mL)
DPR00903-BT	DR-33	9/4/2017 9:30	61.81	trace
DPR00782-BT	MD-11-FS	7/26/2017 8:51	41.70	5.30
DPR00794-BT	MD-13-CO	7/31/2017 9:15	15.76	106.37
DPR00799-BT	MD-14	8/1/2017 9:07	25.62	trace
DPR00800-BT	MD-14-FS	8/1/2017 9:10	30.98	trace
DPR00824-BT	MD-18-FS	8/7/2017 7:45	35.63	trace
DPR00847-BT	MD-22-FS	8/13/2017 8:45	30.70	trace
DPR00862-BT	MD-25-CO	8/19/2017 7:00	62.91	trace
DPR00867-BT	MD-26-FS	8/20/2017 11:00	133.16	5.06
DPR00876-BT	MD-28	8/22/2017 11:04	459.74	trace
DPR00882-BT	MD-29-CO	8/27/2017 9:30	37.09	trace
DPR00728-BT	MD-2-FS	7/10/2017 12:35	15.98	trace
DPR00887-BT	MD-30-FS	8/28/2017 9:38	45.96	6.17
DPR00891-BT	MD-31	8/29/2017 9:13	995.10	477.77
DPR00901-BT	MD-33	9/4/2017 8:45	39.80	5.71
DPR00902-BT	MD-33-CO	9/4/2017 8:45	28.24	trace
DPR00907-BT	MD-34-FS	9/5/2017 8:45	20.75	6.47
DPR00916-BT	MD-36	9/7/2017 8:26	420.65	trace
DPR00752-BT	MD-6-FS	7/17/2017 9:10	13.88	6.45
DPR00769-BT	MD-9	7/20/2017 8:45	128.15	9.08
DPR00874-BT	TL-27	8/21/2017 13:29	61.58	trace
DPR00884-BT	TL-29	8/27/2017 11:30	122.24	5.45
DPR00889-BT	TL-30	8/28/2017 11:19	61.16	trace

Note: Sample MD-13-CO had significant amounts of breakthrough which strongly suggest that the sorbent tubes may have been installed backward on the sampler, or mislabeled.

## 8.0 Summary

Many of the pesticide samples collected were below the method detection limit for both active ingredients methyl bromide and chloropicrin. However, for days where there were quantifiable pesticide concentrations, either one or both active ingredients were detected at all three pesticide monitoring sites: Dorris, Macdoel and Tulelake. This suggests that there may have been pesticide applications in the region on those days. The highest methyl bromide and chloropicrin concentrations were from the Dorris and Macdoel sites which were very similar to historical pesticide-usage as noted in DPR's 2016 Usage Information Report. The urban background site in Weed was purposely chosen for its location far from any pesticide sources and even further from the three high-usage sites. As expected, all but one pesticide sample collected from the Weed site were non-detectable. This indicates that the community of Weed is less impacted by methyl bromide and chloropicrin compared to the communities of Dorris, Macdoel, and Tulelake.