



State of California  
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CALIFORNIA AIR RESOURCES BOARD

Monitoring and Laboratory Division

## **2017 Seasonal Ambient Air Monitoring of Chloropicrin in the Santa Maria Region**

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Prepared by

Megan McKay, Air Pollution Specialist  
Community Air Monitoring North Section

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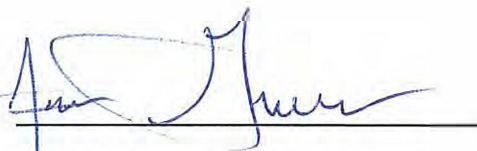
## Report Approval

**Report Title:** 2017 Seasonal Ambient Air Monitoring of Chloropicrin in the Santa Maria Region

**Project Lead:** Megan McKay, Air Pollution Specialist

**Approval:** The following monitoring report has been reviewed and approved by the Monitoring and Laboratory Division.

Signatures:



Joe Guerrero, Manager  
Community Air Monitoring North Section

3-14-19

Date



Kenneth R. Stroud, Chief  
Community Air Monitoring Branch

3-26-19

Date

## Executive Summary

### 2017 Seasonal Ambient Air Monitoring of Chloropicrin in the Santa Maria Region

At the request of the California Department of Pesticide Regulation (DPR), the California Air Resources Board (CARB) performed an ambient air monitoring project for the pesticide chloropicrin. Monitoring was conducted at public schools located in historical high use areas of the Santa Maria region of Santa Barbara County, during the high use months of August through October 2017.

Twenty-four hour ambient air samples were collected on XAD-4 sorbent tubes four days per week for 10 weeks from August 13 through October 19, 2017, at five public schools (in three different school districts: Orcutt Union School District, Santa Maria-Bonita School District, and Guadalupe Union School District). Collected air samples were analyzed by gas chromatography with a mass spectrometer detector (GS/MS) by CARB's Northern Laboratory Branch (NLB) in Sacramento. Of 242 (total) sampled sorbent tubes, there were 230 valid samples including 190 field and 40 quality control (QC) samples.

Due to moisture issues (the sorbent tubes were saturated thus NLB was unable to analyze), five field samples were invalidated. Equipment failure or other issues caused five field and two QC samples to be invalidated.

Of the 190 valid field samples, 17 were reported at less than the analytical method detection limit of <0.01 ppbv (ND), 46 were at trace levels (trace levels are >0.01 but <0.02 ppbv), and 127 had quantifiable results (ranging from 0.02-0.95 ppbv). The two highest values occurred at Kermit McKenzie Junior High School, 0.95 ppbv for the sample beginning on 10/16/2017 and 0.81 ppbv for the sample beginning on 10/13/17. The ten highest values from the project ranged from 0.51-0.95 ppbv (with all other sample values below 0.50 ppbv). Of these ten highest values, four occurred from sampling at Bonita Elementary, three from Calvin C Oakley Elementary, two at Kermit McKenzie Junior High School, and one at Mary Buren Elementary.

**Table of Analytical Sample Results Summary**

<b>Location</b>	<b>Non-Detect Count</b>	<b>Trace Level Count</b>	<b>Quantifiable Count</b>	<b>Average Concentration ppbv</b>	<b>Max Concentration ppbv</b>
Alice Shaw Elementary	0	9	31	0.11	0.32
Bonita Elementary	2	9	25	0.22	0.61
Calvin C Oakley Elementary	0	4	33	0.20	0.67
Kermit McKenzie Junior High School	11	10	19	0.21	0.95
Mary Buren Elementary	4	14	19	0.21	0.69
<b>Total</b>	<b>17</b>	<b>46</b>	<b>127</b>	<b>0.18</b>	<b>0.95</b>

## Table of Contents

<b>Section</b>	<b>Page</b>
MONITORING REPORT APPROVAL.....	i
EXECUTIVE SUMMARY.....	ii
TABLE OF CONTENTS.....	iii
1. INTRODUCTION.....	1
2. SAMPLING LOCATIONS.....	1
3. METHOD.....	3
4. RESULTS.....	5
5. QUALITY CONTROL .....	6
6. DISCUSSION.....	9

### Tables:

Table 1: Sampling Locations.....	2
Table 2: Analytical Sample Results Summary.....	6
Table 3: Field Blank Quality Control Results.....	7
Table 4: Collocation Quality Control Results .....	8
Table 5: Field Spike Quality Control Results .....	8
Table 6: Trip Spike Quality Control Results .....	9
Table 7: Highest Detected Values at Each Location.....	10

### Figures:

Figure 1: Google map route of the selected schools in the Santa Maria region.....	2
Figure 2: Bonita Elementary setup with two samplers. ....	3
Figure 3: Ten Highest Values for the Project .....	9

**Appendices:**

Appendix 1: From DPR: Use Information and Air Monitoring Recommendation for the Active Ingredient Chloropicrin in California

Appendix 2: Sampling Protocol for Chloropicrin Monitoring in Santa Barbara County

Appendix 3: Laboratory Results Report: Chloropicrin Analytical Results for Air Monitoring Samples Collected in Santa Maria Region, August - October 2017

Appendix 4: Location Photos

Appendix 5: Chloropicrin Field Log Sheets

Appendix 6: Analytical Sample Results Table

Appendix 7: Calibration/Certification Report

## 1. Introduction

At the request of the California 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) performed an ambient air monitoring project for the pesticide chloropicrin. Chloropicrin is generally used as a broad spectrum fumigant against microbes, fungi, vegetation, insects, and nematodes.

Data presented by DPR in 2016 (Appendix 1: Use Information and Air Monitoring Recommendation for the Active Ingredient Chloropicrin in California) identified Santa Barbara County as the third highest annual reported chloropicrin usage by county for years 2012 – 2014. The report specified that the total reported use of Chloropicrin in Santa Barbara County for 2012-2014 was 4.09 million pounds. Although Ventura and Monterey Counties had higher total reported usage, monitoring efforts were currently in place in those areas, and thus DPR requested for sampling in Santa Barbara County. Past usage indicates that the highest usage in Santa Barbara County peaks during the months of August, September, and October.

Samples were collected for 10 weeks from August 13 through October 19, 2017, resulting in 230 valid samples (190 field and 40 quality control (QC) samples). The “Sampling Protocol for Chloropicrin Monitoring in Santa Barbara County” is located in Appendix 2.

## 2. Sampling Locations

Locations for this project were selected based on recommendations from DPR (Appendix 1: Use Information and Air Monitoring Recommendation for the Active Ingredient Chloropicrin in California, Section C. Recommendation) and cooperative school districts.

Figure 1 displays the locations of the five schools in the Santa Maria region of Santa Barbara County (in three different school districts) which were selected for monitoring. They are [name, (school district)]:

- Alice Shaw Elementary (Orcutt Union School District),
- Bonita Elementary (Santa Maria-Bonita School District),
- Calvin C Oakley Elementary (Santa Maria-Bonita School District),
- Kermit McKenzie Junior High School (Guadalupe Union School District), and
- Mary Buren Elementary (Guadalupe Union School District).

Unfortunately, the Lucia Mar Unified School District (which includes the areas of Nipomo, Callender, and Arroyo Grande) denied CARB access to locate a monitor at any of their schools. DPR could not recommend a background location in this region, so none was included in this project.

At each school, samplers were placed on top of buildings with the best unobstructed location nearest to agriculture fields. A second sampler was installed at Bonita Elementary School for

quality control samples. The global positioning satellite coordinates for each sampler are included in Table 1, in addition to the sampler probe height above the roof and the ground.

Photos of each sampler at each school, from the four cardinal directions, are included in Appendix 4.

**Table 1: Sampling Locations**

City	School	Coordinates	Probe Height above roof (inches)	Probe Height above ground (feet inches)
Orcutt	Alice Shaw Elementary	34°53'20.4"N 120°25'35.9"W	55"	16'8"
Santa Maria	Bonita Elementary	34°57'27.3"N 120°30'36.7"W	59"	17'2"
Santa Maria	Calvin C Oakley Elementary	34°58'0.5"N 120°27'7.8"W	57"	16'6"
Guadalupe	Kermit McKenzie Jr. High School	34°57'24.4"N 120°34'45.1"W	60"	15'6"
Guadalupe	Mary Buren Elementary	34°58'13.2"N 120°33'58.8"W	60"	16'5"

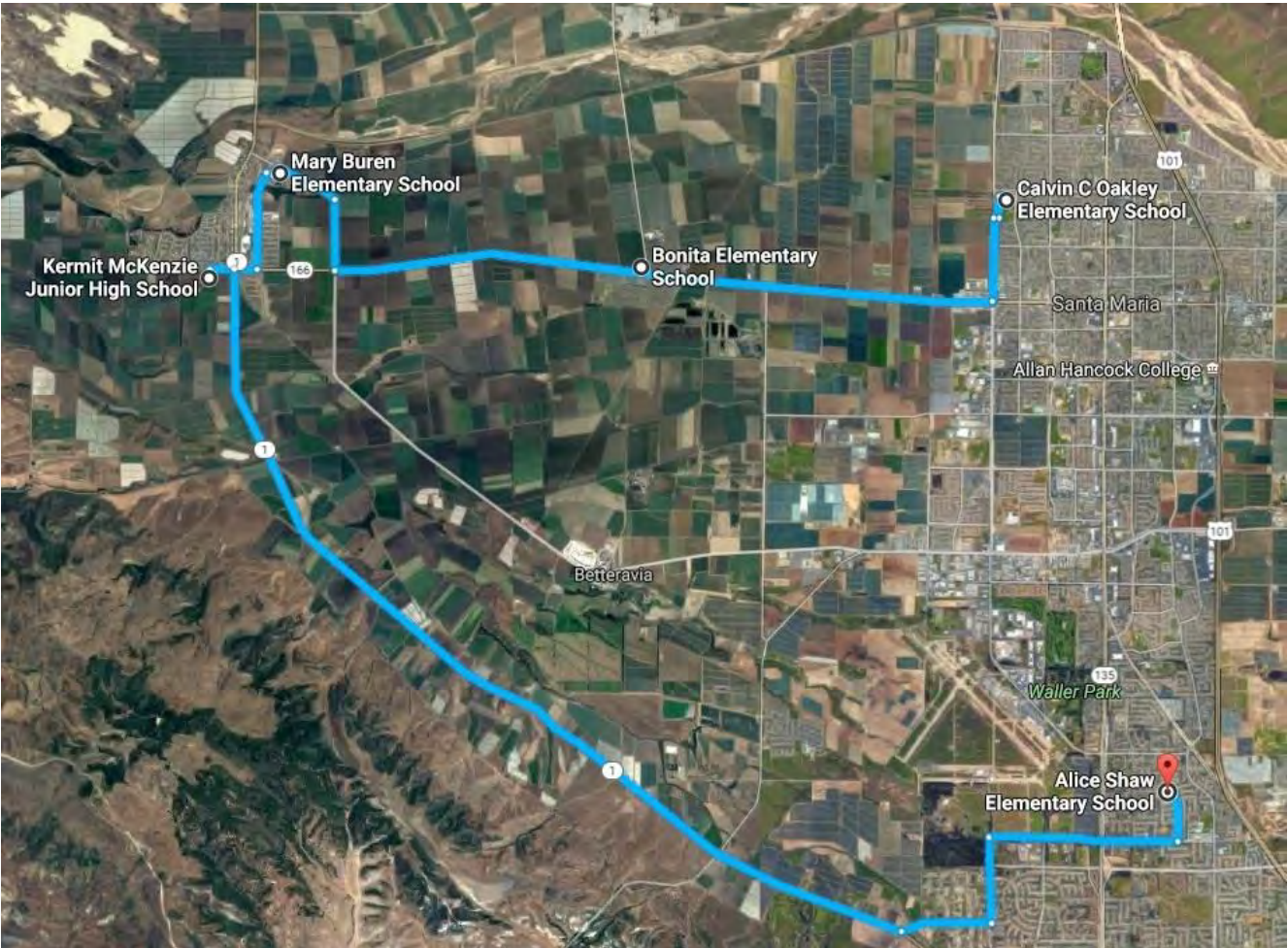


Figure 1: Google map route of the selected schools in the Santa Maria region.

### 3. Method

At each monitoring location, air was drawn continuously through an XAD-4 sorbent tube during the 24-hour sampling period by either an AC or DC pump. Sample flow, targeted at 100 sccm (“Standard Operating Procedure for the Analysis of Trichloronitromethane (Chloropicrin) in Ambient Air using Gas Chromatography/Mass Spectrometry” located in Appendix 2), was controlled by an in-line rotameter during the sampling. Flows were measured using a NIST traceable digital Alicat Whisper mass flow meter (with a range of 0-200 sccm) at both the setup and retrieval of the samples. (The calibration certificate for the mass flow meter used is in Appendix 7.) The averages of the two flow values were used to calculate the volumes of the samples. Upon retrieval, sampled sorbent tubes were placed in a cooler with dry ice to keep below 4°C. As an example, Figure 2 portrays the setup at Bonita Elementary. Notice the PVC tube shielded the sorbent tubes from direct sunlight or rain.

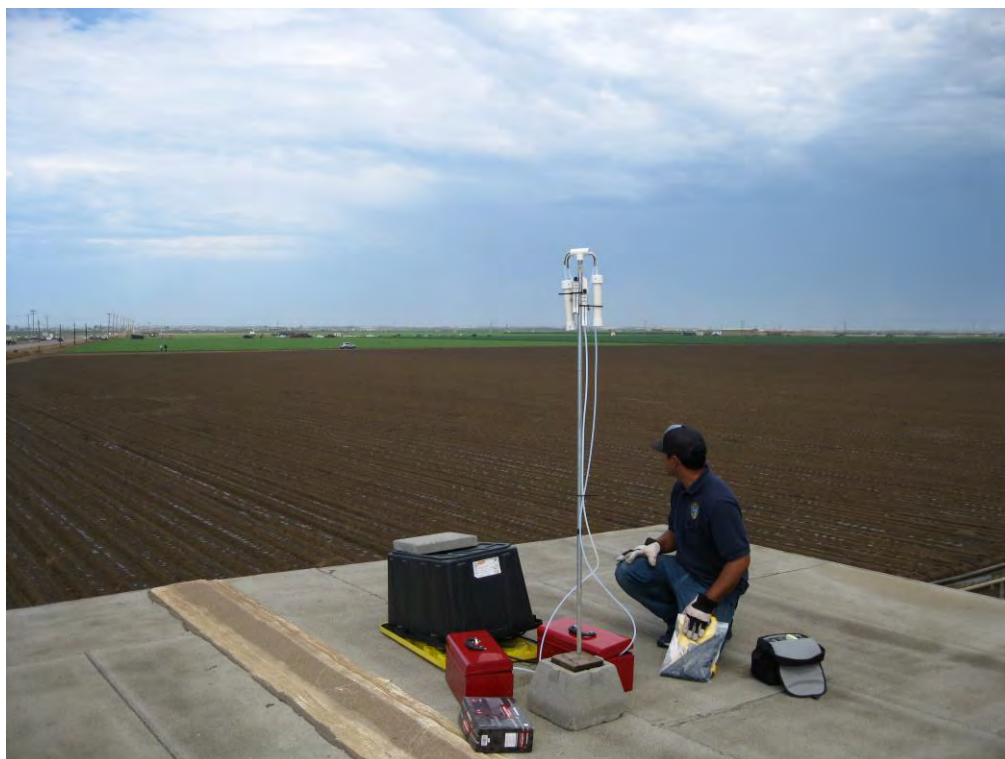


Figure 2: Bonita Elementary setup with two samplers.

Sampling occurred on a weekly schedule, consisting of four consecutive 24-hour samples each week (per location). Sampling commenced on August 13, 2017 and continued for 10 weeks, with the final sample retrieved on October 19, 2017. During the 10-week period, the schedule varied such that sampling included all days, including weekends. The sample start (and end) times varied depending on field staff work schedules. Field spikes, collocated samples, and field blanks were collected once a week, each, at Bonita Elementary.

As is standard practice for CARB, the first sample of each week was installed on the samplers at the end of the previous week’s sampling, and sampling was started with a clock



timer. This was documented on the field log sheets (Appendix 5). To capture any potential passive sampling during this long wait time, the field blanks were also installed at the end of each week, and retrieved along with the first sample of the week at Bonita Elementary.

Field and trip spikes were prepared by CARB's Northern Laboratory Branch (NLB) in Sacramento, by injecting 15.0 µL of a 4000 ng/mL spiking chloropicrin solution (for a final concentration of 20.0 ng/mL chloropicrin after extraction) into an XAD-4 sorbent tube. Both the trip and field spikes were transported and stored under dry ice, before and after use. The field spikes (one each week) were positioned in parallel with the primary samples. The field spikes were removed and handled identically to the other samples. The trip spikes (one each week) were transported and analyzed along with the field spike. The trip spike was treated the same as a field spike with the exception that it was not installed onto a sampler and not sampled.

Field log sheets (Appendix 5) were maintained throughout the project and included sampling day, location names, start and end times, start and end flow rates, sampler elapsed time readings, comments (if applicable), weather conditions, and the start and end initials of the operator. Note, all reported sampling times were reported in Pacific Standard Time (PST).

The XAD-4 sorbent tube air samples were analyzed by gas chromatography with a mass spectrometer detector (GS/MS) by NLB. The laboratory established a method detection limit (MDL) of 1.40 ng/mL (which equates to 4.2 ng/sample or 0.0043 ppbv), and an estimated quantitation limit (EQL) of 7.0 ng/mL (which equates to 21.0 ng/sample or 0.02 ppbv).

Of 242 (total) sampled sorbent tubes there were 230 valid samples including 190 field and 40 quality control (QC) samples.

**Deviations from protocol:**

One deviation occurred during this chloropicrin ambient air monitoring project from the "Sampling Protocol for Chloropicrin Monitoring in Santa Barbara County" located in Appendix 2: Sampling heights above the roof varied from 55-60" (instead of 61-73").

**Location/Sample Identification:**

Sample nomenclature for this study was created from the location of the sampler; a sequential sample number; and if applicable the type of QC sample collected (collocated, blank, or spike).

**Location Name Abbreviations:**

AS = Alice Shaw Elementary  
BE = Bonita Elementary  
CO = Calvin C Oakley Elementary  
KM = Kermit McKenzie Junior High School  
MB = Mary Buren Elementary

## Quality Control Sample Identifications

CO = Collocated

FB = Field Blank

FS = Field Spike

TS = Trip Spike

## Examples

AS-1 = the first day of sampling at Alice Shaw Elementary

BE-4-CO = a collocated sample on the fourth day of sampling at Bonita Elementary

More details of the method can be found in the sampling protocol (Appendix 2) and laboratory report (Appendix 3).

## 4. Results

Appendix 6 presents the Analytical Sample Results Table where the lab analyzed results in ng/sample (Appendix 3) are transformed into sample values (ppbv and  $\mu\text{g}/\text{m}^3$ ) using field information (“Ave Flow” and “Elapsed Minutes” are used to calculate “Volume”). Note the lab analysis does not include any field information (thus invalid samples due to field issues are not necessarily shown as invalid in the lab results). For additional information, please refer to Appendices 3, 5, and 6.

The following 12 samples were invalidated for this project:

- BE-9, BE-15, BE-18, BE-28, and MB-21
  - Due to moisture in the samples. The Bonita Elementary location experienced high levels of fog, and several rain events. Unclear why this location was prone to moisture issues more than the other locations.
- BE-10-FS, CO-29, CO-33, CO-34, MB-5, and MB-33
  - Equipment failures
- BE-1-FB
  - Pump activated

In addition, the following 12 samples are flagged, but included in these results:

- AS-28, AS-35, KM-19, MB-3, MB-13, MB-16, and MB-32
  - These samples have been flagged for having a final flow rate that was out of specifications (>20% from 100 sccm). The variance in flow rates could be attributed to a variety of factors including weak batteries, stuck rotameters, or issues with the wiring. In all cases, the average flow was within the range.
- CO-5
  - This sample was flagged due elapsed timer difference showing a shorter time than the sampler start/final times indicate.
- AS-1, BE-20, CO-37, and MB-20
  - These samples were outside of the 24 hours  $\pm 1$  hour tolerance by 5-8 minutes.

It is presumed that samples BE-33 and BE-33-FB were inadvertently mislabeled in the field.

All quality control information is located in Section 5. "Quality Control."

**Comments from the field notes:**

Aerial spraying was noticed in the southeast direction from Mary Buren Elementary on 8/31/17 and 9/10/17. The assistant principal of Bonita Elementary reported that a crop duster flew over the school on 9/22/17. There were strong smells on the east side of Bonita Elementary on the mornings of 9/25/17 and 9/26/17. DPR stipulates that Chloropicrin is not aerially applied, and therefore these aerial events aren't related to these results.

Of the 190 valid field samples, 17 were reported at less than the analytical method detection limit of <0.004 ppbv (ND), 46 were at trace levels (trace levels are >0.004 and <0.02 ppbv), and 127 had quantifiable results (ranging from 0.02-0.95 ppbv). Table 2 presents the Analytical Results summarized for each location.

**Table 2: Analytical Sample Results Summary**

Location	Non-Detect Count	Trace Level Count	Quantifiable Count	Average Concentration ppbv	Max Concentration ppbv
Alice Shaw Elementary	0	9	31	0.11	0.32
Bonita Elementary	2	9	25	0.22	0.61
Calvin C Oakley Elementary	0	4	33	0.20	0.67
Kermit McKenzie Junior High School	11	10	19	0.21	0.95
Mary Buren Elementary	4	14	19	0.20	0.69
<b>Total</b>	<b>17</b>	<b>46</b>	<b>127</b>	<b>0.18</b>	<b>0.95</b>

**5. Quality Control**

Quality Control samples collected from the field consisted of blanks, collocations, duplicates and spikes. The following summarize the results of these samples. For more detailed information see Tables 3-6 and Appendix 3.

Blanks (Table 3): During this project 12 field blanks were sampled, with one invalid, and 11 were analyzed. Chloropicrin was below the MDL (4.2 ng/sample) for seven field blanks, three were at trace levels (>4.2 ng/sample and <=21.0 ng/sample), and one had quantifiable results (23.5 ng/sample). It is presumed that samples BE-33 and BE-33-FB were inadvertently mislabeled in the field.

Collocation (Table 4): There was one collocation each week, resulting in 10 collocation samples for the project. Two collocated samples and one additional primary were at trace

levels (>0.004 and <0.02 ppbv). For the seven matched quantifiable samples, the relative difference varied from -5% to 11.3%.

Field Spikes (Table 5): Of the 10 field spikes, there are only four quantifiable primary results to compare with. Two of the primary samples were invalid due to moisture, two were ND, and two were at trace level. The spike recovery percent ranged from 67.2% to 92.5%.

Trip Spikes (Table 6): Trip spike recoveries ranged from 80.0% to 121.4%.

Due to rounding of results, calculated values may not match values presented in table.

**Table 3: Field Blank Quality Control Results**

Sample Name	Start Date/Time	Elapsed Minutes	Lab Analysis Chloropicrin (ng/sample)	Corresponding Primary Chloropicrin Sample (ng/sample)
BE-1-FB	8/9/17 12:33	7147	Invalid	trace
BE-4-FB	8/16/17 10:29	1385	ND	trace
BE-5-FB	8/17/17 9:38	7042	ND	61.9
BE-9-FB	8/25/17 5:37	5765	ND	Invalid
BE-13-FB	9/1/17 4:56	7385	trace	102
BE-17-FB	9/7/17 6:05	4318	ND	trace
BE-21-FB	9/13/17 4:30	8716	ND	31.8
BE-25-FB	9/22/17 4:17	5943	trace	574
BE-29-FB	9/29/17 6:15	4527	trace	535
BE-33-FB	10/5/17 8:12	10108	23.5	134.61
BE-37-FB	10/15/17 8:46	1380	ND	362
BE-40-FB	10/18/17 6:06	1433	ND	50.9

Samples marked in purple are invalid.

**Table 4: Collocation Quality Control Results**

Relative % Difference = (Primary-Collocation)/(Average of Primary and Collocation)\*100  
 Due to rounding of results, calculated values may not match values presented in table.

Sample Name	Lab Analysis Chloropicrin (ng/sample)	Corresponding Primary Chloropicrin Sample (ng/sample)	Relative Percent Difference (ng/sample)	Calculated Chloropicrin ppbv	Corresponding Primary Calculated Chloropicrin ppbv	Relative Percent Difference ppbv
BE-2-CO	20.91	trace		0.02		
BE-7-CO	26.88	21.7	-10.6	0.03	0.02	-3.7
BE-11-CO	trace	trace				
BE-14-CO	36.27	38.4	2.9	0.04	0.04	-0.9
BE-19-CO	139.44	128	-4.4	0.15	0.14	-4.1
BE-23-CO	trace	trace				
BE-27-CO	451.23	418	-3.8	0.48	0.44	-5.0
BE-31-CO	488.40	600	10.3	0.50	0.61	9.4
BE-35-CO	33.33	45.0	14.9	0.04	0.05	11.3
BE-39-CO	376.32	398	2.8	0.39	0.42	4.4

**Table 5: Field Spike Quality Control Results**

Spike Recovery % = (Spike Result – Primary Result)/(Spike Amount)\*100  
 Due to rounding of results, calculated values may not match values presented in table.

Sample Name	Spike Amount Chloropicrin (ng/sample)	Lab Analysis Chloropicrin (ng/sample)	Corresponding Primary Chloropicrin Sample (ng/sample)	Spike Recovery Percent	Calculated Chloropicrin ppbv	Corresponding Primary Calculated Chloropicrin ppbv
BE-3-FS	60.0	60.15	trace		0.06	
BE-6-FS	60.0	57.99	ND		0.06	
BE-10-FS	60.0	Invalid	trace		Invalid	
BE-15-FS	60.0	52.47	Invalid		0.05	Invalid
BE-18-FS	60.0	104.97	Invalid		0.11	Invalid
BE-22-FS	60.0	51.18	ND		0.05	
BE-26-FS	60.0	487.35	432	92.5	0.54	0.46
BE-30-FS	60.0	93.30	49.7	72.8	0.10	0.05
BE-34-FS	60.0	168.33	128	67.2	0.19	0.15
BE-38-FS	60.0	582.45	527	91.7	0.62	0.57

Samples marked in purple are invalid.

**Table 6: Trip Spike Quality Control Results**

Spike Recovery % = (Trip Spike Sample Result)/(Spike Amount)\*100

Sample Name	Start Date/Time	Spike Amount Chloropicrin (ng/sample)	Lab Analysis Chloropicrin (ng/sample)	Spike Recovery Percent
Trip Spike	8/15/17 10:54	60.0	57.21	95.4
Trip Spike	8/22/17 6:30	60.0	56.40	94.0
Trip Spike	8/29/17 5:46	60.0	61.23	102.1
Trip Spike	9/5/17 7:52	60.0	58.41	97.4
Trip Spike	9/7/17 14:10	60.0	47.97	80.0
Trip Spike	9/19/17 5:51	60.0	59.04	98.4
Trip Spike	9/26/17 7:15	60.0	63.81	106.4
Trip Spike	10/3/17 9:29	60.0	72.81	121.4
Trip Spike	10/12/17 8:47	60.0	62.46	104.1
Trip Spike	10/16/17 7:52	60.0	64.92	108.2

**6. Discussion**

Of the 190 valid field samples, the two highest values occurred at Kermit McKenzie Junior High School, 0.95 ppbv for the sample beginning on 10/16/2017 and 0.81 ppbv for the sample beginning on 10/13/17. Figure 3 presents the ten highest values from the project which ranged from 0.51-0.95 ppbv (with all other sample values below 0.50 ppbv).

**Highest Detected Values**

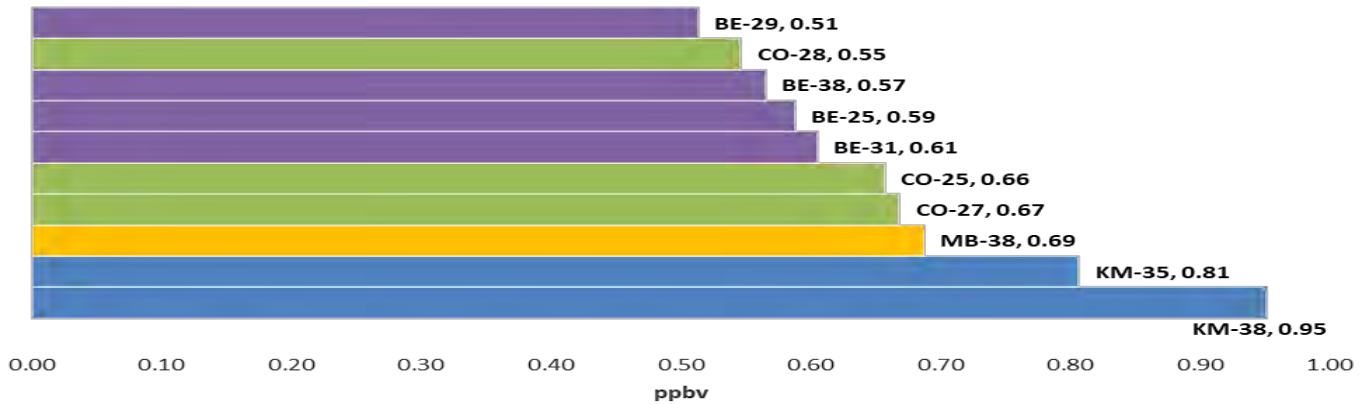


Figure 3: The ten highest detected values for the project (all other values were below 0.50 ppbv). The site location-sample number are labeled, along with actual ppbv value.

Most field blanks were set up to sample for multiple days (between each week of sampling) to provide a “worst case scenario” of passive sampling. Indeed, some passive sampling was observed with three field blanks indicating trace levels (BE-13-FB, BE-25-FB, and BE-29-FB), and one had quantifiable results (BE-33-FB = 23.5 ng/sample).

Table 7 presents the two highest detected values at each location, including the starting date of the 24-hour sample. The ten highest values from the project ranged from 0.51-0.95 ppbv (with all other sample values below 0.50 ppbv). Of these ten highest values, four occurred from sampling at Bonita Elementary, three from Calvin C Oakley Elementary, two at Kermit McKenzie Junior High School, and one at Mary Buren Elementary.

**Table 7: Highest Detected Values at Each Location (ppbv)**

<b>Location</b>	<b>Highest Detected Value (ppbv) - Start Date of Occurrence</b>	<b>Second Highest Detected Value (ppbv) - Start Date of Occurrence</b>
Alice Shaw Elementary	0.32 – 10/13/17	0.22 – 9/25/17
Bonita Elementary	0.61 – 10/3/17	0.59 – 9/25/17
Calvin C Oakley Elementary	0.67 – 9/27/17	0.66 – 9/25/17
Kermit McKenzie Junior High School	0.95 – 10/16/17	0.81 – 10/13/17
Mary Buren Elementary	0.69 – 10/16/17	0.40 – 9/26/17