

Final Results for Spring 2018 Seasonal Ambient Monitoring for Organophosphate Pesticides In Kern County

Prepared By:

Patrick Vaca, Air Pollution Specialist Community Air Monitoring North Section Community Air Monitoring Branch Monitoring and Laboratory Division

March 11, 2019

This report has been reviewed by the staff of the California Air Resources Board (CARB) and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the California Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

#### **Monitoring Report Approval**

**Report Title:** Final Results for Spring 2018 Seasonal Ambient Monitoring for Organophosphate Pesticides in Kern County

Project Lead: Patrick Vaca, Air Pollution Specialist

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

3-11-19

Joe Guerrero, Manager Community Air Monitoring North Section

Kenneth R. Stroud, Chief Community Air Monitoring Branch

Date

3-11-19

Date

#### Executive Summary

#### Spring 2018 Seasonal Ambient Monitoring for Organophosphate Pesticides In Kern County

At the request of the Department of Pesticide Regulation (DPR), the California Air Resources Board (CARB) conducted an air monitoring study for the organophosphate pesticide active ingredients chlorpyrifos, Diazinon, Malathion, chlorpyrifos Oxygen Analog (OA), dichlorvos, dimethoate, dimethoate OA, Diazinon OA, Malathion OA, S,S,S-tributyl trithiophosphate (DEF), and phosmet. The monitoring was conducted in communities near historical high use areas. Sampling was conducted at five locations including three public schools and two CARB ambient air monitoring stations from March 12, 2018 through May 18, 2018.

A total of 235 samples including 199 primary samples and 36 quality control (QC) samples were collected by Community Air Monitoring North (CAMN) staff over the tenweek sampling period. Five primary samplers were deployed to the communities of Arvin, Lost Hills, Wasco, Delano, and Shafter. An additional sampler for Quality Control (QC) samples was set up in Arvin. Samples were collected on polymeric resin contained in glass sorbent tubes with an air sampling flow rate of 1000 standard cubic centimeters per minute (SCCM). The polymeric resin sorbent tube contents were analyzed by gas chromatography with a mass selective detector (GS/MSD) by CARB's Northern Laboratory Branch (NLB) in Sacramento.

13 samples were invalid due to power failures, pump failures, sample time and/or flow rate being out of criteria, and the theft of one sampler. There was a total of 235 sampled sorbent tubes.

#### Organophosphate Sorbent Tube Results

There was a total of 2,475 results provided by the NLB for the eleven organophosphate analytes. Many of the samples (98.6%) were found to be below the Method Detection Limit (MDL) or the Estimated Quantitation Limit (EQL) (which equals five times the MDL). Samples with levels which are higher than the MDL and lower than the EQL are defined as "trace". For chlorpyrifos there were 24 quantifiable samples and 43 trace level samples. For Malathion there were four quantifiable and nine trace level samples. For dichlorvos there were four quantifiable samples. For DEF there was one trace level sample. For chlorpyrifos OA there were four trace level samples. For phosmet there was one quantifiable and one trace level sample. For Malathion OA there were four trace level samples. For Diazanon there was one quantifiable sample. For Diazanon OA, dimethoate, and dimethoate OA there were no quantifiable or trace level samples.

The highest concentration of chlorpyrifos (0.126 ug/m<sup>3</sup>) was seen at the Arvin site on March 18, 2018; the second highest concentration (0.121 ug/m<sup>3</sup>) was seen at the Arvin site on March 20. The highest concentration of Malathion (0.020 ug/m<sup>3</sup>) was seen at the Arvin site on May 8; the second highest concentration (0.017 ug/m<sup>3</sup>) was seen at the

Arvin site on May 6, 2018. The highest concentration of dichlorvos (0.040 ug/m<sup>3</sup>) was seen at John Prueitt Elementary School in Wasco on May 16; the second highest concentration (0.038 ug/m<sup>3</sup>) was seen at the Shafter site on May 16. The highest concentration of phosmet at (0.015 ug/m<sup>3</sup>) was seen at Pioneer School in Delano on April 4. The highest concentration of Diazinon was seen at the Pioneer School on April 5 (0.012 ug/m<sup>3</sup>).

Table of Contents

<u>Section</u>		Page
Monitoring Rep	ort Approval	ii
Executive Sum	mary	iii-i∨
Table of Conter	nts	v-vi
1.0	Introduction	1
2.0	Sampling Sites	1
3.0	Methods	6
4.0	Results	7
5.0	Deviations from Protocol	13
6.0	Quality Assurance/Quality Control	13
7.0	Summary	17
TABLES		
Table 1:	Summary of Sampling Sites	2
Table 2:	Summary of Results for Chlorpyrifos, Malathion, and Diazinon 11	-12
Table 3:	Summary of Results for Phosmet, Malathion OA, and Dichlorvos	12
Table 4:	Summary of Invalid Samples	13
Table 5:	Summary of Collocated Results	14
Table 6:	Field Spike Results for Chlorpyrifos, Malathion, and Diazinon	15
Table 7:	Field Spike Results for Chlorpyrifos OA, Malathion OA and Diazinon OA	15

Table 8:	Field Spike Results for DEF, Dimethoate, and Dimethoate OA	16
Table 9:	Field Spike Results for Phosmet and Dichlorvos	16
Table 10:	Method Detection and Estimated Quantitation Limits	17

#### FIGURES

Figure 1	Map of Kern County OP Monitoring Sites	3
Figure 2	CARB-Arvin Air Monitoring Site	4
Figure 3	Crop Map of CARB-Arvin Site (Spring 2018)	5
Figure 4	CARB-Arvin Valid Samples	7
Figure 5	Lost Hills Valid Samples	8
Figure 6	John L. Prueitt Elementary School Valid Samples	8
Figure 7	Pioneer School Valid Samples	9
Figure 8	CARB-Shafter Valid Samples	9

#### APPENDICES

Appendix 1:	Sampling Protocol for	r Organophosphate	Monitoring in Kern (	County
-------------	-----------------------	-------------------	----------------------	--------

- Appendix 2: Use Information and Air Monitoring Recommendation
- Appendix 3: Sampling Site Photos and Crop Maps (Spring 2018)
- Appendix 4: Mass Flow Meter Certification Report
- Appendix 5: Monitoring Field Log Sheets
- Appendix 6: Laboratory Results Report

#### 1.0 Introduction

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 organophosphate (OP) pesticides chlorpyrifos, chlorpyrifos Oxygen Analog (OA), dichlorvos, dimethoate, dimethoate OA, Diazinon, Diazinon OA, Malathion, Malathion OA, S,S,S-tributyl trithiophosphate (DEF), and phosmet in Kern County. Chlorpyrifos is a clear-to-white crystalline solid insecticide used in agricultural applications for the removal of termites, mosquitos, and roundworms (Christensen et al., 2009). Dichlorovos is a dense colorless liquid which evaporates easily into the atmosphere that is used for insect control in food storage areas, greenhouses and barns. Dimethoate is a white crystalline solid that is used for contact and systemic control of a broad range of insects. Diazinon and Malathion are both colorless liquids with low vapor pressures (ATDR 2003; ATDR 2008) that are used to control insects on fruit, vegetable, nut and field crops. DEF is a colorless to pale yellow liquid that is used as a defoliant for cotton plants. Phosmet is an off-white crystalline solid that is used on a wide variety of fruit crops for the control of aphids, suckers, mites and fruit flies. OP pesticides work through the inhibition of the enzyme acetylcholinesterase (AChE) (ATSDR, 2008). This inhibition results in the accumulation of the neurotransmitter acetylcholine at post-synaptic receptors in the peripheral, neuromuscular, and central nervous systems (ATSDR, 2008).

Data presented by DPR in 2016 showed that Kern County had the highest cumulative annual reported OP usage for years 2012 – 2014. The report showed that for those years, the total reported use in Kern County was over 800,000 pounds of the active ingredients chlorpyrifos, Diazinon, and Malathion. Data indicates that the highest usage in Kern County peaks during the months of March through May.

A total of 222 valid samples, which included 194 primary samples and 36 quality control samples (14 collocated samples, 10 field spikes, and 12 passive samples), were collected from March 12, 2018, through May 18, 2018. Sampling occurred continuously for four 24-hour periods for each week of the study. Weekly sampling commenced upon arrival of the field staff and continued until the fourth/final sample was collected approximately 96 hours later. The "Sampling Protocol for Organophosphate Monitoring in Kern County" is located in Appendix 1.

## 2.0 Sampling Sites

Sampling sites for this study were chosen based on recommendations from DPR (Appendix 2. "Use Information and Air Monitoring Recommendation for the Organophosphate Pesticide Active Ingredients Chlorpyrifos, Diazinon, and Malathion: Seasonal Ambient Air Monitoring Studies in Kern County, Fresno and Tulare Counties, and Imperial County"). Also per the DPR recommendation, schools were given top priority when choosing locations in the listed high OP use cities. CARB staff worked closely with school district office management to locate the schools of highest concern for impacts from OP pesticide applications.

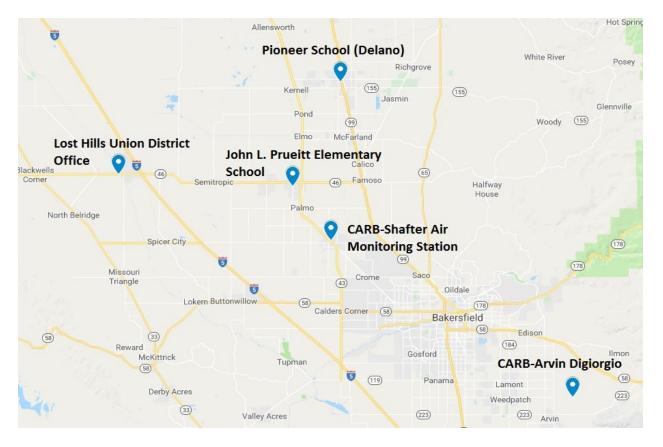
At each site, samplers were installed on top of buildings and one trailer (Arvin-Digiorgio) with unobstructed airflow to the samplers. A collocated sampler was installed at the Arvin-Digiorgio site. All sampler probes were installed at a height of approximately two meters above the level of the rooftop. Photos of each sampler location, and crop maps which indicate prevalence and type of crops nearby, are included in Appendix 3.

Table 1 summarizes the sampling locations including Global Positioning System (GPS) coordinates. GPS coordinates were obtained by Google Earth.

Site Name	Address	GPS Coordinates	Probe Height above ground level (m)
CARB-Arvin-Digiorgio	19405 Buena Vista Ave., Arvin, CA 93203	35.2392, -118.7886	4.26
Lost Hills Union School District	20951 Pavillion Way, Lost Hills, CA 93249	35.6154, -119.7027	4.64
John L. Prueitt Elementary School	3501 7th Street, Wasco, CA 93280	35.5934, -119.3657	4.35
Pioneer School	1001 Hiett Ave., Delano, CA 93215	35.7678, -119.2700	7.62
CARB-Shafter	578 Walker Street, Shafter, CA 93263	35.5035, -119.2726	5.07

#### Table 1 Summary of Sampling Sites

Shown in Figure 1 is a map of the monitoring locations for the study. Figure 2 shows the CARB-Arvin monitoring site. Figure 3 shows a crop map of the Arvin site.



#### Figure 1 Map of Kern County OP Monitoring Sites



Figure 2 CARB-Arvin Air Monitoring Site

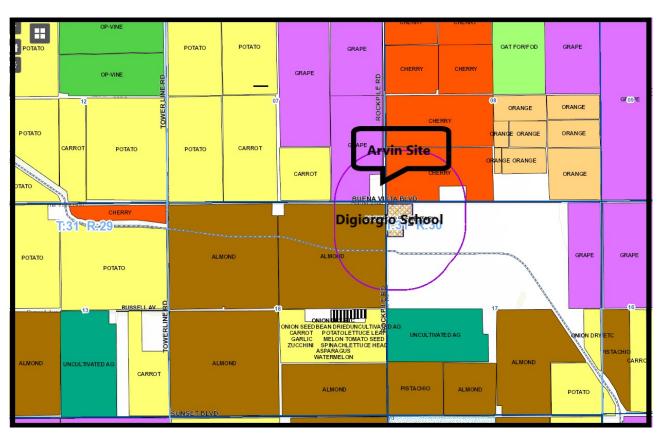


Figure 3 Crop Map of CARB-Arvin Site (Spring 2018)

#### 3.0 Methods

The sampling process was designed to collect organophosphates on polymeric resin contained in glass sorbent tubes (XAD-2). Samples were collected by passing a measured volume of ambient air through the sorbent tubes mounted on the sampling apparatus. A sampler flow check was performed prior to each sampling period. After the sample sorbent tube was installed, the flow rate was set to 1000 SCCM  $\pm$  10% (standard cubic centimeters per minute) using the inline rotameter with a flow range of 0-2 LPM. The flow rate was accurately measured using an Alicat Whisper digital mass flow meter with a range of 0-2 LPM. The flow rate was re-checked at the end of each sampling period just prior to removal of the sorbent tube. For the samples to be acceptable, the average flow rate must have been within 20% of 1000 SCCM (between 800 SCCM and 1200 SCCM). Samples out of the specified flow range were flagged. The certification document for the mass flow meter can be seen in Appendix 4.

The 10-week study began on March 12, 2018, and the final sample was retrieved on May 18, 2018. There was a total of 222 valid samples which included 194 primary samples and 36 quality control samples (14 collocated samples, 10 field spikes, and 12 passive samples). The QC samples were collected at the Arvin-Digiorgio location on a secondary sampler. The spiked sorbent tubes were prepared a day prior to weekly sampling and stored in the laboratory freezer until they were picked up by field staff prior to leaving Sacramento. Upon retrieval, the spikes were immediately put into a cooler with dry ice for transport to the sampling location.

Monitoring occurred continuously for four 24-hour periods each week. Samples were collected in the same sequence for each sampling period (Arvin-Digiorgio, Lost Hills, J.L. Prueitt, Pioneer School, and Shafter).

At the end of each sampling period, the sampled sorbent tubes were placed in individual capped culture tubes with an identification label affixed to each sample. The operating interval and flow rate of each sample was recorded on the log sheet. Each culture tube was then placed in a cooler with dry ice and stored for the remainder of the week. At the end of the week, the collected samples were transported back to CARB Northern Laboratory Branch (NLB) and stored in a freezer until analysis.

The organophosphate field logs which contain the sample start and end times, start and end flow rates, and elapsed time meter readings for each sample can be found in Appendix 5. Site nomenclature for this study was based upon the location of each sampler and the daily sample number. Additional abbreviations were added to identify the type of QC sample collected (collocated, blank, or spike), if applicable.

#### **Sampler Locations**

- AV CARB Arvin Air Monitoring Station
- LH Lost Hills Union District Office
- JP John Prueitt Elementary School
- PS Pioneer School
- SF CARB Shafter Air Monitoring Station

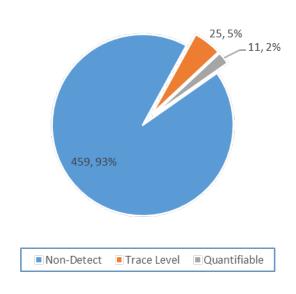
#### **Quality Control**

FB – Passive Sample CO – Collocated Sample FS – Field Spike The NLB extracted and analyzed all of the samples from this pesticide study. The collected sorbent tube samples were analyzed following the laboratory standard operating procedure titled "Standard Operating Procedure for the Determination of Selected Organophosphate Pesticides Collected on XAD-2 Resin by Gas Chromatography-Triple Quadrupole Mass Spectrometry".

#### 4.0 Results

There was a total of 2,475 results provided by NLB for the 11 organophosphate analytes. Many of the samples (98.6%) were found to be below the Method Detection Limit (MDL) or the Estimated Quantitation Limit (EQL). Samples with levels which are higher than the MDL and lower than the EQL are defined as "trace". For chlorpyrifos there were 24 quantifiable level samples and 43 trace level samples. For Malathion there were four quantifiable and nine trace level samples. For dichlorvos there were four quantifiable level samples. For DEF there was one trace level sample. For chlorpyrifos OA there were four trace level samples. For phosmet there was one quantifiable and one trace level sample. For Malathion OA there were four trace level samples. For Diazanon there was one quantifiable sample. For Diazanon OA, dimethoate, and dimethoate OA there were no quantifiable or trace level samples.

The highest concentration of chlorpyrifos (0.126 ug/m<sup>3</sup>) was seen at the Arvin site on March 18, 2018; the second highest concentration (0.121 ug/m<sup>3</sup>) was seen at the Arvin site on March 20. The highest concentration of Malathion (0.020 ug/m<sup>3</sup>) was seen at the Arvin site on May 8; the second highest concentration (0.017 ug/m<sup>3</sup>) was seen at the Arvin site on May 6, 2018. The highest concentration of dichlorvos (0.040 ug/m<sup>3</sup>) was seen at John Prueitt Elementary School on May 16; the second highest concentration of phosmet at (0.015 ug/m<sup>3</sup>) was seen at Pioneer School on April 4. The highest concentration of Diazinon was seen at the Pioneer School on April 5, 2018 (0.012 ug/m<sup>3</sup>). Figures 4-8 summarize the results of the valid primary samples broken down by site.



## Figure 4 CARB-Arvin Valid Samples

## Figure 5 Lost Hills Valid Samples

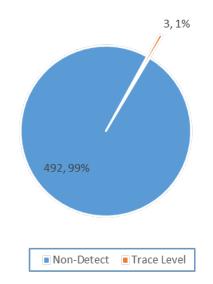
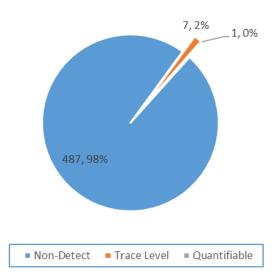


Figure 6 John L. Prueitt Elementary School Valid Samples



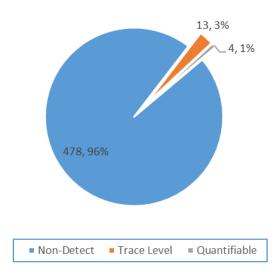
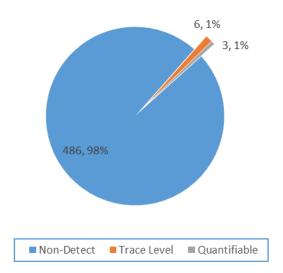


Figure 8 CARB-Shafter Valid Samples



The full sample results are shown in Appendix 6. A summary of the results which only includes trace and quantifiable results for chlorpyrifos, Malathion, and Diazinon is shown in Table 2. Table 3 shows a summary of the results for phosmet, Malathion OA, and dichlorvos.

# Table 2 Summary of Results for Chlorpyrifos, Malathion, and Diazinon

Barcode	Sample Name	Sample Date	Sampling Time (Hours)	Average Flow (SCCM)	Volume (m3)	Chlorpyrifos (µg/sample)	Chlorpyrifos (µg/m3)	Malathion (µg/sample)	Malathion (µg/m3)	Diazinon (µg/sample)	Diazinon (µg/m3)
DPR04000	AV-1	3/12/2018	24.0	1012	1.46	trace	trace	ND	n/a	ND	n/a
DPR04002	LH-1	3/12/2018	23.9	992	1.42	trace	trace	ND	n/a	ND	n/a
DPR04003	JP-1	3/12/2018	23.7	1026	1.46	trace	trace	ND	n/a	ND	n/a
DPR04004	PS-1	3/12/2018	23.2	1043	1.45	0.040	0.028	ND	n/a	ND	n/a
DPR04005	SF-1	3/12/2018	23.3	991	1.39	trace	trace	ND	n/a	ND	n/a
DPR04011	PS-2	3/13/2018	24.4	1002	1.47	trace	trace	ND	n/a	ND	n/a
DPR04014	AV-3	3/14/2018	23.6	1046	1.48	trace	trace	ND	n/a	ND	n/a
DPR04017	JP-3	3/14/2018	23.5	1021	1.44	trace	trace	ND	n/a	ND	n/a
DPR04018	PS-3	3/14/2018	23.7	1025	1.46	0.022	0.015	ND	n/a	ND	n/a
DPR04019	SF-3	3/14/2018	23.7	1011	1.44	trace	trace	ND	n/a	ND	n/a
DPR04021	AV-4	3/15/2018	23.6	1010	1.43	trace	trace	ND	n/a	ND	n/a
DPR04024	JP-4	3/15/2018	23.8	1026	1.47	trace	trace	ND	n/a	ND	n/a
DPR04025	PS-4	3/15/2018	23.6	1050	1.49	trace	trace	ND	n/a	ND	n/a
DPR04026	SF-4	3/15/2018	23.6	1008	1.43	trace	trace	ND	n/a	ND	n/a
DPR04028	AV-5	3/18/2018	24.9	1165	1.74	0.22	0.126	ND	n/a	ND	n/a
DPR04032	PS-5	3/18/2018	24.9	1060	1.58	0.023	0.015	ND	n/a	ND	n/a
DPR04035	AV-6	3/19/2018	23.3	1194	1.67	0.10	0.060	ND	n/a	ND	n/a
DPR04039	PS-6	3/19/2018	23.5	1061	1.50	0.038	0.025	ND	n/a	ND	n/a
DPR04040	SF-6	3/19/2018	23.3	1018	1.43	trace		ND	n/a	ND	n/a
DPR04042	AV-7	3/20/2018	23.4	1179	1.65	0.20	trace 0.121	ND	n/a	ND	n/a
DPR04045	JP-7			1052	1.46	trace		ND		ND	
DPR04046	PS-7	3/20/2018	23.1	1048	1.47	0.022	trace		n/a	ND	n/a
DPR04047	SF-7	3/20/2018	23.3	1020	1.44	trace	0.015	ND	n/a		n/a
DPR04049	AV-8	3/20/2018	23.5	1173	1.62	0.087	trace	ND	n/a	ND	n/a
DPR04050	LH-8	3/21/2018	23.0	935	1.30	trace	0.054	ND	n/a	ND	n/a
DPR04050	JP-8	3/21/2018	23.2	1122	1.56	trace	trace	ND	n/a	ND	n/a
DPR04051	PS-8	3/21/2018	23.1	1075	1.49	0.096	trace	ND	n/a	ND	n/a
DPR04052	SF-8	3/21/2018	23.1	1075	1.49	0.090	0.064	ND	n/a	ND	n/a
DPR04053 DPR04056	5F-0 AV-9	3/21/2018	23.1	1027	1.42		0.016	ND	n/a	ND	n/a
		3/22/2018	23.4			trace	trace	ND	n/a	ND	n/a
DPR04061	SF-9	3/22/2018	23.8	1038	1.48	trace	trace	ND	n/a	ND	n/a
DPR04063	AV-10	3/26/2018	23.0	1001	1.38	trace	trace	ND	n/a	ND	n/a
DPR04067	PS-10	3/26/2018	23.0	1007	1.39	trace	trace	ND	n/a	ND	n/a
DPR04068	SF-10	3/26/2018	23.0	1002	1.38	trace	trace	ND	n/a	ND	n/a
DPR04084	AV-13	4/3/2018	23.0	1003	1.38	trace	trace	ND	n/a	ND	n/a
DPR04095	PS-14	4/4/2018	24.0	1022	1.47	trace	trace	trace	trace	ND	n/a
DPR04098	AV-15	4/5/2018	24.0	1049	1.51	trace	trace	ND	n/a	ND	n/a
DPR04101	JP-15	4/5/2018	23.8	1011	1.44	trace	trace	trace	trace	ND	n/a
DPR04102	PS-15	4/5/2018	24.1	1008	1.46	0.028	0.019	trace	trace	0.018	0.012
DPR04105	AV-16	4/6/2018	23.1	1031	1.43	trace	trace	ND	n/a	ND	n/a
DPR04108	JP-16	4/6/2018	23.2	1005	1.40	0.023	0.016	ND	n/a	ND	n/a
DPR04109	PS-16	4/6/2018	24.0	1025	1.48	0.026	0.018	ND	n/a	ND	n/a
DPR04110	SF-16	4/6/2018	24.0	1011	1.46	0.022	0.015	ND	n/a	ND	n/a
DPR04112	AV-17	4/8/2018	23.4	973	1.37	trace 11	trace	ND	n/a	ND	n/a

# Table 2 Summary of Results for Chlorpyrifos, Malathion, and Diazinon (cont.)

Barcode	Sample Name	Sample Date	Sampling Time (Hours)	Average Flow (SCCM)	Volume (m3)	Chlorpyrifos (µg/sample)	Chlorpyrifos (µg/m3)	Malathion (µg/sample)	Malathion (µg/m3)	Diazinon (µg/sample)	Diazinon (µg/m3)
DPR04116	PS-17	4/8/2018	24.5	1014	1.49	trace	trace	ND	n/a	ND	n/a
DPR04117	SF-17	4/8/2018	23.0	1006	1.39	trace	trace	ND	n/a	ND	n/a
DPR04121	LH-18	4/9/2018	23.0	1008	1.39	trace	trace	ND	n/a	ND	n/a
DPR04124	SF-18	4/9/2018	23.0	996	1.37	trace	trace	ND	n/a	ND	n/a
DPR04157	JP-23	4/17/2018	23.0	1038	1.43	trace	trace	ND	n/a	ND	n/a
DPR04159	SF-23	4/17/2018	23.0	1009	1.39	trace	trace	ND	n/a	ND	n/a
DPR04168	AV-25	4/22/2018	24.8	1003	1.49	0.095	0.064	ND	n/a	ND	n/a
DPR04175	AV-26	4/23/2018	23.1	984	1.36	0.024	0.018	ND	n/a	ND	n/a
DPR04180	SF-26	4/23/2018	23.2	995	1.39	trace	trace	ND	n/a	ND	n/a
DPR04182	AV-27	4/24/2018	23.0	984	1.36	0.025	0.018	ND	n/a	ND	n/a
DPR04189	AV-28	4/25/2018	23.0	1033	1.43	0.028	0.020	ND	n/a	ND	n/a
DPR04207	PS-30	4/30/2018	24.2	1007	1.46	trace	trace	ND	n/a	ND	n/a
DPR04210	AV-31	5/1/2018	24.1	1005	1.45	ND	n/a	trace	trace	ND	n/a
DPR04217	AV-32	5/2/2018	24.0	1015	1.46	ND	n/a	trace	trace	ND	n/a
DPR04224	AV-33	5/6/2018	23.0	998	1.38	ND	n/a	0.024	0.017	ND	n/a
DPR04231	AV-34	5/7/2018	23.0	1006	1.39	trace	trace	trace	trace	ND	n/a
DPR04236	SF-34	5/7/2018	23.0	1030	1.42	trace	trace	ND	n/a	ND	n/a
DPR04238	AV-35	5/8/2018	23.1	995	1.38	0.022	n/a	0.028	0.020	ND	n/a
DPR04245	AV-36	5/9/2018	23.7	1017	1.45	ND	n/a	trace	trace	ND	n/a
DPR04252	AV-37	5/13/2018	23.7	1022	1.45	trace	trace	ND	n/a	ND	n/a
DPR04266	AV-39	5/15/2018	24.3	1001	1.46	0.023	0.016	trace	trace	ND	n/a
DPR04273	AV-40	5/16/2018	24.2	1005	1.46	ND	n/a	trace	trace	ND	n/a

## Table 3 Summary of Results for Phosmet, Malathion OA, and Dichlorvos

Barcode	Sample Name	Sample Date	Sampling Time (Hours)	Average Flow (SCCM)	Volume (m3)	Phosmet (µg/sample)	Phosmet (μg/m3)	Malathion OA (µg/sample)	Malathion OA (µg/m3)	Dichlorvos (µg/sample)	Dichlorvos (µg/m3)
DPR04095	PS-14	4/4/2018	24.0	1022	1.47	trace	trace	ND	na	ND	na
DPR04102	PS-15	4/5/2018	24.1	1008	1.46	0.022	0.015	ND	na	ND	na
DPR04224	AV-33	5/6/2018	23.0	998	1.38	ND	na	trace	trace	ND	na
DPR04238	AV-35	5/8/2018	23.1	995	1.38	ND	na	trace	trace	ND	na
DPR04273	AV-40	5/16/2018	24.2	1005	1.46	ND	na	ND	na	0.023	0.016
DPR04276	JP-40	5/16/2018	24.5	997	1.47	ND	na	ND	na	0.058	0.040
DPR04277	PS-40	5/16/2018	24.3	1017	1.48	ND	na	ND	na	0.022	0.015
DPR04278	SF-40	5/16/2018	24.3	1020	1.49	ND	na	ND	na	0.057	0.038

#### 5.0 Deviations from Protocol

It was initially intended that sampling would be randomized to include all days of the week including weekends. CAMN staff were informed after the commencement of sampling that support staff needed at the school sites would not be able to provide access on Sundays. There were samples collected on one Saturday (4/7/2018). All other samples were collected on a Monday through Thursday schedule.

An additional eight active ingredients: chlorpyrifos OA, dichlorvos, dimethoate, dimethoate OA, Diazinon OA, Malathion OA, S,S,S-tributyl trithiophosphate (DEF) and phosmet were analyzed by NLB and are provided in this report.

#### 6.0 Quality Assurance/Quality Control (QA/QC) Results

There were 13 invalid samples during the campaign. Table 4 summarizes the invalid samples with reasons for invalidation.

Site Name	Sample ID	Date	Reason for Invalidation
Arvin-Passive Sample	DPR04029	3/16/2018	Pump Failure
Arvin-Collocated	DPR04036	3/19/2018	Pump Failure
Arvin-Collocated	DPR04043	3/20/2018	Pump Failure
Arvin-Primary	DPR04119	4/9/2018	Pump Failure
Arvin-Field Spike	DPR04120	4/9/2018	Ending Flow Rate Out of Specification
Arvin-Collocated	DPR04127	4/10/2018	Pump Failure
Arvin-Collocated	DPR04155	4/17/2018	Ending Flow Rate Out of Specification
Arvin-Collocated	DPR04162	4/18/2018	Ending Flow Rate Out of Specification
Lost Hills	DPR04170	4/19/2018	Sample duration >25 hours
John L Prueitt	DPR04171	4/19/2018	Power Failure
Pioneer School	DPR04172	4/19/2018	Sample duration >25 hours
Shafter	DPR04173	4/19/2018	Sample duration >25 hours
John L Prueitt	DPR04199	4/28/2018	Sampler Stolen from Site

#### Table 4 Summary of Invalid Samples

Field QA/QC samples consisted of 14 collocated samples, 10 field spikes, and 12 passive samples. A summary of collocated sample results is shown in Table 5. Only collocated samples with quantifiable amounts of analyte are shown, all others were non-detectable.

Sample Name	Sample Date	Chlorpyrifos (µg/sample) Primary	Chlorpyrifos (µg/sample) Collocated	RPD**	Malathion (µg/sample) Primary	Malathion (µg/sample) Collocated	RPD**	Malathion OA (µg/sample) Primary	Malathion OA (μg/sample) Collocated	RPD**
AV-1	3/12/2018	trace	trace	n/a	ND	ND	n/a	ND	ND	n/a
AV-4	3/15/2018	trace	trace	n/a	ND	ND	n/a	ND	ND	n/a
AV-6	3/19/2018	INV	INV	INV	INV	INV	INV	INV	INV	INV
AV-7	3/20/2018	INV	INV	INV	INV	INV	INV	INV	INV	INV
AV-11	3/27/2018	ND	ND	n/a	ND	ND	n/a	ND	ND	n/a
AV-15	4/5/2018	trace	0.022	n/a	ND	ND	n/a	ND	ND	n/a
AV-19	4/10/2018	INV	INV	INV	INV	INV	INV	INV	INV	INV
AV-23	4/17/2018	INV	INV	INV	INV	INV	INV	INV	INV	INV
AV-24	4/18/2018	INV	INV	INV	INV	INV	INV	INV	INV	INV
AV-26	4/23/2018	0.024	0.05	70.3	ND	ND	n/a	ND	ND	n/a
AV-30	4/30/2018	ND	ND	n/a	ND	ND	n/a	ND	ND	n/a
AV-32	5/2/2018	ND	trace	n/a	trace	0.024	n/a	Trace	Trace	n/a
AV-35	5/8/2018	0.022	0.022	0	0.028	0.030	6.90	Trace	Trace	n/a
AV-38	5/14/2018	ND	ND	n/a	ND	ND	n/a	ND	ND	n/a

## Table 5 Summary of Collocated Results

\*\*Relative Percent Difference.

The Relative Percent Difference (RPD) was calculated as follows:

**RPD** = 2(Collocated μg/sample - Primary μg/sample) Collocated μg/sample + Primary μg/sample

There were five invalid collocated samples (36%) during the study. The highest RPD (70.3%) was seen on 4/23/2018. The lowest RPD (0%) was on 5/8/18.

Field spikes were prepared by injecting an organophosphate solution onto sampling media to a final concentration of 0.40  $\mu$ g/mL after extraction. One field spike was collected per week. Tables 6 through 9 show a summary of field spike samples.

Barcode	Sample Name	Chlorpyrifos (μg/sample)	Chlorpyrifos Lab Result (µg/sample)	Spike % Recovery	Malathion (µg/sample)	Malathion Lab Result (µg/sample)	Spike % Recovery	Diazinon (µg/sample)	Diazinon Lab Result (µg/sample)	Spike % Recovery
DPR04008	AV-2-FS	ND	2.1	132.5	ND	2.0	127.5	ND	2.1	130.0
DPR04050	AV-8-FS	0.087	1.7	102.0	ND	1.6	100.0	ND	1.6	100.0
DPR04064	AV-10-FS	ND	1.7	105.0	ND	1.6	97.5	ND	1.6	102.5
DPR04092	AV-14-FS	ND	1.6	102.5	ND	1.5	97.5	ND	1.6	102.5
DPR04120	AV-18-FS	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
DPR04148	AV-22-FS	ND	1.9	120.0	ND	1.6	100.0	ND	1.8	110.0
DPR04183	AV-27-FS	0.025	1.7	103.4	ND	1.6	100.0	ND	1.6	102.5
DPR04211	AV-31-FS	ND	1.8	115.0	trace	1.7	110.0	ND	1.8	112.5
DPR04232	AV-34-FS	trace	1.7	105.0	trace	1.6	102.5	ND	1.7	107.5
DPR04267	AV-39-FS	0.023	1.8	111.1	trace	1.8	112.5	ND	1.8	115.0

## Table 6 Field Spike Results for Chlorpyrifos, Malathion, and Diazinon

## Table 7 Field Spike Results for Chlorpyrifos OA, Malathion OA, and Diazinon OA

Barcode	Sample Name	Chlorpyrifos OA (µg/sample)	Chlorpyrifos OA Lab Result (µg/sample)	Spike % Recovery	Malathion OA (µg/sample)	Malathion OA Lab Result (μg/sample)	Spike % Recovery	Diazinon OA (µg/sample)	Diazinon OA Lab Result (µg/sample)	Spike % Recovery
DPR04008	AV-2-FS	ND	2.3	145.0	ND	2.2	135.0	ND	2.1	132.5
DPR04050	AV-8-FS	trace	1.9	120.0	ND	1.7	107.5	ND	1.7	105.0
DPR04064	AV-10-FS	ND	1.9	120.0	ND	1.6	100.0	ND	1.6	102.5
DPR04092	AV-14-FS	ND	1.6	97.5	ND	1.5	95.0	ND	1.6	97.5
DPR04120	AV-18-FS	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
DPR04148	AV-22-FS	ND	1.8	110.0	ND	1.6	97.5	ND	1.6	102.5
DPR04183	AV-27-FS	ND	1.7	105.0	ND	1.6	102.5	ND	1.6	100.0
DPR04211	AV-31-FS	ND	1.9	120.0	ND	1.7	107.5	ND	1.7	107.5
DPR04232	AV-34-FS	ND	1.7	105.0	ND	1.6	100.0	ND	1.6	102.5
DPR04267	AV-39-FS	ND	1.8	112.5	ND	1.8	110.0	ND	1.7	107.5

Barcode	Sample Name	DEF (µg/sample)	DEF Lab Result (µg/sample)	Spike % Recovery	Dimethoate (µg/sample)	Dimethoate Lab Result (µg/sample)	Spike % Recovery	Dimethoate OA (µg/sample)	Dimethoate OA Lab Result (µg/sample)	Spike % Recovery
DPR04008	AV-2-FS	ND	2.0	122.5	ND	2.1	130.0	ND	2.3	142.5
DPR04050	AV-8-FS	ND	1.5	97.5	ND	1.7	105.0	ND	2.0	122.5
DPR04064	AV-10-FS	ND	1.5	97.5	ND	1.7	105.0	ND	1.7	107.5
DPR04092	AV-14-FS	ND	1.5	92.5	ND	1.6	97.5	ND	1.4	87.5
DPR04120	AV-18-FS	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
DPR04148	AV-22-FS	ND	1.6	97.5	ND	1.6	97.5	ND	1.6	100.0
DPR04183	AV-27-FS	ND	1.6	100.0	ND	1.6	97.5	ND	1.8	110.0
DPR04211	AV-31-FS	ND	1.7	110.0	ND	1.7	107.5	ND	1.8	110.0
DPR04232	AV-34-FS	ND	1.5	97.5	ND	1.6	102.5	ND	1.7	105.0
DPR04267	AV-39-FS	ND	1.7	102.5	ND	1.8	112.5	ND	1.9	117.5

#### Table 8 Field Spike Results for DEF, Dimethoate, and Dimethoate OA

#### Table 9 Field Spike Results for Phosmet and Dichlorvos

Barcode	Sample Name	Phosmet (μg/sample)	Phosmet Lab Result (µg/sample)	Spike % Recovery	Dichlorvos (µg/sample)	Dichlorvos Lab Result (µg/sample)	Spike % Recovery
DPR04008	AV-2-FS	ND	2.0	122.5	ND	2.3	140.0
DPR04050	AV-8-FS	ND	1.6	100.0	ND	1.8	115.0
DPR04064	AV-10-FS	ND	1.6	102.5	ND	1.7	107.5
DPR04092	AV-14-FS	ND	1.4	87.5	ND	1.5	95.0
DPR04120	AV-18-FS	Invalid	Invalid	Invalid	Invalid	Invalid	Invalid
DPR04148	AV-22-FS	ND	1.6	102.5	ND	1.5	92.5
DPR04183	AV-27-FS	ND	1.6	100.0	ND	1.6	100.0
DPR04211	AV-31-FS	ND	1.9	120.0	ND	1.7	110.0
DPR04232	AV-34-FS	ND	1.6	100.0	ND	1.6	102.5
DPR04267	AV-39-FS	ND	1.8	110.0	ND	1.7	107.5

Twelve passive samples were collected during the campaign. These samples are not considered "field blanks" because the sorbent tubes were exposed to the ambient air for a longer period of time than the regular samples run at the same time. All passive samples were found to be Non-Detectable (ND) for all eleven organophosphate species. Table 10 shows the method detection limits and estimated quantitation limits for all organophosphate species.

Analyte	MDL (ug/mL)	EQL (ug/mL)
chlorpyrifos	0.0011	0.0055
chlorpyrifos OA	0.0015	0.0075
Diazinon	0.0008	0.0040
Diazinon OA	0.0011	0.0055
DEF	0.0017	0.0085
dimethoate	0.0020	0.0100
dimethoate OA	0.0010	0.0050
dichlorvos	0.0010	0.0050
Malathion	0.0009	0.0045
Malathion OA	0.0024	0.0120
phosmet	0.0009	0.0045

#### Table 10 Method Detection and Estimated Quantitation Limits

**MDL - Method Detection Limit** 

**EQL - Estimated Quantitation Limit** 

#### 7.0 Summary

There was a total of 2,475 results provided by the NLB for the eleven organophosphate analytes. Many of the samples (98.6%) were found to be below the Method Detection Limit (MDL) or the Estimated Quantitation Limit (EQL). Samples with levels which are more than the MDL and less than the EQL are defined as "trace". For chlorpyrifos there were 24 quantifiable samples and 43 trace level samples. For Malathion there were four quantifiable and nine trace level samples. For dichlorvos there were four quantifiable samples. For DEF there was one trace level sample. For chlorpyrifos OA there were four trace level samples. For phosmet there was one quantifiable and one trace level sample. For Malathion OA there were four trace level samples. For Diazanon there was one quantifiable sample. For Diazanon OA, dimethoate, and dimethoate OA there were no quantifiable or trace level samples.

The highest concentration of chlorpyrifos (0.126 ug/m<sup>3</sup>) was seen at the Arvin site on March 18; the second highest concentration (0.121 ug/m<sup>3</sup>) was seen at the Arvin site on March 20. The highest concentration of Malathion (0.020 ug/m<sup>3</sup>) was seen at the Arvin site on May 8; the second highest concentration (0.017 ug/m<sup>3</sup>) was seen at the Arvin site on May 6. The highest concentration of dichlorvos (0.040 ug/m<sup>3</sup>) was seen at John Prueitt Elementary School on May 16; the second highest concentration (0.038 ug/m<sup>3</sup>) was seen at the Shafter site on May 16. The highest concentration of phosmet at (0.015 ug/m<sup>3</sup>) was seen at the Pioneer School on April 4. The highest concentration of Diazinon was seen at the Pioneer School on April 5 (0.012 ug/m<sup>3</sup>).

The highest prevalence of quantifiable results (36%) for this study was found at the CARB-Arvin site which indicates a large number of OP pesticide applications in the area during the spring period.

Of these 32 samples, 19 (67.9%) were found to contain the active ingredient chlorpyrifos. An additional 11 (34%) samples had trace amounts of chlorpyrifos. Two samples (6.3%) from the CARB-Arvin site were found to have quantifiable amounts of Malathion with an additional 6 (19%) having trace amounts. One (3.1%) sample had a quantifiable amount of dichlorvos.

Sampling Protocol for Organophosphate Monitoring in Kern County

Use Information and Air Monitoring Recommendation

Sampling Site Photos and Crop Maps

Mass Flow Meter Certification Report

Monitoring Field Log Sheets

Laboratory Results Report