Air Monitoring Network Report:

A Comprehensive Evaluation of Results (2011 – 2016)

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By

Kenneth D. King, Environmental Scientist

Minh Pham, Air Program Supervisor

Edgar Vidrio, Environmental Program Manager

Air Program
Environmental Monitoring Branch
California Department of Pesticide Regulation
1001 I Street
Sacramento, CA 95814

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CONTRIBUTORS

The following Department of Pesticide Regulation staff contributed to the completion of this report.

Section Number	Section Title	Staff
1	Air Monitoring Network	Kenneth D. King & Minh Pham
2	Quality Assurance/Quality Control of Sampling Data	Sue Peoples & Kenneth D. King
3	Pesticide Air Concentrations	Kenneth D. King
4	Pesticide Use Information	Karrin Alstad & Jazmin Gonzalez
5	Air Concentrations and Reported Agricultural Use of Selected Pesticides	Christopher Collins
6	Simple Linear Regression Analysis of Selected Pesticides and their Use	Jazmin Gonzalez
7	Application of Emission Ratios, Gaussian Plume Functions, and Meteorological Data in the Analysis of Use-Concentration Relationships of 1,3-Dichloropropene	Colin Brown
8	Analysis of Sampling Frequency	Jing Tao
9	Analysis of Selected Non-Detected Pesticides	Atac Tuli
10	Assessment of Mitigation Effects Based on Time Series Analysis of Pesticide Air Concentrations	DPR

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Executive Summary

This report reviews and analyzes results from six years of data collected as part of the Air Monitoring Network (AMN) conducted by the Department of Pesticide Regulation (DPR) from February 1, 2011, to December 31, 2016. It provides an analysis of results in greater depth than in previously released annual reports *(available at http://www.cdpr.ca.gov/docs/emon/airinit/air_network_results.htm*).

This report examines pesticide use for the 31 pesticides included in the AMN from 2011 to 2016 in an attempt to assess patterns and trends in the use data, thereby seeking a deeper understanding of the monitoring data through comparison with pesticide use reported in the vicinity of the sampling sites. Additional variables, such as the effects of weather and temporal factors, are also explored in certain sections of this report. We also conduct statistical analyses to better understand the relationship between pesticide air concentrations and reported use.

This Executive Summary provides highlights from each section of the report and refers the reader the specific pages for additional details.

Section 1: Air Monitoring Network *(pages 1 – 15)*

These sections provide background information on the AMN including community locations and pesticides selection. From 2011-2016, AMN consisted of one sampling site in each of the following three communities: Ripon (San Joaquin County), Salinas (Monterey County), and Shafter (Kern County). One 24-hr sample per week at each site was collected by DPR staff and each sample was analyzed for 36 chemicals (31 pesticides and 5 breakdown products). This section includes complete descriptions of the pesticides, sampling locations, field sampling procedures, analytical methods, and quality assurance/control, and health screening levels used for the pesticides monitored.

Section 2: Quality Control/Quality Assurance of Sampling Data *(pages 16 – 22)*

Quality control and quality assurance procedures, alongside their results, are included in this section. Both laboratory and field measures were used to verify the quality of data collected. Laboratory matrix spikes and matrix blanks were included with every set of samples extracted and analyzed at the laboratory and are part of the laboratory QC program. The matrix spikes are conducted to assess accuracy and precision; the blanks are to check for contamination at the laboratory or contamination of the resin packed in the sorption tubes. The blank matrix materials were not fortified but were extracted and analyzed along with

the matrix spikes and field samples. Laboratory matrix spike recovery averages ranged from 72% to 101% for all chemicals analyzed. None of the laboratory matrix spike samples were outside the control limits established from the validation data. A single laboratory blank, for bensulide, resulted in one trace detection. All remaining laboratory blanks resulted in NDs.

Field blanks, field spikes, and duplicate samples are part of DPR's field and laboratory QC program. Field spikes contain a known amount of analyte and are taken to the field by staff and placed on the air samplers for 24-hrs in the same manner as actual field samples. Field spikes are extracted and analyzed in the same manner as the other field samples. In all years sampled, a total of three field blank samples resulted in a detection greater than a ND: two trace detections for malathion OA and one trace detection for chlorthal-dimethyl. All remaining field blanks resulted in non-detections. Field spike average percent recovery results ranged from 0% to 233% depending on the analyte and year. Duplicate samples are samples that are co-located with another sample in the field. These samples serve to evaluate overall precision in sample measurement and analysis. The relative difference was calculated between each quantifiable pair and averaged for each sample media type. Relative percent difference results ranged from 3.1% to 164% depending on the type of collocated sample, analyte and year.

Section 3: Pesticide Air Concentrations *(pages 23 – 48)*

A total of 34,147 analyses were performed from February 1, 2011 to December 31, 2016. Detections (either trace or quantifiable) accounted for 7.5% (2,564 analyses) of the total analyses and only 2.9% (999 analyses) of all samples collected had quantifiable concentrations. 19 chemicals accounted for these quantifiable detections. Of the 19 chemicals, four accounted for 87% of the quantifiable detections: carbon disulfide, methyl isothiocyanate (MITC), 1,3-dichloropropene (1,3-D), and methyl bromide (MeBr). Samples with no detections accounted for 89.6% (30,584 analyses) of all analyses performed.

From 2011 – 2016, the highest percentage of total detections and total quantifiable detections occurred in 2015. Among the three communities, the percentage of total and quantifiable detections was higher in Shafter than in the other two communities, although the differences are small. For all three sites combined, a total of four pesticides had quantifiable detections occurring at least more than 5.0% of the analyses: 1,3-D, carbon disulfide, MeBr and MITC.

The highest observed concentrations over the six years of sampling among the three sites were for 1,3-D. This held across all exposures (24-hr, 4-week rolling average, and 1-year average values). 1,3-D had the highest 24-hour concentration (45,323 ng/m^3) measured at any of the three sampling site locations, followed by chloropicrin (6,384 ng/m^3) and MeBr (6,055 ng/m^3). 1,3-D had the highest rolling 4-week average concentration (18,022 ng/m^3) of any pesticide at any of the three sampling sites for any year samples followed by MeBr (4,124 ng/m^3) then chloropicrin (3,019 ng/m^3). Similarly, 1,3-D had the highest 1-year average concentration (2,589 ng/m^3) of any pesticide sampled followed by MeBr at 1,412 ng/m^3 and carbon disulfide with a concentration of 739 ng/m^3.

No state or federal agency has established health standards for pesticides in air. Therefore, DPR devised health screening levels and regulatory target concentrations to place the measured air concentrations in a health based context. DPR uses the established screening levels as triggers to conduct a detailed evaluation into actual health concerns. Regulatory target concentrations are established after a complete assessment of possible health risks and supersede the screening levels. DPR puts measures in place based on the regulatory target to limit exposures so that adverse effects can be avoided. Exceeding a regulatory target does not necessarily mean an adverse health effect occurs, but it does indicate that the restrictions on the pesticide use may need to be modified.

For monitoring results obtained from 2011-2016, we compiled the maximum air concentrations for each time period: acute (24-hr), Subchronic (4-week or 90-days depending on the AI), and chronic (1-yr). Only 19 pesticides that had quantifiable concentrations for any of the sampling time period (2011-2016) were compared to the established health screening level or regulatory target. For all years included in the monitoring, no pesticide exceeded any of the screening levels or regulatory target concentrations for any of the exposure periods at any of three sampling locations for any of the six years. Diazinon and its OA had the highest percentage of its acute screening level out of all pesticides monitored at 73.5%. 1,3-D had the highest subchronic screening level out of all pesticides monitored at 72.3%. Lastly, MeBr had the highest chronic screening level out of all pesticides monitored at 17.8%.

Cumulative exposures were calculated for 14 organophosphate pesticides included in the AMN that share a common mode of action (cholinesterase inhibition). Cumulative exposure was estimated using a hazard quotient (HQ) and hazard index (HI) approach that relies on the ratio between the detected air

concentration and the screening level (or regulatory target). The organophosphate cumulative exposures were estimated for each community and exposure period.

None of the HIs exceeded a value of 1.0 at any of the sampling locations during any of the sampling years, indicating that the screening levels were not exceeded for the combined 14 organophosphates. The highest acute HI of any site was at Shafter with an acute HI of 0.740 in 2011. Shafter also had the highest subchronic HI and chronic HI with values of 0.229 in 2011 and 0.088 in 2013, respectively. Additionally, using air concentrations for the 14 organophosphates for the sampling years 2011-2016, a 6-year chronic HI of 0.066 was determined for the Shafter sampling site which was the highest of the three sampling locations.

This report evaluates cancer risk of three pesticides measured at quantifiable concentrations that have been designated as potential carcinogens by California and by the United States Environmental Protection Agency (U.S. EPA): 1,3-D, chlorothalonil, and DDVP. DPR calculated the annual and 6-year average individual cancer risks for 1,3-D, chlorothalonil, and DDVP for each sampling location. Although individual annual cancer risk values were calculated and are included in this report, standard risk assessment procedures assume chronic exposure occurs every single day for a lifetime (70 years), therefore, the use of these shorter timeframes (annual estimates) are less suitable for comparison to a 70-year target and are shown for illustrative purposes only. Calculations in this report show that the total 2011-2016 cancer risk levels for each pesticide determined at all three sampling sites were in the range of what DPR considers to be negligible (risk in the range of 10^{-5} to 10^{-6} or less).

Section 4: Pesticide Use Information *(pages 49– 64)*

Pesticide use data near the sampling sites in Ripon, Salinas, and Shafter was obtained from DPR's pesticide use reporting (PUR) system from February 1, 2011 to December 31, 2016. A 5-mi radius around each of the sites was overlaid onto a Public Land Survey System's (PLSS) section map layer in ArcGIS and section ID numbers were extracted. A proportion value was assigned to each section depending on the actual portion of that section that was within the specified distance from the site location. Each record of lbs of AI was then multiplied by the proportion factor to yield the adjusted pounds (Adj. Lbs). In this section we display total pesticide amount used for each of the 31 pesticides included in the AMN occurring within a 5-mile radius of each sampling site. Annual sums within the 5-mile radius of each site ranged from 0 to 304,358 pounds depending on the pesticide and location. Of the 31 pesticides, the pesticides with the largest sums of pounds applied at all three sampling sites from 2011 to 2016 were: 1,3-D, MITC, and MeBr, in that order.

Section 5: Air Concentrations and Reported Agricultural Use of Selected Pesticides *(pages 65 – 84)*

This section displays measured air concentrations and compares them to reported pesticide use over time at each of the three sampling locations. The pesticides in this section were selected because they had a high percentage of quantifiable detections each year. The pesticides included in this section include the fumigants 1,3-D, chloropicrin, MeBr, and MITC as well as two organophosphates, chlorpyrifos and diazinon. Both air concentrations and reported use are expressed as rolling 4-week averages. They are shown over time (2011-2016) for each pesticide at each sampling site, allowing six years of data to be viewed together. No overall patterns are evident from this simple visual comparison but allow the reader to visually assess if detections occur during times of high use. It is worth noting that one cannot tell from a visual inspection alone whether observed trends are statistically significant. Therefore, Sections 6, 7, and 10 provide additional advanced statistical analyses of varying levels to better address this question.

Section 6: Simple Linear Regression Analysis of Selected Pesticides and Their Use *(pages 85 – 114)*

DPR is interested in examining what relationships exist between pesticide use and air concentrations for subchronic and chronic time periods over the years 2011 - 2016 at the sampling sites of Ripon, Salinas, and Shafter. We begin by applying a simple linear regression model to reported pesticide use and concentration to test whether a relationship exists between the two quantitative variables. In later sections, we use more complex analyses. A selection of six pesticides and two degradates were included in this model: 1,3-D, chloropicrin, chlorpyrifos and its oxygen analog, diazinon and its oxygen analog, MITC, and MeBr. Model results showed a weak positive relationship between pesticide use and measured concentrations for most of the pesticides analyzed at all three sampling locations for subchronic time periods. While, for chronic time periods, only data from the Shafter sampling location showed any statistically significant relationship between use and concentrations for all pesticides analyzed with the exception of MeBr and diazinon. Several factors contributed to the difficulty of correlating subchronic and chronic concentrations with reported use data: the large number of non-detections, weeks with no reported use but with detected concentrations, and multiple changes to laboratory analytical methods that resulted in decreasing detection limits.

Section 7: Application of Emission Ratios, Gaussian Plume Functions, and Meteorological Data in the Analysis of Use-Concentration Relationships of 1,3-Dichloropropene *(pages 115 – 129)*

In this section, we attempt to explain 1,3-D use-concentration relationship using pesticide use data along with several additional variables. Additional variables include refined estimates of the proportion of mass emitted from fumigated fields depending on application method (called 'emission ratios', or 'ERs'), flux profiles (fumigant mass emitted from a field over time), meteorological data, and spatial data (including distance and direction of a fumigation from a monitoring site). Rather than applying these data as variables in a multiple linear regression, these variables were implemented into a function that attempts to estimate air concentration based on use data and environmental conditions, which is then compared to measured air concentration data using regression methods. The process uses a relatively simple pollutant dispersion function to approximate the relative impact of an application in accordance with meteorological conditions, application method, and distance from an air sampling location.

We found evidence of a positive relationship between predicted and measured 1,3-D concentrations at all three sampling locations. The predicted concentrations exceeded measured concentration by approximately an order of magnitude, but produced fits with the measured data that were approximately linear. Goodness-of-fit measures varied substantially by site, with R^2 values of 0.50 at Shafter, 0.79 at Salinas, and 0.93 at Ripon.

The value of slope coefficients varied by site, indicating the presence of some site- or region-specific variables for which we were unable to account. The slope between predicted and measured concentration at Shafter was approximately 3 times greater at Ripon, and 8 times greater than Salinas. The difference appears to result from a greater increased in measured 1,3-D air concentrations per unit mass applied at Shafter as compared to the other two locations, a relationship for which the model is unable to fully account.

The results of this work suggest that fumigant air concentrations can be estimated based on fumigant use data using this simple model provided the availability of high-quality meteorological data and accurate flux estimates. However, additional work is still needed to better understand and account for the sources of site-to-site variations.

Section 8: Analysis of Sampling Frequency *(pages 130 – 136)*

Previous sampling frequency analysis determined that no significant differences existed in the sampling results of different days of a week and different locations of a community. Based on this analysis, DPR determined that sampling once a week at one location in each of three communities was sufficient to provide a representative weekly air concentration for the AMN. After collecting 6-years' worth of weekly

air sampling data at the three sampling site locations, we revisit the sampling frequency questions with this larger data set. We compared sampling results between different days of a week for all the pesticides that had a certain amount of detections during 2011 – 2016. For some pesticides showing certain patterns, further analysis was performed to evaluate the possible cause and its impact on the AMN results.

Due to the high portion of non-detects in the AMN data, several non-parametric statistical methods were used in the analysis. Results from the sampling frequency analysis showed that the sampling was not equally distributed among all seven days of the week during the 2011–2016 sampling period, instead data analysis shows that the actual distribution of sampling days was skewed towards Monday, Tuesday and Wednesdays with more than 90% of the sampling started on Monday to Thursday. Given this section information, DPR improved the AMN's random sampling schedule by ensuring that sampling start days include Fridays to Sundays more consistently.

Although the skewed sampling frequency limited our capability to analyze differences in sample results based on different days of the week. Using data for chlorothalonil and carbon disulfide, we were able to show a lack of significant difference between days of a week and measured concentrations. A linear regression model was used to establish that the percentage of quantifiable detections increases on average by 3.8 for every 100 additional collected samples. As a result, although larger sample size could result in more detections, the effect is relatively weak.

Section 9: Analysis of Selected Non-Detected Pesticides *(pages 137 – 145)*

Six pesticides were never detected at quantifiable concentrations at any of the sampling sites. They are: cypermethrin, DEF, dicofol, dimethoate, endosulfan sulfate, and oxydemeton-methyl. We explored the pesticide's volatility, meteorological information, and reported use within a 5-mi radius of each sampling site location to explain why none of these pesticides were detected at any of the sampling sites during the 2011 - 2016 sampling period.

Pesticide use data indicated DEF, Dicofol, and endosulfan had little to no reported use within a 5-mi radius of a sampling site location which explains the lack of AMN detections of these three pesticides. Although there was some reported cypermethrin use within 5-miles from the three sampling site locations, the low volatility associated with the pesticide may have resulted in this AI having no quantifiable air concentrations at any of the sampling site locations in any year. Reported pesticide use for dimethoate and oxydemeton-methyl near the sampling sites was mostly applied via ground application methods, which could of limit off-

site movement during and immediately following applications leading to a lack of AMN detections of this AI.

Section 10: Assessment of Mitigation Effects Based on Time Series Analysis of Pesticide Air Concentrations

(pages 146 – 171)

The AMN is designed to monitor ambient air concentrations of soil fumigants and other pesticides in agricultural communities of high pesticide use. Over the last few years (2011 – 2016), DPR and the U.S. EPA have put mitigation procedures in place to control off-site emissions of the several fumigants including: MeBr, MITC, and 1,3-D. In this section, a time series analysis of air concentrations of MeBr, MITC, and 1,3-D was conducted to assess the effect of implemented mitigation actions (interventions) on measured air concentrations. For this analysis, we used an ARIMA model with input series to estimate the effect of the intervention (mitigation action), this process is often referred to as intervention analysis or interrupted time series analysis.

Although multiple mitigation measures adopted by DPR or U.S. EPA were used in this intervention analysis, assessing the specific implementation timing of the mitigation measures was almost impossible to determine due to implementation time lags and other factors that make it difficult to incorporate in the statistical models used for this analysis. Therefore, the intervention analysis was based on a combination of multiple measures occurring at different points in time, rather than due to a unique action at a specific point in time. Overall significant relationships were established between air concentrations and mitigation measures at some sampling sites depending on the fumigant. MeBr air concentrations showed a significant decreasing pattern resulting from interventions occurring at the end of 2015 in all three locations. In general, there was a small but significant decrease in MITC concentrations in 2015 for Ripon and Salinas, resulting from U.S. EPA and DPR actions aimed at restricting use. Contrary to the other two fumigants, the model was unable to determine any significant correlation between the 1,3-D use series and corresponding air concentration series with the available data and model used. This is likely due an increase in 2011–2016 demand in its use to compensate for the decline in MeBr use.

Caution should be taken when attempting to expand on these ARIMA results in a mechanistic way, because additional unknown covariates may also be responsible for driving fumigant air concentrations. However, this empirical approach does provide DPR with another tool to investigate the possible effects of mitigation measures on air concentrations.

Collecting samples and conducting over 34,000 analyses for 36 chemicals as well as analyzing both concentration and use data collected for six years adds substantially to our knowledge of pesticides in air, and not just in the three communities where sampling sites were located. Data from this report can be extrapolated to predict pesticide air concentrations in many other communities that share similar pesticide use, cropping patterns, geography, meteorological conditions, and other factors.

The AMN data also meet DPR's mandate for "continuous evaluation." California law requires DPR to conduct "continuous evaluation" of currently registered pesticides. DPR uses this data to evaluate use practices to detect possible problems, determine if current regulatory measures are effective, or if further regulatory measures are required. The AMN provides a powerful tool to accomplish these legal requirements, helping to ensure that pesticide exposure is below any level of concern.

Contents

Section 1:

Air Monitoring Network

Introduction

From 2011 – 2016, the Department of Pesticide Regulation (DPR) conducted the first of its kind intensive pesticide ambient air monitoring study in three sampling locations in California. As part of the initial Air Monitoring Network (AMN), DPR collected weekly 24-hr air samples at each sampling location for six years. Collected air samples were analyzed for at least 36 pesticide and pesticidal breakdown products. Each year, DPR has released an AMN annual report to highlight air concentrations measured the previous year. Although these annual reports provide detailed sampling results, they focus only on measured air concentrations for that year and tend to lack additional information and analyses (e.g., comparison with reported pesticide use and statistical analysis of the results). DPR is not able to provide the most recent pesticide use data that would make concentration vs use and other statistical analyses possible because of the inherent pesticide use reporting time lag. Reported pesticide use is not finalized by DPR until 12 to 24 months following the calendar year in which the applications took place to ensure that all reported use data is properly vetted and accurate. For example DPR will not officially release 2017 use information until sometime in 2019. Therefore, since use data of the same year as the air sampling would be limited or incomplete, DPR has not conducted advanced analysis of the AMN measured air concentrations in its annual reports. For the first time in this report we provide a comprehensive evaluation of measured air concentrations collected in the AMN from 2011 to 2016 and relate that information to use and other variables in a variety of complex analyses. The specific goals of this report are the following:

- Provide pesticide air concentration data for the first six years of the study
- Describe quality assurance and quality control procedures of the sampling data
- Provide reported pesticide use information near the sampling site locations
- Graphically present air concentration data and reported use data for six years
- Use linear regressions to analyze measured air concentrations and reported use data
- Perform advanced statistical analysis using multiple variables to assess use-concentration relationship for the fumigant 1,3-dichloropropoene (1,3-D)
- Reevaluate AMN sampling frequency to ensure sampling schedule meets the needs of the AMN

- Determine why several pesticides have not been detected by the AMN
- Assess effects of mitigation measures on fumigant air concentrations near sampling site locations.

Some of the above objectives have been requested by multiple stakeholders during the various AMN annual report comment periods; while others are ones that DPR planned to accomplish with this larger dataset in order to view the results more comprehensively, to help plan future monitoring activities, and to ensure that the resources available for air monitoring are being used effectively. This report includes data from February 1, 2011 to December 31, 2016.

Background

In February 2011, DPR implemented the AMN to measure multiple pesticides in various agricultural communities (Neal et al. 2010). The goals of the AMN are to provide data that assists in assessing potential health risks, developing measures to mitigate risks, and measuring the effectiveness of regulatory requirements. Specifically, the AMN objectives are to:

- Identify pesticides in air and determine seasonal, annual, and multiple-year concentrations,
- Compare concentrations to subchronic and chronic health screening levels,
- Track trends in air concentrations over time,
- Estimate cumulative exposure to multiple pesticides with common physiological modes of action in humans (e.g., cholinesterase inhibitors), and
- Attempt to correlate concentrations with use and weather patterns.

As part of the initial process to select sampling site locations for the AMN, communities were prioritized based on pesticide use (both local and regional), demographic data, and availability of other exposure and health data (Neal et al. 2010). Based on these factors, the three communities of Salinas (Monterey County), Shafter (Kern County), and Ripon (San Joaquin County) were selected for the AMN. Starting in February 2011, a randomized 24-hr weekly air sample set was collected at each of the three AMN sampling locations. The collected air samples were analyzed for 31 pesticides and 5 pesticide breakdown products.

Communities and Sampling Site Locations

Ripon

Ripon, a town of 4.2 square miles in area, is located approximately 20 miles south of Stockton in San Joaquin County (Figure 1). The monitoring site is located in an open area behind the police station on 259 N Wilma Avenue near the western side of the city.

Shafter

Shafter, a city of 18 square miles in area, is located approximately 18 miles west-northwest of Bakersfield in Kern County (Figure 1). The monitoring site is situated at a city well location adjacent to Shafter High School in the northeastern edge of the city.

Salinas

Salinas, a city of 19 square miles in area, is located approximately 15 miles northeast of the city of Monterey in Monterey County (Figure 1). The monitoring site is located at the Salinas Airport in the southeastern section of the city.

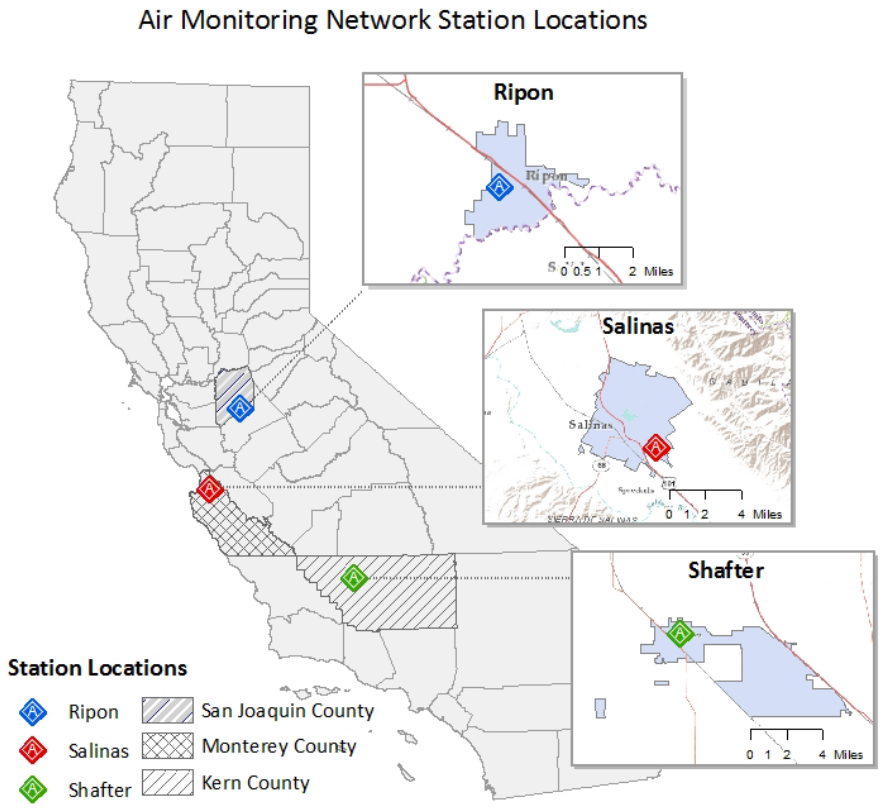


Figure 1. Map showing the locations of the three communities and monitoring sites.

Pesticides Monitored

As part of the AMN, DPR monitored for 36 chemicals (31 pesticides and 5 pesticide breakdown products). Chemicals included in the AMN were selected based primarily on potential health risk (Vidrio et al. 2013). Four analytical methods were used to analyze the collected air samples: (1) multi-pesticide residue analysis, (2) volatile organic compounds (VOC) analysis, (3) methyl isothiocyanate (MITC) analysis, and (4) chloropicrin analysis.

Multi-Pesticide Residue Analysis

Prior to sampling, personnel from the California Department of Food and Agriculture's (CDFA's) Center for Analytical Chemistry washed, rinsed, and packed 30 mL of XAD-4 sorbent material into a custom built Teflon® cartridge (4.8" in length and 1.9" in diameter) to collect for the 32 analytes to be analyzed in the multi-pesticide residue analysis. As part of sample collection, ambient air was drawn through the XAD-4 media with an SKC® AirChek HV30 air pump, calibrated at a flow rate of 15 L/min (± 10%) for a continuous 24-hr period. The cartridge was connected to the pump using a combination of threaded ABS plastic fittings, nitrile rings, and approximately 8 feet of Tygon® (or similar) tubing which were all downstream of the sample media. The Teflon® tube containing the sample media was kept sealed prior to sampling at which time the inlet of the cartridge itself was open to the ambient air. Bios Defender 530® or DC-Lite® flow meters were used to obtain flow rates at the start and end of the sampling period.

Multi-pesticide residue analysis using XAD-4 resin was performed by CDFA's Center for Analytical Chemistry laboratory using gas chromatography–mass spectrometry (GC-MS) and liquid chromatography–mass spectrometry (LC-MS) methods as described elsewhere (CDFA 2008). This analysis can detect a variety of fungicides, insecticides, herbicides, and defoliants. The breakdown products of chlorpyrifos, diazinon, dimethoate, endosulfan and malathion were also included in the multi-pesticide residue analysis method. Table 1 lists the 32 analytes included in the multi-pesticide residue analysis.

Table 1. Target analytes in the multi-pesticide residue analysis.

Pesticide Group	Chemical Class	Chemical
Defoliant	Organophosphate	DEF (SSS-tributylphosphorotrithioate)
Fungicide	Chloronitrile	Chlorothalonil
	Dicarboximide	Iprodione
Herbicide	Carbamate	EPTC
	Chloracetanilide	Metolachlor
	Dinitroaniline	Oryzalin
		Trifluralin
	Diphenyl ether	Oxyfluorfen
	Organophosphate	Bensulide
	Phthalate	Chlorthal-dimethyl
	Pyridazinone	Norflurazon
	Triazine	Simazine
	Urea	Diuron
Insecticide	Organochlorine	Dicofol
		Endosulfan
	Organophosphate	Acephate
		Chlorpyrifos
		Diazinon
		Dimethoate
		Malathion
		Methidathion
		DDVP
		Oxydemeton-methyl
		Phosmet
	Organosulfite	Propargite
	Pyrethroid	Cypermethrin
		Permethrin
Degradate	Organochlorine	Endosulfan Sulfate
	Organophosphate	Chlorpyrifos Oxygen Analog
		Diazinon Oxygen Analog
		Dimethoate Oxygen Analog
		Malathion Oxygen Analog

Volatile Organic Compound Analysis

A 6-L SilcoCan® canister (cat. # 24142) was pre-evacuated to a pressure of -30 ”Hg for VOC analysis. A Restek flow controller (cat. # 24160) was attached to the canister inlet to achieve a flow rate of 3.0 mL/min (± 10%) for a continuous 24-hr sampling period. The inlet of the flow controller assembly was extended to match the sampling height of the sorbent tubes with approximately 8 feet of 1/16” internal diameter PTFE

(Teflon®) tubing. Bios Defender 530® or DC-Lite® flow meters were used to check the flow rate at the start and end of the sampling period.

Collected air canisters were analyzed for the presence of three analytes (Table 2) using a VOC GC-MS method similar to the U.S. Environmental Protection Agency's (U.S. EPA) TO-15 method as described by CDFA (2008).

MITC

SKC® Anasorb® CSC sorbent sample tubes containing coconut charcoal as the activated sampling media (cat. # 226-16-02) were used to collect the analyte MITC. These tubes measured 10mm in diameter by 160mm in length and contained 1,800 mg of sorbent in the primary sample region. Ambient air was drawn through the media by an SKC® XR series pump (PCXR8 or PCXR4) at a flow rate of 1.5 L/min (± 10%) for a continuous 24-hr sampling period. The glass tube containing the sample media was connected to the pump with approximately 8 feet of Tygon® tubing, downstream of the sample media. The glass tips sealing the sampling media were broken open immediately prior to sampling. Bios Defender 530® or DC-Lite® flow meters were used to obtain flow rates at the start and end of the sampling period.

Samples collected on these sorbent tubes were analyzed for residues of MITC by GC-MS as described by CDFA (2004). MITC extraction from the sorbent medium involves using carbon disulfide in ethyl acetate with subsequent analysis using a gas chromatography-nitrogen phosphorous detector (GC-NPD).

Chloropicrin

SKC® XAD-4 sorbent sample tubes (cat. # 226-175) were used to collect the analyte chloropicrin. These tubes measured 8mm in diameter and 150 mm in length and contained 400 mg of sorbent material in the primary sample region. Ambient air was drawn through the media by an SKC® XR series pump (PCXR8 or PCXR4) at a flow rate of 50 mL/min (± 10%) for a continuous 24-hr sampling period. The glass tube containing the sample media was connected to an adjustable low-flow single tube holder (SKC cat. # 224-26-01) which was in turn connected to the pump with approximately 8 feet of Tygon® tubing, all of which were downstream of the sample media. The glass tips sealing the sampling media were broken open to allow airflow immediately prior to sampling and the inlet was open directly to the ambient air. Bios Defender 530® or DC-Lite® flow meters were used to obtain flow rates at the start and end of the sampling period.

SKC® XAD-4 sample tubes were analyzed for residues of chloropicrin by gas chromatography-electron capture detector (GC-ECD) as described by CDFA (1999). Each tube was desorbed in hexane and analyzed by a gas chromatograph equipped with GC-ECD.

Table 2. Target analytes in the volatile organic compound and individual analyte residue analysis.

Pesticide	Pesticide Group	Chemical Class
VOC Analysis		
1,3-Dichloropropene	Fumigant	Halogenated organic
Methyl Bromide	Fumigant	Halogenated organic
Carbon Disulfide	Fumigant	Inorganic
Individual Analyte Analysis		
MITC	Fumigant	-
Chloropicrin	Fumigant	Halogenated organic

Field Sampling Procedure

Chain of custody (COC) forms, sample analysis request forms, and sample labels including the study number and unique sample identification numbers were supplied to field sampling personnel to be attached to sampling tubes, cartridges, and canisters prior to sampling.

Each of the four sample types detailed above were set up and started at the same time, except for the occasional make-up sample needed to replace an invalidated sample. These make-up samples were typically run on the day following an invalidation event. Reasons why samples might be deemed invalid include but are not limited to the following: sampling period out of range, ending flow or pressure out of acceptable range, power interruptions, glass tube breakage during removal (e.g., damaged sampling media), and inoperative sampling equipment. The starting flow rates were measured prior to air sample collection and if any were determined to be out of the acceptable range (± 10% of target flow value), that sampling equipment was recalibrated to within an acceptable tolerance. As the air sampling commences at each monitoring site, the sample tracking number, date, time, staff initials, weather conditions, and air sampler flow rate were documented on a COC form.

Sampling Procedure

One 24-hr sample set was collected each week at each of the three sites. The starting day varied each week with the actual dates being randomly selected. Actual sampling start times were left to the discretion of the field sampling personnel, but sampling always started anywhere from 7:30 a.m. to 3:30 p.m.

Quality Control Methods

In addition to the primary samples, DPR collected quality control samples including trip blanks, field spikes, and co-located duplicate samples at a rate of 10% of primary samples. A later section of this report summarizes the results of these quality control procedures.

A trip blank sample provides information on possible contamination of samples. For the manufactured pre-packed XAD-4 and charcoal sample tubes, the ends were broken open, capped and placed on dry ice with the field samples. The multi-pesticide residue XAD cartridges were opened in the field, capped, and placed on dry ice to be stored and shipped with the field samples. No air canister trip blanks were collected. Trip blanks collected from each sampling site were randomly selected and collected at least once every month of sampling. If any trip blank sample contained detectable amounts of any of the pesticides, that would indicate a problem with contamination during transport or during laboratory extraction.

A field spike is a sample with a known amount of chemical spiked onto the sample media, which is placed next to a primary sample that undergoes the same air flow and run time conditions. The field spike is stored under dry ice (-78.5°C) during transport for sorbent tubes and cartridges, and at ambient temperature for canisters. It is treated similarly to a field sample, undergoing the same storage and shipping conditions. The field spiked sample, when compared to the primary sample, provides some information about any change in the ability to recover the analyte during air sampling. DPR collected one field spike sample per month for each sample type. The multi-pesticide residue XAD cartridge was spiked with two different analytes every month. For chloropicrin- and MITC-spiked samples, spiked concentrations varied every month. VOC canister spike samples were collected at a randomly selected site every other month.

An acceptable range of spike recoveries for the AMN was established by analyzing blank-matrix spike samples at five replicate analyses at five different spike levels. The mean percent recovery and standard deviation (SD) were determined based on these 25 data points. The control limits were then established as the mean percent recovery ± 3 SDs. Spike samples outside of the control limits established for each pesticide does not necessarily indicate that the obtained results are deemed invalid or unusable, however, it would indicate the need for a further and more refined assessment of the field and laboratory procedures to determine the cause. Depending on the results of this assessment, DPR may deem that changes to field and laboratory procedures are necessary.

Additionally, to look for sample analyte breakthrough in the sampling media, a method trapping efficiency was conducted for the AMN samples. Two-stage air samples were collected and analyzed to determine the proportion of the spike trapped in the bottom stage to assess for possible sample breakthrough.

A duplicate sample is a sample that is co-located with a regular field sample. These samples evaluate overall precision in sample measurement and analysis. DPR collected one duplicate sample for each sample type once per month.

Method calibration

The laboratory verified calibration by analyzing a series of standard samples (samples containing known amounts of analyte dissolved in a solvent). The linear range of calibration was determined by analyzing standards of increasing concentration. Within the linear range, the calibration was determined by regressing the standard concentration on the response of the instrument (peak height or peak area of the chromatogram) using at least five concentrations. The minimum acceptable correlation coefficient of the calibration was given in the standard operating procedure for each method, but in general was at least 0.95.

Method detection limits and limits of quantitation

The method detection limit (MDL) is the lowest concentration of a pesticide (analyte) that a chemical method can reliably detect. The laboratory determined the MDL for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. This standard is analyzed at least 7 times, and the MDL is determined by calculating the 99% confidence interval of the mean.

The limit of quantitation (LOQ) is the level at which concentrations may be reliably measured quantitatively and is set at a certain factor above the MDL. The level of interference determines the magnitude of this factor; the more interference, the higher the factor. Table 3 lists the MDLs and LOQs for the AMN analytes. During the study some of these limits were lowered due to increased sensitivity of the analytical processes being used. For the VOC samples collected in the summa canister, the MDL and LOQ remained the same; therefore, all those samples were either quantifiable or non-detects, with no possibility of trace detections.

Table 3. Method detection limits and limits of quantitation for Air Monitoring Network analytes.

Analyte	MDL (ng/m^3)	LOQ (ng/m^3)
1,3-D **	-	-
10/16/13 - 12/31/16	45.4 (0.01 ppb)*	45.4 (0.01 ppb)*
6/20/11 - 10/15/13	454 (0.1 ppb)*	454 (0.1 ppb)*
1/1/11 - 6/19/11	4540 (1.0 ppb)*	4540 (1.0 ppb)*

Analyte	MDL (ng/m^3)	LOQ (ng/m^3)
Acephate	1	9.3
Bensulide	1.4	9.3
Carbon Disulfide **	-	-
10/16/13 - 12/31/16	31.1 (0.01 ppb)*	31.1 (0.01 ppb)*
6/20/11 - 10/15/13	311 (0.1 ppb)*	311 (0.1 ppb)*
1/1/11 - 6/19/11	3110 (1.0 ppb)*	3110 (1.0 ppb)*
Chloropicrin **	-	-
6/19/13 - 12/31/16	222	694
1/1/11 - 6/18/13	222	2778
Chlorothalonil	13.7	23.1
Chlorpyrifos	5	23.1
Chlorpyrifos OA	2.9	9.3
Cypermethrin	4.7	23.1
Chlorthal-dimethyl	1.7	9.3
DDVP	3.2	23.1
DEF	1.8	9.3
Diazinon	1.2	9.3
Diazinon OA	2.1	9.3
Dimethoate	2.3	9.3
Dimethoate OA	1.9	9.3
Diuron	5.1	9.3
Endosulfan	3.2	23.1
Endosulfan Sulfate	4.6	23.1
EPTC	1.7	23.1
Iprodione	1.1	23.1
Malathion	2.2	9.3
Malathion OA	1.3	9.3
Methidathion	1.4	9.3
Methyl Bromide **	-	-
10/16/13 - 12/31/16	39.6 (0.01 ppb)*	39.6 (0.01 ppb)*
6/20/11 - 10/15/13	396 (0.1 ppb)*	396 (0.1 ppb)*
1/1/11 - 6/19/11	3960 (1.0 ppb)*	3960 (1.0 ppb)*
Metolachlor	2.7	9.3
MITC	5.6	23.1
Norflurazon	3.8	9.3
Oryzalin	1.4	23.1
Oxydemeton methyl	2.3	9.3
Oxyfluorfen	6.4	23.1
Permethrin	7.2	23.1
Phosmet	8	9.3
pp-Dicofol	2.1	23.1
Propargite	3.8	23.1
Simazine	1.2	9.3
Trifluralin	1.7	23.1

*For VOC analysis target analytes, MDL equals LOQ.

** Refinements in analytical methods caused these limits to decrease over time as shown.

Air Concentration Calculations

For the sorbent tube and cartridge samples, air concentrations were calculated as an amount of pesticide captured from a volume of air moving through the sampling media. Analytical results are presented in micrograms per sample (µg/sample). The concentrations are converted from µg/sample to nanograms per cubic meter (ng/m^3) of sample air using the following calculation:

$$\frac{Sample\,results\,(\mu g) \times 1000\,L/m^3}{Flow\,rate\,of\;sampler\,(L/\min) \times Run\,time\,(\min)} \text{ x 1000 ng/µg = ng/m}^3$$

The VOC concentrations were reported as parts per billion (ppb) and converted to ng/m^3 using the following calculations:

$$\frac{\text{Sample results (ppb)x Molecular weight (g mol}^{-1})}{24.45} \text{x } 1000 = \text{ng/m}^3$$

The calculation above assumes 1 atmosphere of pressure at 25°C and 24.45 is obtained from multiplication of the Universal Gas Constant (R) (82.06 atm.cm^3/(mol·K)) and temperature in degrees Kelvin (298 K) with appropriate unit conversions based on the ideal gas law[1].

Per standard DPR practice, when calculating average concentrations from multiple samples, samples with no detectable amounts were assumed to contain one-half the MDL (ND=0.5*MDL), and samples with trace amounts were assumed to contain the value halfway between the MDL and the LOQ (Trace= 0.5*(MDL+LOQ)).

Health Evaluation Methods

Pesticides can cause a variety of health effects when present at concentrations above health-protective levels. The pesticides included in the AMN were selected in part because (1) risk assessments indicate the potential for high exposure, or (2) they are high priority for risk assessment due to toxicity and/or exposure concerns. Some of the pesticides in the AMN can cause adverse effects such as respiratory illnesses,

[1] Ideal gas law: pV = nRT
where p = pressure, V = volume, n = number of moles, R = universal gas constant, and T = temperature

damage to the nervous system, cancer, and birth defects. Vidrio et al. (2013) summarize the potential health effects of each pesticide.

Health Screening Levels and Regulatory Targets

No state or federal agency has established health standards for pesticides in air. Therefore, DPR, in consultation with the Office of Environmental Health Hazard Assessment (OEHHA) and others, developed a health-based framework. Using this framework, measured air concentrations can then be compared to health screening levels or regulatory targets to evaluate potential human exposure.

Health screening levels are based on a preliminary assessment of possible health effects and are used as triggers for DPR to conduct a more detailed evaluation. A measured air concentration below the screening level for a given pesticide would not be considered a significant health concern and the pesticide would not undergo further evaluation at this time. A measured concentration above the screening level would not necessarily indicate a significant health concern, but would indicate the need for a further, more refined evaluation. Vidrio et al. (2013) summarize more information on DPR-determined screening levels including information on deriving screening levels for each pesticide.

Once a complete assessment of possible health risks is completed, regulatory targets are established, which supersede screening levels. Based on these regulatory targets, DPR puts measures in place to limit the exposures and avoid any adverse effects. Exceeding a regulatory target does not necessarily mean an adverse health effect has occurred, but it does indicate that the restrictions on the pesticide use may need to be modified. DPR normally establishes a regulatory target after completing a formal risk assessment of a chemical's toxicity and potential exposures. DPR management determines a regulatory target based on a comprehensive risk assessment, which draws upon input from other agencies, pesticide use patterns, potential effects on use of alternative or replacement pesticides, and various other factors. A regulatory target is based on a more comprehensive evaluation than is done for a health screening level. Therefore, a regulatory target supersedes a health screening level (i.e., a specific pesticide and exposure duration will have either a regulatory target or a health screening level, but not both). Four of the pesticides monitored in the AMN (chloropicrin, methyl bromide (MeBr), methyl isothiocyanate (MITC), and 1,3-D) have regulatory targets for one or more exposure periods (Table 4).

Table 4. Screening levels for each analyte and exposure period.

	Screening Levels (ng/m^3)		
Analyte	Acute (1-day)	Subchronic (4-wk)	Chronic (1-yr)
1,3-Dichloropropene	505,000	14,000	9,000
Acephate	12,000	8,500	8,500
Bensulide	259,000	24,000	24,000
Carbon Disulfide	1,550,000	800,000	800,000
Chloropicrin	491,000 *	2,300	1,800
Chlorothalonil	34,000	34,000	34,000
Chlorpyrifos	1,200	850	510
Chlorpyrifos OA	1,200	850	510
Cypermethrin	113,000	81,000	27,000
Chlorthal-dimethyl	23,500,000	470,000	47,000
DDVP	11,000	2,200	770
DEF	8,800	8,800	N/A - Seasonal
Diazinon	130	130	130
Diazinon OA	130	130	130
Dimethoate	4,300	3,000	300
Dimethoate OA	4,300	3,000	300
Diuron	170,000	17,000	5,700
Endosulfan	3,300	3,300	330
Endosulfan Sulfate	3,300	3,300	330
EPTC	230,000	24,000	8,500
Iprodione	939,000	286,000	286,000
Malathion	112,500	80,600	8,100
Malathion OA	112,500	80,600	8,100
Methidathion	3,100	3,100	2,500
Methyl Bromide	820,000 *	19,400 *	3,900
Metolachlor	85,000	15,000	15,000
MITC	66,000 *	3,000	300
Norflurazon	170,000	26,000	26,000
Oryzalin	420,000	230,000	232,000
Oxydemeton methyl	39,200	610	610
Oxyfluorfen	510,000	180,000	51,000
Permethrin	168,000	90,000	90,000
Phosmet	77,000	26,000	18,000
pp-Dicofol	68,000	49,000	20,000
Propargite	14,000	14,000	14,000
Simazine	110,000	31,000	31,000
Trifluralin	1,200,000	170,000	41,000

* These values are regulatory targets rather than screening levels.

Cumulative Exposures

Cumulative exposures were estimated using a hazard quotient (HQ) and hazard index (HI) approach for pesticides that have a common mode of action (e.g., cholinesterase inhibitors). The potential risk of the measured concentrations of a pesticide in air was evaluated by comparing the air concentration measured over a specified time (e.g., 24 hr, 4 week, or 1 year) with the screening level derived for a similar exposure (i.e., acute, subchronic, or chronic). The ratio of measured air concentration of a pesticide to a reference concentration or screening level for that pesticide is called the HQ. In this case,

$$\text{Hazard Quotient} = \frac{\text{Air Concentration Detected } (ng / m^3)}{\text{Screening Level } (ng / m^3)}$$

If the HQ is greater than 1, then the air concentration exceeds the screening level, which would indicate the need for further and more refined evaluation. Similarly, the risk from multiple pesticides (cumulative risk) is evaluated using the HI approach, which sums all of the HQs for the pesticides monitored.

$$HI = HQ_1 \text{ (pesticide 1)} + HQ_2 \text{ (pesticide 2)} + HQ_3 \text{ (pesticide 3)} + \ldots \text{ (and so forth)}$$

A HI greater than 1 indicates that the cumulative toxicity of the multiple pesticides should be further evaluated and that potential health impacts may have been missed by considering the pesticides individually.

Important Notes

Please note that the measured air concentrations for methyl iodide and acrolein are excluded from this report. Although these two pesticides were initially included in the AMN in 2011, these two pesticides have since been removed from the AMN due to either cancellation of sale of products containing the pesticide or due to the number of non-pesticidal sources of the active ingredient (AI) as previously detailed elsewhere (Vidrio et al., 2013; Tuli et al., 2017). Additionally, although carbon disulfide was also removed from the AMN at the end of 2016 (King et al., 2017), results for carbon disulfide are included in this report since the timeframe in which the pesticide was being monitored does include the complete timeframe included in this report, 2011-2016.

Due to the refinement of analytical techniques by the laboratory, the MDL and LOQ have been significantly lowered for a few of the analytes monitored. This includes successive refinements for the VOC's monitored using the air canister method. Therefore, depending on the data requirements of the statistical analysis being performed, not all collected air and use data are treated uniformly across all analysis performed as part of this report. In each section, each methodology used is explained as well as any data use deviations. Examples of using data differently include dividing a pesticide's air concentrations in several segments to account for analytical method date changes that can cause subtle data differences (e.g., 10-fold LOQ decrease).

Section 2:

Quality Assurance/Quality Control of Sampling Data

Method Validation

An acceptable range of spike recoveries was established by analyzing laboratory spike samples in five replicate analyses at five different spike levels. The mean percent recovery and SD were determined based on these 25 data points. The control limits were established as the mean percent recovery ± 3 SD. In addition, for the multi-pesticide sample, MITC, and chloropicrin methods, a method trapping efficiency was determined by collecting 2-stage air samples that were analyzed to determine the proportion of the spike trapped in the bottom stage to assess for possible sample breakthrough.

General Continuing Quality Control

Samples were stored at the DPR facility in West Sacramento under the care of the laboratory liaison until scheduled delivery to the CDFA analytical laboratory. Storage stability was evaluated for the longest anticipated holding period with at least four sampling intervals and two replicate samples at each sampling interval. All analytes have storage stability data for a minimum of 28 days. Each extraction set consisted of 5 to 20 actual samples and quality control (QC) samples which include a reagent blank, a matrix blank, and a matrix spiked sample. Any subsequent matrix spiked samples outside the control limits required the set of samples associated with that spike to be reanalyzed. Also, about 10% of the actual samples are accompanied by laboratory-spiked samples disguised as real samples (blind spike).

Quality Control Results

Laboratory matrix spikes and matrix blanks were included with every set of samples extracted and analyzed at the laboratory and are part of the laboratory QC program. The matrix spikes are conducted to assess accuracy and precision; the blanks are to check for contamination at the laboratory or contamination of the resin packed in the sorption tubes. The blank matrix materials were not fortified but were extracted and analyzed along with the matrix spikes and field samples.

Table 5 lists the averages for the laboratory blank samples that were extracted and analyzed with the air samples for the entire monitoring period. Table 6 lists the averages for the laboratory spike samples that were extracted and analyzed with the air samples for the entire monitoring period. Laboratory matrix spike

recovery averages ranged from 72% to 101% for all chemicals analyzed. None of the laboratory matrix spike samples were outside the control limits established from the validation data. A single laboratory blank, for bensulide, resulted in one trace detection. All remaining laboratory blanks resulted in NDs.

Table 5. Laboratory blank results.

	Year					
Chemical	2011	2012	2013	2014	2015	2016
Acephate	ND	ND	ND	ND	ND	ND
Bensulide	ND	ND	ND	ND	ND	†
Carbon Disulfide	ND	ND	ND	ND	ND	ND
Chloropicrin	ND	ND	ND	ND	ND	ND
Chlorothalonil	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND
Chlorpyrifos OA	ND	ND	ND	ND	ND	ND
Cypermethrin	ND	ND	ND	ND	ND	ND
Chlorthal-dimethyl	ND	ND	ND	ND	ND	ND
DDVP	ND	ND	ND	ND	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND
Diazinon OA	ND	ND	ND	ND	ND	ND
1,3-Dichloropropene	ND	ND	ND	ND	ND	ND
Dicofol	ND	ND	ND	ND	ND	ND
Dimethoate	ND	ND	ND	ND	ND	ND
Dimethoate OA	ND	ND	ND	ND	ND	ND
Diuron	ND	ND	ND	ND	ND	ND
Endosulfan	ND	ND	ND	ND	ND	ND
Endosulfan Sulfate	ND	ND	ND	ND	ND	ND
EPTC	ND	ND	ND	ND	ND	ND
Iprodione	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	ND	ND	ND	ND
Malathion OA	ND	ND	ND	ND	ND	ND
Methidathion	ND	ND	ND	ND	ND	ND
Methyl Bromide	ND	ND	ND	ND	ND	ND
Metolachlor	ND	ND	ND	ND	ND	ND
MITC	ND	ND	ND	ND	ND	ND
Norflurazon	ND	ND	ND	ND	ND	ND
Oryzalin	ND	ND	ND	ND	ND	ND
Oxydemeton methyl	ND	ND	ND	ND	ND	ND
Oxyfluorfen	ND	ND	ND	ND	ND	ND
Permethrin	ND	ND	ND	ND	ND	ND
Phosmet	ND	ND	ND	ND	ND	ND
Propargite	ND	ND	ND	ND	ND	ND
Simazine	ND	ND	ND	ND	ND	ND
SSS-tributyltriphosphorotrithioate (DEF)	ND	ND	ND	ND	ND	ND
Trifluralin	ND	ND	ND	ND	ND	ND

ND = None detected

† There was one trace detection for bensulide in 2016, all others were non-detects

Table 6. Laboratory spike average percent recoveries

	Percent Recovery by Year					
Chemical	2011	2012	2013	2014	2015	2016
Acephate	92	94	89	94	96	88
Bensulide	94	94	86	94	95	92
Carbon Disulfide	97	98	96	95	97	97
Chloropicrin	95	92	91	94	95	94
Chlorothalonil	91	95	90	96	97	75
Chlorpyrifos	92	96	92	95	98	92
Chlorpyrifos OA	95	94	86	93	95	89
Cypermethrin	91	97	90	95	95	91
Chlorthal-dimethyl	93	95	92	95	97	87
DDVP	88	89	87	91	94	83
Diazinon	95	94	89	90	94	94
Diazinon OA	95	95	87	95	96	93
cis-1,3-Dichloropropene	100	101	98	98	100	97
trans-1,3-Dichloropropene	99	101	97	98	100	96
Dicofol	97	98	93	98	98	87
Dimethoate	94	92	89	96	95	90
Dimethoate OA	96	94	89	96	95	94
Diuron	92	91	87	96	96	99
Endosulfan	94	95	92	95	97	88
Endosulfan Sulfate	96	98	92	97	98	90
EPTC	86	87	85	85	96	93
Iprodione	90	96	89	95	97	93
Malathion	95	98	94	96	99	92
Malathion OA	91	88	92	97	96	95
Methidathion	96	95	91	89	94	92
Methyl Bromide	98	95	96	97	97	96
Metolachlor	96	94	87	93	94	94
MITC	81	81	77	73	72	72
Norflurazon	96	93	87	96	96	95
Oryzalin	96	94	87	94	97	92
Oxydemeton methyl	96	95	92	87	93	92
Oxyfluorfen	94	98	94	99	99	80
Permethrin	90	99	89	94	95	92
Phosmet	95	94	87	96	95	91
Propargite	94	94	89	97	95	93
Simazine	96	94	86	95	95	93
SSS-tributyltriphosphorotrithioate (DEF)	97	96	91	91	94	90
Trifluralin	91	94	92	95	97	89

Field blanks, field spikes, and duplicate samples are part of DPR's field and laboratory QC program. The field spikes were fortified by a CDFA chemist. Field spikes contain a known amount of analyte and are taken to the field by staff and placed on the air samplers for 24-hrs in the same manner as actual field samples. Field spikes are extracted and analyzed in the same manner as the other field samples. Table 7 lists the field blank results for all years. In all years sampled, a total of three field blank samples resulted in a detection greater than a ND: two trace detections for malathion OA and one trace detection for chlorthal-dimethyl. All remaining field blanks resulted in non-detections. Table 8 lists the field spike average percent recovery results which ranged from 0% to 233% depending on the analyte and year.

Table 7. Field blank results.

	Year					
Chemical	2011	2012	2013	2014	2015	2016
Acephate	ND	ND	ND	ND	ND	ND
Bensulide	ND	ND	ND	ND	ND	ND
Carbon Disulfide	ND	ND	ND	ND	ND	ND
Chloropicrin	ND	ND	ND	ND	ND	ND
Chlorothalonil	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND
Chlorpyrifos OA	ND	ND	ND	ND	ND	ND
Cypermethrin	ND	ND	ND	ND	ND	ND
Chlorthal-dimethyl	ND	ND	ND	ND	ND	‡
DDVP	ND	ND	ND	ND	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND
Diazinon OA	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND
trans-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND
Dicofol	ND	ND	ND	ND	ND	ND
Dimethoate	ND	ND	ND	ND	ND	ND
Dimethoate OA	ND	ND	ND	ND	ND	ND
Diuron	ND	ND	ND	ND	ND	ND
Endosulfan	ND	ND	ND	ND	ND	ND
Endosulfan Sulfate	ND	ND	ND	ND	ND	ND
EPTC	ND	ND	ND	ND	ND	ND
Iprodione	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	ND	ND	ND	ND
Malathion OA	†	ND	ND	ND	ND	ND
Methidathion	ND	ND	ND	ND	ND	ND
Methyl Bromide	ND	ND	ND	ND	ND	ND
Metolachlor	ND	ND	ND	ND	ND	ND
MITC	ND	ND	ND	ND	ND	ND
Norflurazon	ND	ND	ND	ND	ND	ND
Oryzalin	ND	ND	ND	ND	ND	ND
Oxydemeton methyl	ND	ND	ND	ND	ND	ND
Oxyfluorfen	ND	ND	ND	ND	ND	ND
Permethrin	ND	ND	ND	ND	ND	ND
Phosmet	ND	ND	ND	ND	ND	ND
Propargite	ND	ND	ND	ND	ND	ND
Simazine	ND	ND	ND	ND	ND	ND
SSS-tributyltriphosphorotrithioate (DEF)	ND	ND	ND	ND	ND	ND
Trifluralin	ND	ND	ND	ND	ND	ND

ND = None detected

†There were two trace detections for Malathion OA in 2011, all others were non-detects

‡There was a single detection for Chlorthal-dimethyl in 2016, all others were non-detects

Table 8. Field spike average percent recoveries.

	Percent Recovery by Year					
Chemical	2011	2012	2013	2014	2015	2016
Acephate	80	83	83	72	74	117
Bensulide	77	94	82	70	90	67
Carbon Disulfide	NS	NS	NS	NS	NS	NS
Chloropicrin	73	81	80	86	81	100
Chlorothalonil	67	90	56	93	NS	77
Chlorpyrifos	71	NS	86	NS	75	102
Chlorpyrifos OA	67	NS	93	88	100	65
Cypermethrin	NS	72	80	60	74	81
Chlorthal-dimethyl	81	NS	98	83	95	111
DDVP	82	75	NS	83	79	133
Diazinon	NS	75	NS	91	47	50
Diazinon OA	NS	NS	NS	92	NS	0
cis-1,3-Dichloropropene	NS	91	132	96	71	79
trans-1,3-Dichloropropene	NS	NS	129	121	102	104
Dicofol	NS	124	121	NS	125	233
Dimethoate	NS	58	NS	84	79	72
Dimethoate OA	NS	78	NS	96	94	126
Diuron	NS	60	65	77	87	98
Endosulfan	NS	83	NS	90	87	98
Endosulfan Sulfate	NS	77	NS	96	91	95
EPTC	NS	70	NS	76	69	47
Iprodione	83	97	52	83	77	49
Malathion	NS	74	83	NS	72	96
Malathion OA	NS	51	96	NS	104	131
Methidathion	82	NS	195	NS	99	97
Methyl Bromide	NS	87	46	65	30	77
Metolachlor	NS	89	82	115	89	99
MITC	54	72	58	63	78	64
Norflurazon	NS	79	64	63	58	87
Oryzalin	43	56	0	44	1	NS
Oxydemeton methyl	71	NS	NS	29	47	46
Oxyfluorfen	NS	43	0	75	96	113
Permethrin	NS	83	NS	NS	NS	40
Phosmet	94	62	82	97	83	90
Propargite	NS	NS	70	76	115	77
Simazine	NS	81	NS	92	58	38
SSS-tributyltriphosphorotrithioate (DEF)	86	NS	104	87	70	NS
Trifluralin	NS	NS	49	53	NS	46

ND = None detected; NS = Field sample not spiked with the chemical.

Tables 9-12 summarize the results of duplicate samples per sampling analytical method (multi-pesticide, VOC, MITC, and chloropicrin). A duplicate sample is a sample that is co-located with another sample in the field. These samples serve to evaluate overall precision in sample measurement and analysis. The relative difference was calculated between each quantifiable pair and averaged for each sample media type. Relative percent difference results ranged from 3.1% to 164% depending on the type of collocated sample, analyte and year.

Table 9. Comparison of multi-pesticide co-located (duplicate) samples.

	Number of matches by year					
Primary/duplicate results	2011	2012	2013	2014	2015	2016
ND[a] / ND	213	507	445	443	397	331
Trace[b] / trace	6	18	21	28	16	20
ND / trace	4	18	8	6	2	1
ND / >LOQ	0	1	4	1	0	0
trace / >LOQ	0	0	0	0	0	0
>LOQ / >LOQ	1	0	2	2	1	0
Relative Difference[c]	6.6%	-	3.1%	7.5%	8.2%	-

[a] ND = None detected.

[b] Trace = Pesticide detection confirmed, but less than the quantitation limit.

[c] For pairs with both concentrations >LOQ.

Table 10. Comparison of VOC co-located (duplicate) samples.

	Number of matches by year					
Primary/duplicate results	2011	2012	2013	2014	2015	2016
ND[a] / ND	6	43	18	31	36	26
Trace[b] / trace	0	0	0	0	0	0
ND / trace	0	0	0	0	0	0
ND / >LOQ	0	0	3	3	1	0
trace / >LOQ	0	0	0	0	0	0
>LOQ / >LOQ	0	0	6	10	15	25
Relative Difference[c]	-	-	24.3%	29.1%	55.0%	36.9%

[a] ND = None detected.

[b] Trace = Pesticide detection confirmed, but less than the quantitation limit.

[c] For pairs with both concentrations >LOQ.

Table 11. Comparison of MITC co-located (duplicate) samples.

	Number of matches by year					
Primary/duplicate results	2011	2012	2013	2014	2015	2016
ND[a] / ND	5	8	11	10	12	8
trace[b] / trace	0	0	1	0	0	1
ND / trace	0	0	0	1	0	0
ND / >LOQ	0	2	4	2	1	0
trace / >LOQ	0	0	0	0	1	0
>LOQ / >LOQ	1	4	3	3	2	2
Relative Difference[c]	164.0%	11.3%	11.6%	12.8%	5.3%	5.5%

[a] ND = None detected.

[b] Trace = Pesticide detection confirmed, but less than the quantitation limit.

[c] For pairs with both concentrations >LOQ.

Table 12. Comparison of chloropicrin co-located (duplicate) samples.

	Number of matches by year					
Primary/duplicate results	2011	2012	2013	2014	2015	2016
ND[a] / ND	7	7	17	16	16	13
trace[b] / trace	0	0	0	0	0	0
ND / trace	0	0	0	0	0	0
ND / >LOQ	0	0	0	0	0	0
trace / >LOQ	0	0	0	0	0	0
>LOQ / >LOQ	0	0	0	0	0	0

[a] ND = None detected.

[b] Trace = Pesticide detection confirmed, but less than the quantitation limit.

Section 3:

Pesticide Air Concentrations

Pesticide Detections

From February 1, 2011, through December 31, 2016, there were 34,147 total analyses performed on air samples collected from all sampling site locations (Table 13). The number of analyses consists of the number of samples collected multiplied by the number of chemicals analyzed in each sample type (i.e., 1 multi-residue sample = 32 analyses). Of these 34,147 analyses, 7.5% (2,564 analyses) showed detectable concentrations, which include both quantifiable and trace detections (Table 14). Samples with quantifiable concentrations accounted for 2.9% (999 analyses) of all analyses performed (Table 15). Samples with no detections accounted for 89.6% (30,584 analyses) of all analyses performed.

Some deviations from the typical number of samples collected occurred for the following reasons: (1) a smaller number of total analyses performed were collected among all sites during the 2011 calendar year because sampling did not begin until February 2011, resulting in 11 (not 12) months of sampling data, and (2) some samples were invalidated for various reasons outlined in individual AMN annual reports available online (http://www.cdpr.ca.gov/docs/emon/airinit/air_network_results.htm).

Table 13. Total number of analyses performed during the 2011-2016 sampling period, by site.

	Total Analyses Performed			
Year	Ripon	Salinas	Shafter	Total
2011	1,769	1,744	1,739	5,252
2012	1,924	1,891	1,924	5,739
2013	1,923	1,955	1,961	5,839
2014	1,961	1,924	1,924	5,809
2015	1,921	1,924	1,892	5,737
2016	1,924	1,924	1,923	5,771
Total	**11,422**	**11,362**	**11,363**	**34,147**

Table 14. Percentage and count of positive detections during the 2011-2016 sampling period, by site.

	Total Detections (Trace or Quantifiable)			
Row Labels	Ripon	Salinas	Shafter	Total
2011	5.8% (103)	6.8% (118)	6.6% (115)	6.4% (336)
2012	4.7% (90)	5.4% (102)	6.7% (129)	5.6% (321)
2013	5.6% (107)	5.1% (99)	9.9% (194)	6.9% (400)
2014	7.4% (146)	6.4% (123)	10.4% (200)	8.1% (469)
2015	9.6% (184)	7.9% (152)	11.7% (222)	9.7% (558)
2016	8.2% (157)	6.8% (130)	10.0% (193)	8.3% (480)
Total	**6.9% (787)**	**6.4% (724)**	**9.3% (1,053)**	**7.5% (2,564)**

Table 15. Percentage and count of quantifiable detections during the 2011-2016 sampling period, by site.

	Quantifiable Detections			
Year	Ripon	Salinas	Shafter	Total
2011	1.8% (31)	1.2% (21)	1.8% (32)	1.6% (84)
2012	0.9% (18)	0.7% (14)	2.2% (43)	1.3% (75)
2013	1.5% (28)	1.9% (37)	3.5% (69)	2.3% (134)
2014	3.3% (64)	2.4% (46)	4.5% (86)	3.4% (196)
2015	4.3% (83)	3.5% (68)	5.7% (107)	4.5% (258)
2016	4.2% (80)	3.7% (72)	5.2% (100)	4.4% (252)
Total	**2.7% (304)**	**2.3% (258)**	**3.8% (437)**	**2.9% (999)**

The percentages of detections show minor fluctuations when considered across all sampling years (Table 14). From 2011 – 2016, the highest percentage of total detections and total quantifiable detections occurred in 2015 (Tables 14 and 15). Among the three communities, the percentage of total and quantifiable detections was higher in Shafter than in the other two communities, although the differences are small. Table 16 shows that only four pesticides had quantifiable detections occurring at least more than 5% of the analyses: 1,3-D, carbon disulfide, MeBr and MITC.

Table 16. Percentages and counts of detection types across all sites and years, by analyte.

Analyte	Total Analyses Performed	Total Detections	Quantifiable Detections
1,3-Dichloropropene	921	19.0% (175)	19.0% (175)
Acephate	923	0.2% (2)	0
Bensulide	923	0.8% (7)	0
Carbon Disulfide	921	40.9% (377)	40.9% (377)
Chloropicrin	924	4.0% (37)	2.1% (19)
Chlorothalonil	923	35.8% (330)	1.6% (15)
Chlorpyrifos	923	26.4% (244)	2.5% (23)
Chlorpyrifos OA	923	25.1% (232)	1.8% (17)
Cypermethrin	923	0	0
Chlorthal-dimethyl	923	21.2% (196)	0.1% (1)
DDVP	923	5.5% (51)	0.5% (5)
DEF	923	0	0
Diazinon	923	3.6% (33)	0.4% (4)
Diazinon OA	923	3.1% (29)	0.3% (3)
Dimethoate	923	0.1% (1)	0
Dimethoate OA	923	0.4% (4)	0
Diuron	923	7.5% (69)	0.5% (5)
Endosulfan	923	0.9% (8)	0
Endosulfan Sulfate	923	0	0
EPTC	923	3.3% (30)	2.4% (22)
Iprodione	923	3.7% (34)	0.3% (3)
Malathion	923	4.4% (41)	0.4% (4)
Malathion OA	923	14.1% (130)	0.1% (1)
Methidathion	923	0.4% (4)	0
Methyl Bromide	921	13.1% (121)	13.1% (121)
Metolachlor	923	0.5% (5)	0
MITC	924	26.2% (242)	21.8% (201)
Norflurazon	923	0.4% (4)	0
Oryzalin	923	1.5% (14)	0.2% (2)
Oxydemeton methyl	923	0	0
Oxyfluorfen	923	1.3% (12)	0.1% (1)
Permethrin	923	0.9% (8)	0
Phosmet	923	0.1% (1)	0
pp-Dicofol	923	0	0
Propargite	923	3.6% (33)	0
Simazine	923	3.1% (29)	0
Trifluralin	923	6.6% (61)	0
Total	**34,147**	**7.5% (2,564)**	**2.9% (999)**

Air Sampling Results by Sampling Location

Salinas

A total of 11,362 analyses were collected at Salinas from 2011 – 2016 (Table 17). Of the 11,362 analyses, 724 (6%) resulted in detections: 258 were quantifiable (2% of analyses performed). Chlorthal-dimethyl had the highest number of detections in Salinas; the number of samples resulting in any detection (trace or quantifiable) ranged from 40% to 67% depending on the year (Table 18). However, only one of these detections was quantifiable and in one year only (2014). All other chlorthal-dimethyl detections were at trace levels (Tables 18 and 19). The percentage of total detections for carbon disulfide was 41%; lower percentages of total detections occurred in the early years. The lower percentages of detections may be due to the higher analytical method limits used during the early AMN years. These adjustments occurred in 2011 and 2013. However, as detailed in King et al. (2017), carbon disulfide levels are believed to originate from non-pesticidal sources. The oxygen analog (OA) of malathion was the last analyte for which analyses produced more than 25% of the total detections, although none of these were quantifiable (Tables 18 and 19). Monitoring for the parent compound itself, malathion, resulted in 11% of samples showing a detection, of which only 1% (4 samples) were quantifiable.

Table 17. Count of individual analyses performed for each analyte per year for Salinas.

	Total Analyses Performed						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	48	52	51	52	52	52	307
Acephate	47	51	53	52	52	52	307
Bensulide	47	51	53	52	52	52	307
Carbon Disulfide	48	52	51	52	52	52	307
Chloropicrin	47	52	53	52	52	52	308
Chlorothalonil	47	51	53	52	52	52	307
Chlorpyrifos	47	51	53	52	52	52	307
Chlorpyrifos OA	47	51	53	52	52	52	307
Cypermethrin	47	51	53	52	52	52	307
Chlorthal-dimethyl	47	51	53	52	52	52	307
DDVP	47	51	53	52	52	52	307
DEF	47	51	53	52	52	52	307
Diazinon	47	51	53	52	52	52	307
Diazinon OA	47	51	53	52	52	52	307
Dimethoate	47	51	53	52	52	52	307
Dimethoate OA	47	51	53	52	52	52	307
Diuron	47	51	53	52	52	52	307
Endosulfan	47	51	53	52	52	52	307
Endosulfan Sulfate	47	51	53	52	52	52	307
EPTC	47	51	53	52	52	52	307
Iprodione	47	51	53	52	52	52	307
Malathion	47	51	53	52	52	52	307
Malathion OA	47	51	53	52	52	52	307
Methidathion	47	51	53	52	52	52	307
Methyl Bromide	48	52	51	52	52	52	307
Metolachlor	47	51	53	52	52	52	307
MITC	49	51	53	52	52	52	309
Norflurazon	47	51	53	52	52	52	307
Oryzalin	47	51	53	52	52	52	307
Oxydemeton methyl	47	51	53	52	52	52	307
Oxyfluorfen	47	51	53	52	52	52	307
Permethrin	47	51	53	52	52	52	307
Phosmet	47	51	53	52	52	52	307
pp-Dicofol	47	51	53	52	52	52	307
Propargite	47	51	53	52	52	52	307
Simazine	47	51	53	52	52	52	307
Trifluralin	47	51	53	52	52	52	307
Total	**1,744**	**1,891**	**1,955**	**1,924**	**1,924**	**1,924**	**11,362**

Table 18. Percentage and count of total detections during the 2011-2016 sampling period in Salinas.

	Total Detections						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	6% (3)	2% (1)	16% (8)	4% (2)	19% (10)	25% (13)	12% (37)
Acephate	2% (1)	0	0	0	0	0	0% (1)
Bensulide	9% (4)	0	0	0	2% (1)	0	2% (5)
Carbon Disulfide	0	2% (1)	14% (7)	44% (23)	88% (46)	92% (48)	41% (125)
Chloropicrin	6% (3)	0	13% (7)	10% (5)	15% (8)	13% (7)	10% (30)
Chlorothalonil	0	0	4% (2)	12% (6)	10% (5)	6% (3)	5% (16)
Chlorpyrifos	23% (11)	24% (12)	2% (1)	2% (1)	0	0	8% (25)
Chlorpyrifos OA	11% (5)	8% (4)	0	0	0	0	3% (9)
Chlorthal-dimethyl	40% (19)	51% (26)	49% (26)	63% (33)	65% (34)	67% (35)	56% (173)
DDVP	6% (3)	8% (4)	13% (7)	12% (6)	17% (9)	0	9% (29)
Diazinon	23% (11)	2% (1)	2% (1)	0	2% (1)	0	5% (14)
Diazinon OA	17% (8)	0	2% (1)	0	0	0	3% (9)
Diuron	4% (2)	39% (20)	19% (10)	8% (4)	2% (1)	4% (2)	13% (39)
Endosulfan	0	0	0	2% (1)	0	0	0% (1)
EPTC	0	0	0	2% (1)	0	0	0% (1)
Malathion	9% (4)	12% (6)	15% (8)	12% (6)	13% (7)	8% (4)	11% (35)
Malathion OA	30% (14)	31% (16)	13% (7)	27% (14)	37% (19)	21% (11)	26% (81)
Methidathion	9% (4)	0	0	0	0	0	1% (4)
Methyl Bromide	17% (8)	10% (5)	10% (5)	27% (14)	13% (7)	10% (5)	14% (44)
Metolachlor	11% (5)	0	0	0	0	0	2% (5)
MITC	10% (5)	6% (3)	15% (8)	12% (6)	8% (4)	4% (2)	9% (28)
Norflurazon	4% (2)	0	0	0	0	0	1% (2)
Oryzalin	2% (1)	0	0	0	0	0	0% (1)
Oxyfluorfen	0	0	2% (1)	0	0	0	0% (1)
Phosmet	2% (1)	0	0	0	0	0	0% (1)
Simazine	6% (3)	4% (2)	0	2% (1)	0	0	2% (6)
Trifluralin	2% (1)	2% (1)	0	0	0	0	1% (2)
Total	**7% (118)**	**5% (102)**	**5% (99)**	**6% (123)**	**8% (152)**	**7% (130)**	**6% (724)**

Table 19 Percentage and count of quantifiable detections during the 2011-2016 sampling period in Salinas.

	Quantifiable Detections						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	6% (3)	2% (1)	16% (8)	4% (2)	19% (10)	25% (13)	12% (37)
Carbon Disulfide	0	2% (1)	14% (7)	44% (23)	88% (46)	92% (48)	41% (125)
Chloropicrin	6% (3)	0	11% (6)	2% (1)	4% (2)	10% (5)	6% (17)
Chlorthal-dimethyl	0	0	0	2% (1)	0	0	0% (1)
DDVP	0	0	4% (2)	0	0	0	1% (2)
Diazinon	0	0	2% (1)	0	0	0	0% (1)
Diazinon OA	0	0	2% (1)	0	0	0	0% (1)
Diuron	0	8% (4)	0	2% (1)	0	0	2% (5)
Malathion	4% (2)	0	2% (1)	0	2% (1)	0	1% (4)
Methyl Bromide	17% (8)	10% (5)	10% (5)	27% (14)	13% (7)	10% (5)	14% (44)
MITC	10% (5)	6% (3)	9% (5)	8% (4)	4% (2)	2% (1)	6% (20)
Oxyfluorfen	0	0	2% (1)	0	0	0	0% (1)
Total	**1% (21)**	**1% (14)**	**2% (37)**	**2% (46)**	**4% (68)**	**4% (72)**	**2% (258)**

Shafter

A total of 11,363 analyses were collected at Shafter from 2011 – 2016 (Table 20). Of the 11,363 analyses, 9% (1,053 analyses) produced either trace or quantifiable detections and 4% (437 analyses) of the total detections resulted in quantifiable detections (Tables 21 and 22). Chlorpyrifos had the highest percentage of total detections (54%, 165 analyses), followed closely by chlorothalonil and chlorpyrifos OA at 52% (160 analyses each). Carbon disulfide had the highest percentage of quantifiable detections (42%, 129 analyses), followed by MITC (37%, 114 analyses) and 1,3-D (27%, 84 analyses). Because the VOC analysis method does not differentiate between an MDL and LOQ, all detections were at quantifiable concentrations. The lower count of 1,3-D detections in earlier years may be due to a higher MDL during that period.

Table 20. Count of individual analyses performed for each analyte per year for Shafter.

	Total Analyses Performed						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	47	52	53	52	52	52	308
Acephate	47	52	53	52	51	52	307
Bensulide	47	52	53	52	51	52	307
Carbon Disulfide	47	52	53	52	52	52	308
Chloropicrin	47	52	53	52	52	51	307
Chlorothalonil	47	52	53	52	51	52	307
Chlorpyrifos	47	52	53	52	51	52	307
Chlorpyrifos OA	47	52	53	52	51	52	307
Cypermethrin	47	52	53	52	51	52	307
Chlorthal-dimethyl	47	52	53	52	51	52	307
DDVP	47	52	53	52	51	52	307
DEF	47	52	53	52	51	52	307
Diazinon	47	52	53	52	51	52	307
Diazinon OA	47	52	53	52	51	52	307
Dimethoate	47	52	53	52	51	52	307
Dimethoate OA	47	52	53	52	51	52	307
Diuron	47	52	53	52	51	52	307
Endosulfan	47	52	53	52	51	52	307
Endosulfan Sulfate	47	52	53	52	51	52	307
EPTC	47	52	53	52	51	52	307
Iprodione	47	52	53	52	51	52	307
Malathion	47	52	53	52	51	52	307
Malathion OA	47	52	53	52	51	52	307
Methidathion	47	52	53	52	51	52	307
Methyl Bromide	47	52	53	52	52	52	308
Metolachlor	47	52	53	52	51	52	307
MITC	47	52	53	52	52	52	308
Norflurazon	47	52	53	52	51	52	307
Oryzalin	47	52	53	52	51	52	307
Oxydemeton methyl	47	52	53	52	51	52	307
Oxyfluorfen	47	52	53	52	51	52	307
Permethrin	47	52	53	52	51	52	307
Phosmet	47	52	53	52	51	52	307
pp-Dicofol	47	52	53	52	51	52	307
Propargite	47	52	53	52	51	52	307
Simazine	47	52	53	52	51	52	307
Trifluralin	47	52	53	52	51	52	307
Total	**1,739**	**1,924**	**1,961**	**1,924**	**1,892**	**1,923**	**11,363**

Table 21. Percentage and count of total detections during the 2011-2016 sampling period in Shafter.

	Total Detections						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	0	6% (3)	26% (14)	37% (19)	42% (22)	50% (26)	27% (84)
Acephate	0	2% (1)	0	0	0	0	0% (1)
Bensulide	2% (1)	0	0	0	0	0	0% (1)
Carbon Disulfide	0	0	15% (8)	50% (26)	90% (47)	92% (48)	42% (129)
Chlorothalonil	13% (6)	23% (12)	60% (32)	77% (40)	75% (38)	62% (32)	52% (160)
Chlorpyrifos	53% (25)	48% (25)	75% (40)	56% (29)	61% (31)	29% (15)	54% (165)
Chlorpyrifos OA	45% (21)	48% (25)	55% (29)	62% (32)	53% (27)	50% (26)	52% (160)
Chlorthal-dimethyl	15% (7)	0	8% (4)	0	2% (1)	15% (8)	7% (20)
DDVP	2% (1)	0	6% (3)	2% (1)	8% (4)	2% (1)	3% (10)
Diazinon	11% (5)	4% (2)	6% (3)	0	0	0	3% (10)
Diazinon OA	4% (2)	8% (4)	8% (4)	0	0	2% (1)	4% (11)
Dimethoate OA	0	4% (2)	0	0	0	0	1% (2)
Diuron	6% (3)	12% (6)	2% (1)	10% (5)	10% (5)	0	7% (20)
EPTC	17% (8)	4% (2)	9% (5)	12% (6)	10% (5)	6% (3)	9% (29)
Iprodione	2% (1)	4% (2)	4% (2)	6% (3)	8% (4)	8% (4)	5% (16)
Malathion	0	2% (1)	4% (2)	2% (1)	0	0	1% (4)
Malathion OA	6% (3)	10% (5)	9% (5)	6% (3)	6% (3)	0	6% (19)
Methyl Bromide	9% (4)	4% (2)	4% (2)	15% (8)	13% (7)	8% (4)	9% (27)
MITC	38% (18)	52% (27)	57% (30)	42% (22)	35% (18)	42% (22)	44% (137)
Norflurazon	2% (1)	0	0	0	2% (1)	0	1% (2)
Oryzalin	2% (1)	2% (1)	2% (1)	2% (1)	6% (3)	0	2% (7)
Permethrin	2% (1)	0	2% (1)	0	0	0	1% (2)
Propargite	2% (1)	0	11% (6)	0	0	0	2% (7)
Simazine	4% (2)	12% (6)	0	4% (2)	4% (2)	6% (3)	5% (15)
Trifluralin	9% (4)	6% (3)	4% (2)	4% (2)	8% (4)	0	5% (15)
Total	**7% (115)**	**7% (129)**	**10% (194)**	**10% (200)**	**12% (222)**	**10% (193)**	**9% (1,053)**

Table 22. Percentage and count of quantifiable detections during the 2011-2016 sampling period in Shafter.

	Quantifiable Detections						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	0	6% (3)	26% (14)	37% (19)	42% (22)	50% (26)	27% (84)
Carbon Disulfide	0	0	15% (8)	50% (26)	90% (47)	92% (48)	42% (129)
Chlorothalonil	0	0	8% (4)	13% (7)	4% (2)	4% (2)	5% (15)
Chlorpyrifos	4% (2)	6% (3)	9% (5)	8% (4)	12% (6)	6% (3)	7% (23)
Chlorpyrifos OA	2% (1)	8% (4)	8% (4)	6% (3)	6% (3)	0	5% (15)
DDVP	0	0	0	0	0	2% (1)	0% (1)
Diazinon	2% (1)	0	2% (1)	0	0	0	1% (2)
Diazinon OA	2% (1)	2% (1)	0	0	0	0	1% (2)
EPTC	11% (5)	4% (2)	9% (5)	6% (3)	8% (4)	6% (3)	7% (22)
Iprodione	0	0	0	0	0	2% (1)	0% (1)
Malathion OA	0	2% (1)	0	0	0	0	0% (1)
Methyl Bromide	9% (4)	4% (2)	4% (2)	15% (8)	13% (7)	8% (4)	9% (27)
MITC	38% (18)	52% (27)	49% (26)	31% (16)	29% (15)	23% (12)	37% (114)
Oryzalin	0	0	0	0	2% (1)	0	0% (1)
Total	**2% (32)**	**2% (43)**	**4% (69)**	**4% (86)**	**6% (107)**	**5% (100)**	**4% (437)**

Ripon

A total of 11,422 analyses were collected at the Ripon sampling site from 2011 – 2016 (Table 23). Of the 11,422 analyses, 7% (787 analyses) resulted in trace or quantifiable detections and 3% were quantifiable (Tables 24 and 25). Chlorothalonil samples resulted in the highest number of total detections among the monitored analytes (50% [154 analyses] of all samples analyzed); however, none of these samples produced any quantifiable concentrations (Tables 24 and 25). Carbon disulfide was detected in 40% of the analyses, but as stated and explained by King et al. (2017); these are believed to have originated from non-pesticidal sources (Table 24). Monitoring of MITC concentrations in Ripon produced 25% (77) detections with 22% (67) quantifiable (Table 25).

Table 23. Count of individual analyses performed for each analyte per year for Ripon.

	Total Analyses Performed						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	46	52	52	53	51	52	306
Acephate	48	52	52	53	52	52	309
Bensulide	48	52	52	53	52	52	309
Carbon Disulfide	46	52	52	53	51	52	306
Chloropicrin	48	52	52	53	52	52	309
Chlorothalonil	48	52	52	53	52	52	309
Chlorpyrifos	48	52	52	53	52	52	309
Chlorpyrifos OA	48	52	52	53	52	52	309
Cypermethrin	48	52	52	53	52	52	309
Chlorthal-dimethyl	48	52	52	53	52	52	309
DDVP	48	52	52	53	52	52	309
DEF	48	52	52	53	52	52	309
Diazinon	48	52	52	53	52	52	309
Diazinon OA	48	52	52	53	52	52	309
Dimethoate	48	52	52	53	52	52	309
Dimethoate OA	48	52	52	53	52	52	309
Diuron	48	52	52	53	52	52	309
Endosulfan	48	52	52	53	52	52	309
Endosulfan Sulfate	48	52	52	53	52	52	309
EPTC	48	52	52	53	52	52	309
Iprodione	48	52	52	53	52	52	309
Malathion	48	52	52	53	52	52	309
Malathion OA	48	52	52	53	52	52	309
Methidathion	48	52	52	53	52	52	309
Methyl Bromide	46	52	52	53	51	52	306
Metolachlor	48	52	52	53	52	52	309
MITC	47	52	51	53	52	52	307
Norflurazon	48	52	52	53	52	52	309
Oryzalin	48	52	52	53	52	52	309
Oxydemeton methyl	48	52	52	53	52	52	309
Oxyfluorfen	48	52	52	53	52	52	309
Permethrin	48	52	52	53	52	52	309
Phosmet	48	52	52	53	52	52	309
pp-Dicofol	48	52	52	53	52	52	309
Propargite	48	52	52	53	52	52	309
Simazine	48	52	52	53	52	52	309
Trifluralin	48	52	52	53	52	52	309
Total	**1,769**	**1,924**	**1,923**	**1,961**	**1,921**	**1,924**	**11,422**

Table 24. Percentage and count of total detections during the 2011-2016 sampling period in Ripon.

	Total Detections						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	4% (2)	0	15% (8)	19% (10)	31% (16)	35% (18)	18% (54)
Bensulide	0	0	0	0	0	2% (1)	0% (1)
Carbon Disulfide	0	0	12% (6)	49% (26)	88% (45)	88% (46)	40% (123)
Chloropicrin	0	0	6% (3)	4% (2)	2% (1)	2% (1)	2% (7)
Chlorothalonil	38% (18)	21% (11)	42% (22)	66% (35)	65% (34)	65% (34)	50% (154)
Chlorpyrifos	19% (9)	13% (7)	19% (10)	15% (8)	27% (14)	12% (6)	17% (54)
Chlorpyrifos OA	25% (12)	19% (10)	23% (12)	17% (9)	23% (12)	15% (8)	20% (63)
Chlorthal-dimethyl	6% (3)	0	0	0	0	0	1% (3)
DDVP	0	2% (1)	8% (4)	2% (1)	10% (5)	2% (1)	4% (12)
Diazinon	4% (2)	4% (2)	4% (2)	0	2% (1)	4% (2)	3% (9)
Diazinon OA	2% (1)	2% (1)	2% (1)	2% (1)	6% (3)	4% (2)	3% (9)
Dimethoate	0	0	0	0	0	2% (1)	0% (1)
Dimethoate OA	0	0	2% (1)	0	0	2% (1)	1% (2)
Diuron	0	10% (5)	2% (1)	4% (2)	4% (2)	0	3% (10)
Endosulfan	0	2% (1)	2% (1)	4% (2)	6% (3)	0	2% (7)
Iprodione	2% (1)	2% (1)	10% (5)	2% (1)	10% (5)	10% (5)	6% (18)
Malathion	2% (1)	0	2% (1)	0	0	0	1% (2)
Malathion OA	13% (6)	10% (5)	13% (7)	8% (4)	12% (6)	4% (2)	10% (30)
Methyl Bromide	20% (9)	8% (4)	8% (4)	30% (16)	20% (10)	13% (7)	16% (50)
MITC	43% (20)	23% (12)	20% (10)	23% (12)	25% (13)	19% (10)	25% (77)
Oryzalin	0	6% (3)	0	0	6% (3)	0	2% (6)
Oxyfluorfen	4% (2)	6% (3)	0	2% (1)	6% (3)	4% (2)	4% (11)
Permethrin	4% (2)	0	2% (1)	2% (1)	2% (1)	2% (1)	2% (6)
Propargite	4% (2)	13% (7)	4% (2)	11% (6)	12% (6)	6% (3)	8% (26)
Simazine	2% (1)	10% (5)	0	2% (1)	2% (1)	0	3% (8)
Trifluralin	25% (12)	23% (12)	12% (6)	15% (8)	0	12% (6)	14% (44)
Total	**6% (103)**	**5% (90)**	**6% (107)**	**7% (146)**	**10% (184)**	**8% (157)**	**7% (787)**

Table 25. Percentage and count of quantifiable detections during the 2011-2016 sampling period in Ripon.

	Quantifiable Detections						
Analyte	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	4% (2)	0	15% (8)	19% (10)	31% (16)	35% (18)	18% (54)
Carbon Disulfide	0	0	12% (6)	49% (26)	88% (45)	88% (46)	40% (123)
Chloropicrin	0	0	0	4% (2)	0	0	1% (2)
Chlorpyrifos OA	0	2% (1)	0	0	0	2% (1)	1% (2)
DDVP	0	2% (1)	0	0	2% (1)	0	1% (2)
Diazinon	0	0	2% (1)	0	0	0	0% (1)
Iprodione	0	0	0	0	4% (2)	0	1% (2)
Methyl Bromide	20% (9)	8% (4)	8% (4)	30% (16)	20% (10)	13% (7)	16% (50)
MITC	43% (20)	23% (12)	18% (9)	19% (10)	15% (8)	15% (8)	22% (67)
Oryzalin	0	0	0	0	2% (1)	0	0% (1)
Total	**2% (31)**	**1% (18)**	**1% (28)**	**3% (64)**	**4% (83)**	**4% (80)**	**3% (304)**

Highest detected concentrations

Highest detected concentrations among all sites

The highest observed concentrations over the six years of sampling among the three sites were for 1,3-D (Table 26). This held across all exposures (24-hr, 4-week rolling average, and 1-year average values). 1,3-D had the highest 24-hour concentration (45,323 ng/m^3) measured at any of the three sampling site locations, followed by chloropicrin (6,384 ng/m^3) and MeBr (6,055 ng/m^3) (Tables 26 – 35). 1,3-D had the highest rolling 4-week average concentration (18,022 ng/m^3) of any pesticide at any of the three sampling sites for any year samples followed by MeBr (4,124 ng/m^3) then chloropicrin (3,019 ng/m^3). Similarly, 1,3-D had the highest 1-year average concentration (2,589 ng/m^3) of any pesticide sampled followed by MeBr at 1,412 ng/m^3 and carbon disulfide with a concentration of 739 ng/m^3. The subsections below present these concentrations in greater detail by timeframe, site, and year. Where analyses of certain chemicals did not produce quantifiable detections, or in some cases any detections at all, default values were used as adjusted concentrations for the required calculations. Non-detections (NDs) were assumed to be one-half of the MDL, while trace detections were assumed to be the midpoint of the MDL and the LOQ. See Appendix A for complete sampling data for samples collected from 2011 – 2016.

Table 26. Highest concentrations among all sites from 2011-2016.

	Highest Concentration (ng/m^3)		
Chemical	Acute (24-hr)	Subchronic (rolling 4-wk)	Chronic (1-yr)
1,3-Dichloropropene	45,322.6	18,022.1	2,588.8
Acephate	Trace (5.2)	(1.7)	(0.6)
Bensulide	Trace (5.4)	(3)	(1.1)
Carbon Disulfide	3,125.3	1,565.0	738.6
Chloropicrin	6,383.9	3,019.2	397.6
Chlorothalonil	117.7	67.2	21.8
Chlorpyrifos	422.5	113.3	20.4
Chlorpyrifos OA	143.1	43.7	7.6
Cypermethrin	ND (2.4)	(2.4)	(2.4)
Chlorthal-dimethyl	10.3	6.7	4.0
DDVP	68.8	27.9	4.2
DEF	ND (0.9)	(0.9)	(0.9)
Diazinon	59.6	17.7	2.3
Diazinon OA	36.0	11.0	1.9
Dimethoate	Trace (5.8)	(2.3)	(1.2)
Dimethoate OA	Trace (5.6)	(3.3)	(1.1)
Diuron	31.8	19.6	5.3
Endosulfan	Trace (13.2)	(10.3)	(2.3)
Endosulfan Sulfate	ND (2.3)	(2.3)	(2.3)
EPTC	250.3	139.4	11.8
Iprodione	17.0	12.2	1.7
Malathion	12.5	6.9	1.9
Malathion OA	10.7	5.3	2.3
Methidathion	Trace (5.4)	(3)	(1.1)
Methyl Bromide	6,055.0	4,124.0	1,415.5
Metolachlor	Trace (6)	(3.7)	(1.8)
MITC	930.4	563.5	73.0
Norflurazon	Trace (6.6)	(4.2)	(2.1)
Oryzalin	62.4	16.1	2.4
Oxydemeton methyl	ND (1.2)	(1.2)	(1.2)
Oxyfluorfen	52.7	15.6	4.1
Permethrin	Trace (15.2)	(6.5)	(4.1)
Phosmet	Trace (8.7)	(5.2)	(4.1)
pp-Dicofol	ND (1.1)	(1.1)	(1.1)
Propargite	Trace (13.5)	(13.5)	(3.5)
Simazine	Trace (5.3)	(4.1)	(1.1)
Trifluralin	Trace (12.4)	(12.4)	(3.7)

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Highest detected concentrations at Salinas

Table 27. 24-hr concentrations for all analytes with at least one detection (trace or quantifiable) at Salinas, 2011-2016.

	Maximum 24-Hr Concentration (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	10,071.7	3,429.8	4,319.0	440.1	3,643.0	1,560.7	10,071.7
Acephate	Tr (5.2)	ND (0.5)	ND (0.5)	ND (0.5)	ND (0.5)	ND (0.5)	Tr (5.2)
Bensulide	Tr (5.4)	ND (0.7)	ND (0.7)	ND (0.7)	Tr (5.4)	ND (0.7)	Tr (5.4)
Carbon Disulfide	ND (1,555)	616.3	152.5	691.0	3,125.3	846.7	3,125.3
Chloropicrin	3,926.4	ND (111)	6,383.9	4,809.0	3,023.4	2,824.3	6,383.9
Chlorothalonil	ND (6.9)	ND (6.9)	Tr (18.4)	Tr (18.4)	Tr (18.4)	Tr (18.4)	Tr (18.4)
Chlorpyrifos	Tr (14.1)	Tr (14.1)	Tr (14.1)	Tr (14.1)	ND (2.5)	ND (2.5)	Tr (14.1)
Chlorpyrifos OA	Tr (6.1)	Tr (6.1)	ND (1.5)	ND (1.5)	ND (1.5)	ND (1.5)	Tr (6.1)
Chlorthal-dimethyl	Tr (5.5)	Tr (5.5)	Tr (5.5)	10.3	Tr (5.5)	Tr (5.5)	10.3
DDVP	Tr (13.2)	Tr (13.2)	52.1	Tr (13.2)	Tr (13.2)	ND (1.6)	52.1
Diazinon	Tr (5.3)	Tr (5.3)	39.2	ND (0.6)	Tr (5.3)	ND (0.6)	39.2
Diazinon OA	Tr (5.7)	ND (1.1)	25.8	ND (1.1)	ND (1.1)	ND (1.1)	25.8
Diuron	Tr (7.2)	31.8	Tr (7.2)	14.4	Tr (7.2)	Tr (7.2)	31.8
Endosulfan	ND (1.6)	ND (1.6)	ND (1.6)	Tr (13.2)	ND (1.6)	ND (1.6)	Tr (13.2)
EPTC	ND (0.9)	ND (0.9)	ND (0.9)	Tr (12.4)	ND (0.9)	ND (0.9)	Tr (12.4)
Malathion	12.5	Tr (5.8)	9.6	Tr (5.8)	10.5	Tr (5.8)	12.5
Malathion OA	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)
Methidathion	Tr (5.4)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	Tr (5.4)
Methyl Bromide	6,055.0	2,526.8	4,424.8	3,062.5	178.5	438.6	6,055.0
Metolachlor	Tr (6)	ND (1.4)	ND (1.4)	ND (1.4)	ND (1.4)	ND (1.4)	Tr (6)
MITC	50.5	181.8	233.8	71.9	72.8	26.3	233.8
Norflurazon	Tr (6.6)	ND (1.9)	ND (1.9)	ND (1.9)	ND (1.9)	ND (1.9)	Tr (6.6)
Oryzalin	Tr (12.3)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	Tr (12.3)
Oxyfluorfen	ND (3.2)	ND (3.2)	52.7	ND (3.2)	ND (3.2)	ND (3.2)	52.7
Phosmet	Tr (8.7)	ND (4)	ND (4)	ND (4)	ND (4)	ND (4)	Tr (8.7)
Simazine	Tr (5.3)	Tr (5.3)	ND (0.6)	Tr (5.3)	ND (0.6)	ND (0.6)	Tr (5.3)
Trifluralin	Tr (12.4)	Tr (12.4)	ND (0.9)	ND (0.9)	ND (0.9)	ND (0.9)	Tr (12.4)

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.
Tr indicates Trace Detections, which are measured concentrations between the LOQ and MDL
ND indicates measured concentrations below the MDL

Table 28. Maximum rolling 4-wk concentrations for all analytes with at least one quantifiable detection at Salinas, 2011-2016.

	Maximum Rolling 4-wk Concentration (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	2,688.2	1,027.7	2,611.0	157.6	1,907.7	1,245.4	2,688.2
Carbon Disulfide	(1,555)	270.7	270.7	319.1	977.4	914.4	(1,555)
Chloropicrin	1,808.7	(111)	3,019.2	1,545.7	1,551.3	1,493.4	3,019.2
Chlorthal-dimethyl	(5.5)	(5.5)	(5.5)	6.7	(5.5)	(5.5)	6.7
DDVP	(4.5)	(4.5)	27.9	(7.4)	(10.3)	(1.6)	27.9
Diazinon	(5.3)	(1.8)	10.2	(0.6)	(1.8)	(0.6)	10.2
Diazinon OA	(3.4)	(1.1)	7.2	(1.1)	(1.1)	(1.1)	7.2
Diuron	(4.9)	19.6	(6)	7.8	(3.7)	(3.7)	19.6
Malathion	4.6	(5.8)	6.7	(4.6)	6.9	(4.6)	6.9
Methyl Bromide	4,124.0	1,097.5	1,870.9	1,261.6	119.5	256.2	4,124.0
MITC	14.7	71.0	88.7	35.7	23.2	8.7	88.7
Oxyfluorfen	(3.2)	(3.2)	15.6	(3.2)	(3.2)	(3.2)	15.6

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Table 29. Average yearly concentrations for all analytes with at least one quantifiable detection at Salinas, 2011-2016.

	1-yr Average Concentrations (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	Highest
1,3-Dichloropropene	1,351.1	288.6	406.7	33.1	200.6	186.6	1,351.1
Carbon Disulfide	(738.6)	164.4	136.4	87.1	272.7	263.2	738.6
Chloropicrin	329.8	(111)	397.6	228.0	248.5	246.9	397.6
Chlorthal-dimethyl	(2.7)	(3.2)	(3.1)	3.9	(3.9)	(4)	4.0
DDVP	(2.3)	(2.5)	4.2	(2.9)	(3.6)	(1.6)	4.2
Diazinon	(1.7)	(0.7)	1.3	(0.6)	(0.7)	(0.6)	1.7
Diazinon OA	(1.8)	(1.1)	1.5	(1.1)	(1.1)	(1.1)	1.8
Diuron	(2.7)	5.3	(3.4)	3.0	(2.6)	(2.7)	5.3
Malathion	1.7	(1.6)	1.9	(1.6)	1.8	(1.5)	1.9
Methyl Bromide	1,415.5	354.5	300.7	186.8	35.2	40.6	1,415.5
MITC	5.6	8.1	11.7	6.2	5.6	3.5	11.7
Oxyfluorfen	(3.2)	(3.2)	4.1	(3.2)	(3.2)	(3.2)	4.1

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Highest detected concentrations at Shafter

Table 30. 24-hr concentrations for all analytes with at least one detection (trace or quantifiable) at Shafter, 2011-2016.

	Maximum 24-Hr Concentration (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	ND (2,270)	3,643.0	39,969.2	9,250.5	9,713.3	45,322.6	45,322.6
Acephate	ND (0.5)	Tr (5.2)	ND (0.5)	ND (0.5)	ND (0.5)	ND (0.5)	Tr (5.2)
Bensulide	Tr (5.4)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	Tr (5.4)
Carbon Disulfide	ND (1,555)	ND (155.5)	896.5	547.9	812.5	946.3	946.3
Chlorothalonil	Tr (18.4)	Tr (18.4)	79.7	117.7	38.6	58.5	117.7
Chlorpyrifos	27.4	130.9	422.5	337.9	77.8	52.1	422.5
Chlorpyrifos OA	9.2	17.4	143.1	109.6	13.4	Tr (6.1)	143.1
Chlorthal-dimethyl	Tr (5.5)	ND (0.9)	Tr (5.5)	ND (0.9)	Tr (5.5)	Tr (5.5)	Tr (5.5)
DDVP	Tr (13.2)	ND (1.6)	Tr (13.2)	Tr (13.2)	Tr (13.2)	49.0	49.0
Diazinon	59.6	Tr (5.3)	29.3	ND (0.6)	ND (0.6)	ND (0.6)	59.6
Diazinon OA	36.0	10.1	Tr (5.7)	ND (1.1)	ND (1.1)	Tr (5.7)	36.0
Dimethoate OA	ND (1)	Tr (5.6)	ND (1)	ND (1)	ND (1)	ND (1)	Tr (5.6)
Diuron	Tr (7.2)	Tr (7.2)	Tr (7.2)	Tr (7.2)	Tr (7.2)	ND (2.6)	Tr (7.2)
EPTC	187.4	18.1	250.3	216.3	28.6	27.3	250.3
Iprodione	Tr (12.1)	Tr (12.1)	Tr (12.1)	Tr (12.1)	Tr (12.1)	17.0	17.0
Malathion	ND (1.1)	Tr (5.8)	Tr (5.8)	Tr (5.8)	ND (1.1)	ND (1.1)	Tr (5.8)
Malathion OA	Tr (5.3)	10.7	Tr (5.3)	Tr (5.3)	Tr (5.3)	ND (0.7)	10.7
Methyl Bromide	2,934.4	2,134.8	208.8	962.6	283.3	112.6	2,934.4
MITC	930.4	346.6	762.4	112.6	231.9	108.9	930.4
Norflurazon	Tr (6.6)	ND (1.9)	ND (1.9)	ND (1.9)	Tr (6.6)	ND (1.9)	Tr (6.6)
Oryzalin	Tr (12.3)	Tr (12.3)	Tr (12.3)	Tr (12.3)	62.4	ND (0.7)	62.4
Permethrin	Tr (15.2)	ND (3.6)	Tr (15.2)	ND (3.6)	ND (3.6)	ND (3.6)	Tr (15.2)
Propargite	Tr (13.5)	ND (1.9)	Tr (13.5)	ND (1.9)	ND (1.9)	ND (1.9)	Tr (13.5)
Simazine	Tr (5.3)	Tr (5.3)	ND (0.6)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)
Trifluralin	Tr (12.4)	Tr (12.4)	Tr (12.4)	Tr (12.4)	Tr (12.4)	ND (0.9)	Tr (12.4)

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.
Tr indicates Trace Detections, which are measured concentrations between the LOQ and MDL
ND indicates measured concentrations below the MDL

Table 31. Maximum rolling 4-wk concentrations for all analytes with at least one quantifiable detection at Shafter, 2011-2016.

	Maximum Rolling 4-wk Concentration (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	
1,3-Dichloropropene	(2270)	1,081.0	18,022.1	17,524.2	5,137.9	13,659.2	18,022.1
Carbon Disulfide	(1,555)	(155.5)	340.7	303.5	410.1	482.5	(1,555)
Chlorothalonil	(12.6)	(18.4)	38.0	67.2	48.3	24.5	67.2
Chlorpyrifos	14.5	49.6	113.3	92.1	59.6	39.4	113.3
Chlorpyrifos OA	6.9	13.1	43.7	32.0	9.1	(6.1)	43.7
DDVP	(4.5)	(1.6)	(7.4)	(4.5)	(7.4)	13.5	13.5
Diazinon	17.7	(2.9)	10.1	(0.6)	(0.6)	(0.6)	17.7
Diazinon OA	11.0	5.6	(5.7)	(1.1)	(1.1)	(2.2)	11.0
EPTC	75.9	7.1	139.4	85.7	18.6	9.7	139.4
Iprodione	(3.4)	(3.4)	(6.3)	(6.3)	(9.2)	10.4	10.4
Malathion OA	(1.8)	4.3	(4.1)	(3)	(1.8)	(0.7)	4.3
Methyl Bromide	1,980.0	682.2	198.0	389.3	186.4	80.6	1,980.0
MITC	563.5	556.8	318.9	258.9	156.2	51.0	563.5
Oryzalin	(3.6)	(3.6)	(3.6)	(3.6)	16.1	(0.7)	16.1

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Table 32. Average yearly concentrations for all analytes with at least one quantifiable concentration at Shafter, 2011-2016.

	1-yr Average Concentrations (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	Highest
1,3-Dichloropropene	(1052.9)	384.4	2,588.8	909.1	800.1	1,558.7	2,588.8
Carbon Disulfide	(721.3)	(155.5)	149.1	86.3	216.5	227.2	721.3
Chlorothalonil	(8.3)	(9.5)	16.0	21.8	16.0	14.6	21.8
Chlorpyrifos	9.0	10.9	20.4	16.0	13.9	7.8	20.4
Chlorpyrifos OA	3.6	4.4	7.6	6.8	4.2	(3.8)	7.6
DDVP	(1.8)	(1.6)	(2.3)	(1.8)	(2.5)	2.5	2.5
Diazinon	2.3	(0.8)	1.3	(0.6)	(0.6)	(0.6)	2.3
Diazinon OA	1.9	1.5	(1.4)	(1.1)	(1.1)	(1.1)	1.9
EPTC	8.5	1.3	11.8	7.8	2.6	1.7	11.8
Iprodione	(0.8)	(1)	(1)	(1.2)	(1.5)	1.5	1.5
Malathion OA	(0.9)	1.2	(1.1)	(0.9)	(0.9)	(0.6)	1.2
Methyl Bromide	1,053.8	247.1	162.6	70.1	40.4	26.0	1,053.8
MITC	73.0	51.1	65.7	20.7	27.3	17.4	73.0
Oryzalin	(0.9)	(0.9)	(0.9)	(0.9)	2.4	(0.7)	2.4

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Highest detected concentrations at Ripon

Table 33. 24-hr concentrations for all analytes with at least one detection (trace or quantifiable) at Ripon, 2011-2016.

	Maximum 24-Hr Concentration (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	2011-2016
1,3-Dichloropropene	12,249.3	ND (227)	14,744.6	3,511.5	4,074.0	2,917.2	14,744.6
Bensulide	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	ND (0.7)	Tr (5.4)	Tr (5.4)
Carbon Disulfide	ND (1,555)	ND (155.5)	463.8	370.4	2,842.0	603.9	2,842.0
Chloropicrin	ND (111)	ND (111)	Tr (1389)	1,150.4	Tr (458)	Tr (458)	1,150.4
Chlorothalonil	Tr (18.4)	Tr (18.4)	Tr (18.4)	Tr (18.4)	Tr (18.4)	Tr (18.4)	Tr (18.4)
Chlorpyrifos	Tr (14.1)	Tr (14.1)	Tr (14.1)	Tr (14.1)	Tr (14.1)	Tr (14.1)	Tr (14.1)
Chlorpyrifos OA	Tr (6.1)	13.2	Tr (6.1)	Tr (6.1)	Tr (6.1)	14.9	14.9
Chlorthal-dimethyl	Tr (5.5)	ND (0.9)	ND (0.9)	ND (0.9)	ND (0.9)	ND (0.9)	Tr (5.5)
DDVP	ND (1.6)	68.8	Tr (13.2)	Tr (13.2)	25.9	Tr (13.2)	68.8
Diazinon	Tr (5.3)	Tr (5.3)	48.7	ND (0.6)	Tr (5.3)	Tr (5.3)	48.7
Diazinon OA	Tr (5.7)	Tr (5.7)	Tr (5.7)	Tr (5.7)	Tr (5.7)	Tr (5.7)	Tr (5.7)
Dimethoate	ND (1.2)	ND (1.2)	ND (1.2)	ND (1.2)	ND (1.2)	Tr (5.8)	Tr (5.8)
Dimethoate OA	ND (1)	ND (1)	Tr (5.6)	ND (1)	ND (1)	Tr (5.6)	Tr (5.6)
Diuron	ND (2.6)	Tr (7.2)	Tr (7.2)	Tr (7.2)	Tr (7.2)	ND (2.6)	Tr (7.2)
Endosulfan	ND (1.6)	Tr (13.2)	Tr (13.2)	Tr (13.2)	Tr (13.2)	ND (1.6)	Tr (13.2)
Iprodione	Tr (12.1)	Tr (12.1)	Tr (12.1)	Tr (12.1)	14.7	Tr (12.1)	14.7
Malathion	Tr (5.8)	ND (1.1)	Tr (5.8)	ND (1.1)	ND (1.1)	ND (1.1)	Tr (5.8)
Malathion OA	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)	Tr (5.3)
Methyl Bromide	2,934.4	2,666.5	1,152.8	2,328.9	2,980.9	1,160.6	2,980.9
MITC	308.2	90.1	852.2	202.8	373.0	73.2	852.2
Oryzalin	ND (0.7)	Tr (12.3)	ND (0.7)	ND (0.7)	44.8	ND (0.7)	44.8
Oxyfluorfen	Tr (14.8)	Tr (14.8)	ND (3.2)	Tr (14.8)	Tr (14.8)	Tr (14.8)	Tr (14.8)
Permethrin	Tr (15.2)	ND (3.6)	Tr (15.2)	Tr (15.2)	Tr (15.2)	Tr (15.2)	Tr (15.2)
Propargite	Tr (13.5)	Tr (13.5)	Tr (13.5)	Tr (13.5)	Tr (13.5)	Tr (13.5)	Tr (13.5)
Simazine	Tr (5.3)	Tr (5.3)	ND (0.6)	Tr (5.3)	Tr (5.3)	ND (0.6)	Tr (5.3)
Trifluralin	Tr (12.4)	Tr (12.4)	Tr (12.4)	Tr (12.4)	ND (0.9)	Tr (12.4)	Tr (12.4)

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.
Tr indicates Trace Detections, which are measured concentrations between the LOQ and MDL
ND indicates measured concentrations below the MDL

Table 34. Maximum rolling 4-wk concentrations for all analytes with at least one quantifiable detection at Ripon, 2011-2016.

	Maximum Rolling 4-wk Concentration (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	
1,3-Dichloropropene	3,985.7	(227)	7,992.7	7,476.6	3,271.0	2,126.6	7,992.7
Carbon Disulfide	(1,555)	(155.5)	169.6	226.5	1,565.0	442.8	1,565.0
Chloropicrin	(111)	(111)	(1069.5)	577.5	(197.8)	(197.8)	1,069.5
Chlorpyrifos OA	(6.1)	7.9	(6.1)	(6.1)	(6.1)	6.0	7.9
DDVP	(1.6)	18.4	(10.3)	(4.5)	10.3	(4.5)	18.4
Diazinon	(1.8)	(1.8)	13.8	(0.6)	(1.8)	(2.9)	13.8
Iprodione	(3.4)	(3.4)	(12.1)	(3.4)	12.2	(12.1)	12.2
Methyl Bromide	1,980.0	1,118.8	1,118.8	866.6	1,639.9	594.0	1,980.0
MITC	143.6	128.3	271.6	97.6	150.4	41.4	271.6
Oryzalin	(0.7)	(6.5)	(0.7)	(0.7)	11.7	(0.7)	11.7

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Table 35. Average yearly concentrations for all analytes with at least one quantifiable detection at Ripon, 2011-2016.

	1-yr Average Concentrations (ng/m^3)						
Chemical	2011	2012	2013	2014	2015	2016	Highest
1,3-Dichloropropene	1,397.7	(227)	883.2	301.9	379.6	389.6	1,397.7
Carbon Disulfide	(733.6)	(155.5)	142.1	76.3	351.5	228.6	733.6
Chloropicrin	(111)	(111)	(184.7)	146.2	(117.7)	(117.7)	184.7
Chlorpyrifos OA	(2.6)	2.5	(2.5)	(2.2)	(2.5)	2.3	2.6
DDVP	(1.6)	2.9	(2.5)	(1.8)	3.0	(1.8)	3.0
Diazinon	(0.8)	(0.8)	1.6	(0.6)	(0.7)	(0.8)	1.6
Iprodione	(0.8)	(0.8)	(1.7)	(0.8)	1.7	(1.7)	1.7
Methyl Bromide	1,203.0	315.2	195.4	171.6	171.0	79.7	1,203.0
MITC	35.1	14.2	37.9	14.8	22.8	9.8	37.9
Oryzalin	(0.7)	(1.4)	(0.7)	(0.7)	2.0	(0.7)	2.0

() values in parentheses indicate the use of assigned concentrations for trace and non-detects to estimate rolling-4 week average and 1-year average concentrations.

Comparisons of Maximum Air Concentrations to Health Screening Levels

No state or federal agency has established health standards for pesticides in air. Therefore, DPR devised health screening levels and regulatory target concentrations to place the measured air concentrations in a health based context. DPR uses the established screening levels as triggers to conduct a detailed evaluation into actual health concerns. Regulatory target concentrations are established after a complete assessment of possible health risks and supersede the screening levels. DPR puts measures in place based on the regulatory target to limit exposures so that adverse effects can be avoided. Exceeding a regulatory target does not necessarily mean an adverse health effect occurs, but it does indicate that the restrictions on the pesticide use may need to be modified.

For monitoring results obtained from 2011-2016, we compiled the maximum air concentrations for each time period: acute (24-hr), Subchronic (4-week or 90-days depending on the AI), and chronic (1-yr). Only pesticides with quantifiable concentrations for any of the sampling time period (2011-2016) were compared to the established health screening level or regulatory target. Table 36 summarizes the magnitude of the highest measured air concentrations relative to the screening level for each time period for the 19 chemicals with quantifiable concentrations in at least one sample from the three sampling locations for any of the 6-yr sampling period. Pesticides with maximum concentrations of trace and ND were excluded from these tables.

For all years included in the monitoring, no pesticide exceeded any of the screening levels or regulatory target concentrations for any of the exposure periods at any of three sampling locations for any of the six years. Diazinon and its OA had the highest percentage of its acute screening level out of all pesticides monitored at 73.5%. 1,3-D had the highest subchronic screening level out of all pesticides monitored at 72.3%. Lastly, MeBr had the highest chronic screening level out of all pesticides monitored at 17.8%.

Table 36. Maximum measured air concentrations relative to the screening levels for chemicals with quantifiable concentrations for all sampling locations, 2011-2016.

Pesticide	% of Acute Screening Level	% of Subchronic Screening Level	% of Chronic Screening Level
1,3-Dichloropropene	24.98% (2013)	72.28% * (2014)	7.90% (2016)
Carbon Disulfide	0.20% (2015)	0.20% (2015)	0.04% (2015)
Chloropicrin	1.30% ** (2013)	55.62% * (2013)	12.99% (2013)
Chlorothalonil	0.35% (2014)	0.23% (2014)	0.04% (2014)
Chlorpyrifos + OA	47.13% (2013)	18.47% (2013)	2.04% (2013)
Chlorthal-dimethyl	0.00% (2014)	0.00% (2014)	0.00% (2014)
DDVP	0.63% (2013)	1.27% (2013)	0.40% (2013)
Diazinon + OA	73.54% (2011)	21.17% (2011)	2.22% (2011)
Diuron	0.02% (2012)	0.12% (2012)	0.07% (2012)
EPTC	0.11% (2013)	0.58% (2013)	0.05% (2013)
Iprodione	0.00% (2015)	0.00% (2015)	0.00% (2015)
Malathion + OA	0.01% (2013)	0.02% (2013)	0.02% (2013)
Methyl Bromide	0.74% ** (2011)	21.26% ** (2011)	17.82% (2011)
MITC	1.41% ** (2013)	10.63% (2013)	12.74% (2013)
Oryzalin	0.02% (2015)	0.01% (2015)	0.00% (2015)
Oxyfluorfen	0.01% (2013)	0.01% (2013)	0.01% (2013)

*Maximum 90-day average air concentrations used for this time period
** These values were calculated using regulatory targets rather than screening levels.
A percentage greater than 100% of the screening level suggests the need for further evaluation.
Parentheses denotes the year in which the maximum air concentration relative to its screening levels was observed.

Cumulative Exposure Estimates

Cumulative exposures were only calculated for organophosphate pesticides included in the AMN because these are the only pesticides in the AMN that have a common mode of action (cholinesterase inhibition) that were detected at quantifiable concentrations. The 14 organophosphates included in the AMN are:

1. Acephate
2. Bensulide
3. Chlorpyrifos
4. Chlorpyrifos OA
5. DDVP
6. Diazinon
7. Diazinon OA
8. Dimethoate
9. Dimethoate OA
10. Malathion
11. Malathion OA
12. Oxydemeton methyl
13. Phosmet
14. DEF

While organophosphates can have additional potential health effects, they all inhibit cholinesterase, an enzyme in the nervous system. Although EPTC, an N-methyl carbamate herbicide, inhibits cholinesterase, it has a different mechanism of toxicity and toxicity profile than the organophosphate insecticides; therefore, it would not be appropriate to group it with the organophosphates in a cumulative exposure calculation. As described in Section 1, the cumulative exposure was estimated using a HQ and HI approach that relies on the ratio between the detected air concentration and the screening level (or regulatory target). The organophosphate cumulative exposures were estimated for each community and exposure period.

Tables 37 through 39 show the HIs for the combined 14 organophosphates in each community for each exposure duration for 2011 to 2016. None of the HIs exceeded a value of 1.0 at any of the sampling locations during any of the sampling years, indicating that the screening levels were not exceeded for the combined 14 organophosphates. The highest acute HI of any site was at Shafter with an acute HI of 0.740 in 2011 (Table 37). Shafter also had the highest subchronic HI with a value of 0.229 in 2011 (Table 38). The Shafter sampling site also had the highest chronic HI with a value of 0.088 in 2013 (Table 39). Additionally, using air concentrations for the 14 organophosphates for the sampling years 2011-2016, a 6-year chronic HI of 0.066 was determined for the Shafter sampling site (Table 39).

Table 37. Highest 24-hr hazard index values determined for the combined 14 organophosphates included in the monitoring from 2011 to 2016.

	Acute hazard index†						
Community	2011	2012	2013	2014	2015	2016	2011-2016 Max
Salinas	0.102	0.053	0.504	0.026	0.053	0.017	**0.504**
Shafter	0.740	0.135	0.485	0.386	0.084	0.062	**0.740**
Ripon	0.088	0.053	0.433	0.053	0.098	0.088	**0.433**

† A hazard quotient or hazard index greater than one suggests the need for further evaluation.

Table 38. Highest rolling 4-week average hazard index values determined for the combined 14 organophosphates included in the monitoring from 2011 to 2016.

	Subchronic hazard index†						
Community	2011	2012	2013	2014	2015	2016	2011-2016 Max
Salinas	0.078	0.039	0.144	0.026	0.031	0.021	**0.144**
Shafter	0.229	0.085	0.201	0.162	0.094	0.070	**0.229**
Ripon	0.039	0.039	0.142	0.033	0.070	0.057	**0.142**

† A hazard quotient or hazard index greater than one suggests the need for further evaluation.

Table 39. Highest 1-yr average hazard index values determined for the combined 14 organophosphates included in the monitoring from 2011 to 2016.

	Chronic hazard index†							
Community	2011	2012	2013	2014	2015	2016	2011-2016 Max	2011-2016 Average
Salinas	0.054	0.040	0.045	0.034	0.036	0.032	**0.054**	**0.040**
Shafter	0.068	0.060	0.088	0.069	0.061	0.049	**0.088**	**0.066**
Ripon	0.041	0.041	0.048	0.038	0.045	0.040	**0.048**	**0.042**

† A hazard quotient or hazard index greater than one suggests the need for further evaluation.

Cancer Risk Estimates

The AMN collects samples for eight pesticides that have been designated as potential carcinogens by Proposition 65[2] or by U.S. EPA's B2 list. These chemicals are: 1,3-D, carbon disulfide, chlorothalonil, DDVP, diuron, iprodione, oxydemeton methyl, and propargite. Cancer risk is expressed as a probability for the occurrence of cancer (e.g., 1 in 1,000,000 or 10^{-6}, 1 in 100,000 or 10^{-5}, etc.), and is estimated based on the following calculation:

Cancer risk of single pesticide = (cancer potency) X (chronic air concentration) X (respiratory rate)

It is a standard default assumption that exposure to a carcinogen takes place over a lifetime, so DPR uses a default respiratory rate for an adult of 0.28 m^3 /kg-day over 70 years. Table 40 lists the cancer potency factor information for the pesticides included in the AMN that have at least one quantifiable detection at any sampling location from 2011-2016.

Table 40. Cancer Potency Factors for Pesticides Included in the AMN with Quantifiable Detections

Pesticide	Cancer Potency Factor $(mg/kg\text{-}day)^{-1}$	Reference
1,3-Dichloropropene	0.014	DPR 2015
Chlorothalonil	0.016	DPR 2018
DDVP	0.35	DPR 1996
Diuron	NA	NA
Iprodione	NA	NA

NA = DPR has not established a cancer potency value for these pesticides

Risk in the range of 10^{-5} to 10^{-6} or less is generally considered to be at the limit of what is considered to be negligible. DPR has set a cancer risk regulatory goal of 1.00×10^{-5} for 1,3-D and has not established a cancer risk regulatory target for chlorothalonil or DDVP.

The 6-year average risks for 1,3-D, chlorothalonil, and DDVP are shown in Table 41. The individual annual risk values used to calculate the 6-year averages are also shown, but these are for illustrative purposes only as these shorter timeframes are less suitable for comparison to a 70-year target.

[2] The official name of Proposition 65 is The Safe Drinking Water and Toxic Enforcement Act of 1986

Table 41. Annual and 6-year average individual cancer risks for 1,3-dichloropropene and chlorothalonil for each sampling site (2011-2016).

Community	2011	2012	2013	2014	2015	2016	6-year Average
	1,3-D						
Salinas	3.22E-6	1.06E-6	1.51E-6	1.23E-7	7.10E-7	7.24E-7	1.22E-6
Shafter	ND	1.48E-6	1.16E-5	3.41E-6	3.01E-6	5.68E-6	4.35E-6
Ripon	2.57E-6	ND	3.52E-6	1.30E-6	1.63E-6	1.51E-6	1.90E-6
Chlorothalonil							
Salinas	3.07E-08	3.07E-08	3.33E-08	3.51E-08	3.46E-08	3.35E-08	3.30E-08
Shafter	3.73E-08	4.22E-08	7.09E-08	9.91E-08	7.24E-08	6.48E-08	6.49E-08
Ripon	5.04E-08	4.19E-08	5.24E-08	6.52E-08	6.44E-08	6.39E-08	5.65E-08
DDVP							
Salinas	2.29E-07	2.46E-07	4.16E-07	2.87E-07	3.53E-07	1.57E-07	2.83E-07
Shafter	1.81E-07	1.57E-07	2.21E-07	1.79E-07	2.46E-07	2.46E-07	2.05E-07
Ripon	1.57E-07	2.83E-07	2.44E-07	1.78E-07	2.9E-07	1.79E-07	2.22E-07

Section 4:

Pesticide Use Information

Introduction

DPR's pesticide use reporting (PUR) system is one of the leading pesticide use accounting systems worldwide. DPR requires applicators to report all agriculture pesticide use to the county agricultural commissioner (CAC), and for each CAC to submit this reported use data to DPR. Report information includes: date and location of application, crop type, the size of application area, as well as operator and site ID numbers associated with the material applications permit. The California legal definition of "agricultural use" also includes applications to parks, golf course, cemeteries, rangeland, pastures, and road side rights-of-way. Additionally, non-agricultural applications including commodity and structural fumigations are reported. Only home and garden uses are excluded from the PUR accounting program (DPR 2000).

Data Quality

The PUR data is subjected to an array of QC routines and validity checks, both in the county-based reporting system, CalAgPermits, and at DPR (2017a). Several statistical routines are implemented at DPR to detect potential outliers in the data fields for acres treated and pounds (lbs) of pesticide used (DPR, 2017a). Additional QC procedures are conducted by the Air Program prior to any data analysis that includes PUR data. These additional procedures include flagging or removing use reports with application rates greater than 110% of the product maximum label rate. Other reasons for flagging results include reporting of: (1) applications with the incorrect application method (such as an aerial application of a fumigant), or (2) fumigations where the reported acreage was greater than 110% the statewide allowed maximum.

Reported Use

To better understand the links between PUR data and the AMN, PUR data associated with the sites located in Ripon, Salinas, and Shafter was accessed. A 5-mi radius around each of the sites was overlaid onto a Public Land Survey System's (PLSS) section map layer in ArcGIS and section ID numbers were extracted. A proportion value was assigned to each section depending on the actual portion of that section that was within the specified distance from the site location. Each record of lbs of AI was then multiplied by the proportion factor to yield the adjusted pounds (Adj. Lbs). Tables 42-44 present this use information. Figures

2-13 display the total use of the top four pesticides applied within a 5-mi radius around each of the sites from 2011-2016. In a later section, we analyze the relationship between use and detections.

Salinas

Table 42. Annual adjusted pound sum of reported pesticide use of 31 active ingredients within a 5-mi radius of the Salinas sampling site location.

SALINAS							
Active Ingredient	2011	2012	2013	2014	2015	2016	SUM
CHLOROPICRIN*	514,141	608,746	543,311	643,274	523,018	670,421	3,502,913
1,3-D*	208,745	290,428	266,181	259,390	126,086	154,346	1,305,178
METHYL BROMIDE*	275,437	201,897	151,141	78,510	40,593	23,802	771,384
MITC*	9,938	8,737	3,892	56,734	53,408	52,949	185,660
MALATHION	19,606	14,805	10,291	9,741	10,610	5,240	70,295
BENSULIDE	7,250	6,882	7,946	13,790	13,290	14,969	64,129
PERMETHRIN	6,616	6,847	7,529	7,811	6,748	4,954	40,507
CHLORTHAL-DIMETHYL	5,299	5,282	5,109	7,900	7,417	8,242	39,252
ACEPHATE	4,669	3,900	3,858	3,495	4,256	5,738	25,918
CHLOROTHALONIL	1,567	1,154	2,178	2,816	2,686	2,315	12,719
DDVP	2,688	3,718	2,679	1,318	1,068	518	11,992
CHLORPYRIFOS*	5,516	3,350	1,469	161	30	–	10,529
OXYDEMETON METHYL	3,793	2,475	971	815	355	37	8,446
IPRODIONE	2,160	1,358	1,349	1,325	544	376	7,115
OXYFLUORFEN	491	576	564	710	823	780	3,945
DIMETHOATE	1,404	534	407	288	318	885	3,835
DIAZINON*	2,339	345	111	1	22	1	2,818
CYPERMETHRIN	442	335	339	437	423	546	2,522
DIURON	78	56	105	195	514	460	1,411
TRIFLURALIN	125	63	103	51	12	35	391
S-METOLACHLOR	48	1	4	7	20	34	117
METHIDATHION	39	54	–	–	–	–	93
ORYZALIN	–	19	25	15	–	–	60
DEF	–	–	–	–	–	–	–
DICOFOL	–	–	–	–	–	–	–
ENDOSULFAN	–	–	–	–	–	–	–
EPTC	–	–	–	–	–	–	–
NORFLURAZON	–	–	–	–	–	–	–
PHOSMET	–	–	–	–	–	–	–
PROPARGITE	–	–	–	–	–	–	–
SIMAZINE	–	–	–	–	–	–	–

* Data was queried from the PUR database on 01-19-2018 and was subjected to the additional Air Program QC procedures described above and in Craig (2017). Non-asterisked AIs were queried on 3-1-2018 and are displayed as retrieved from PUR database.

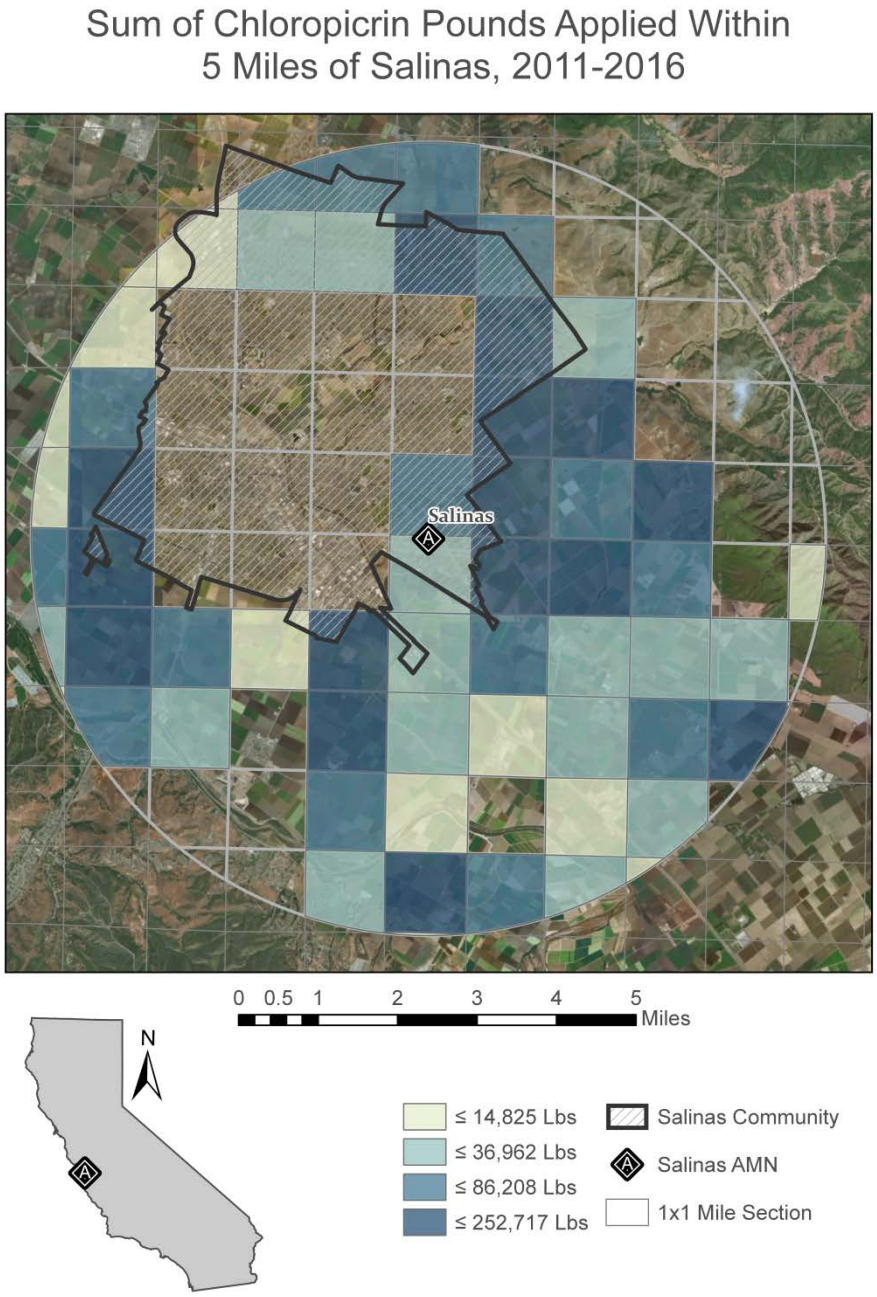


Figure 2. Sum of Chloropicrin pounds applied within 5 miles of Salinas, 2011-2016.

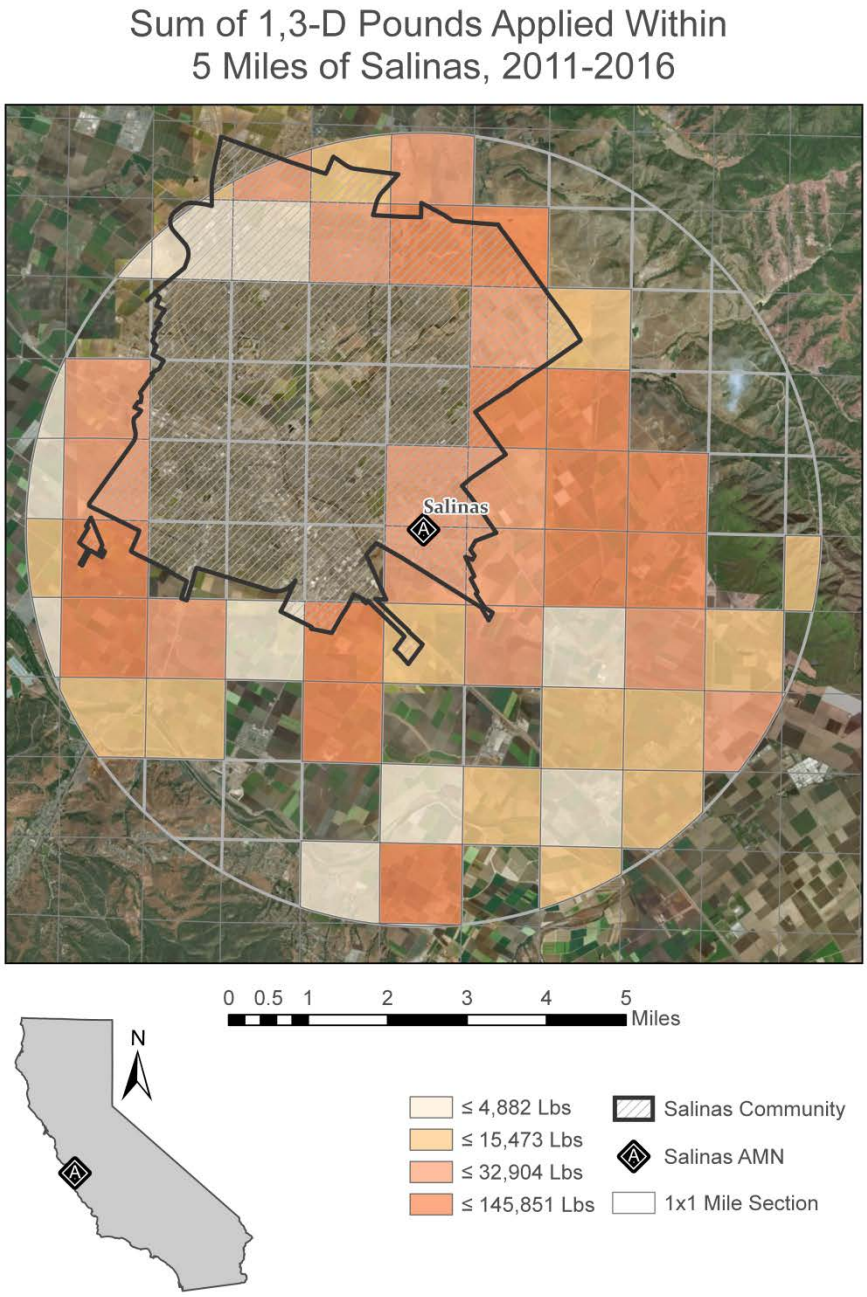


Figure 3. Sum of 1,3-dichloropropene pounds applied within 5 miles of Salinas, 2011-2016.

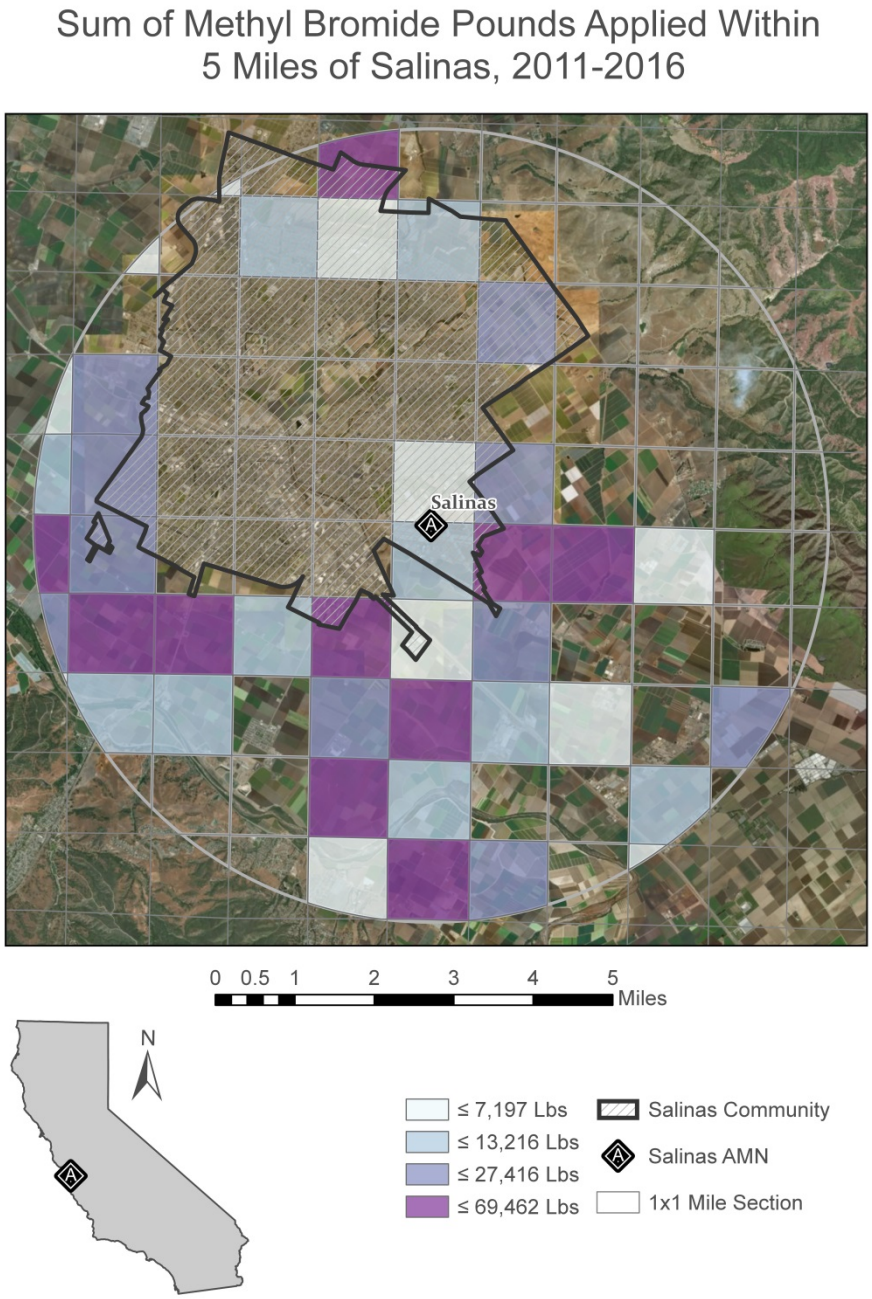


Figure 4. Sum of methyl bromide pounds applied within 5 miles of Salinas, 2011-2016.

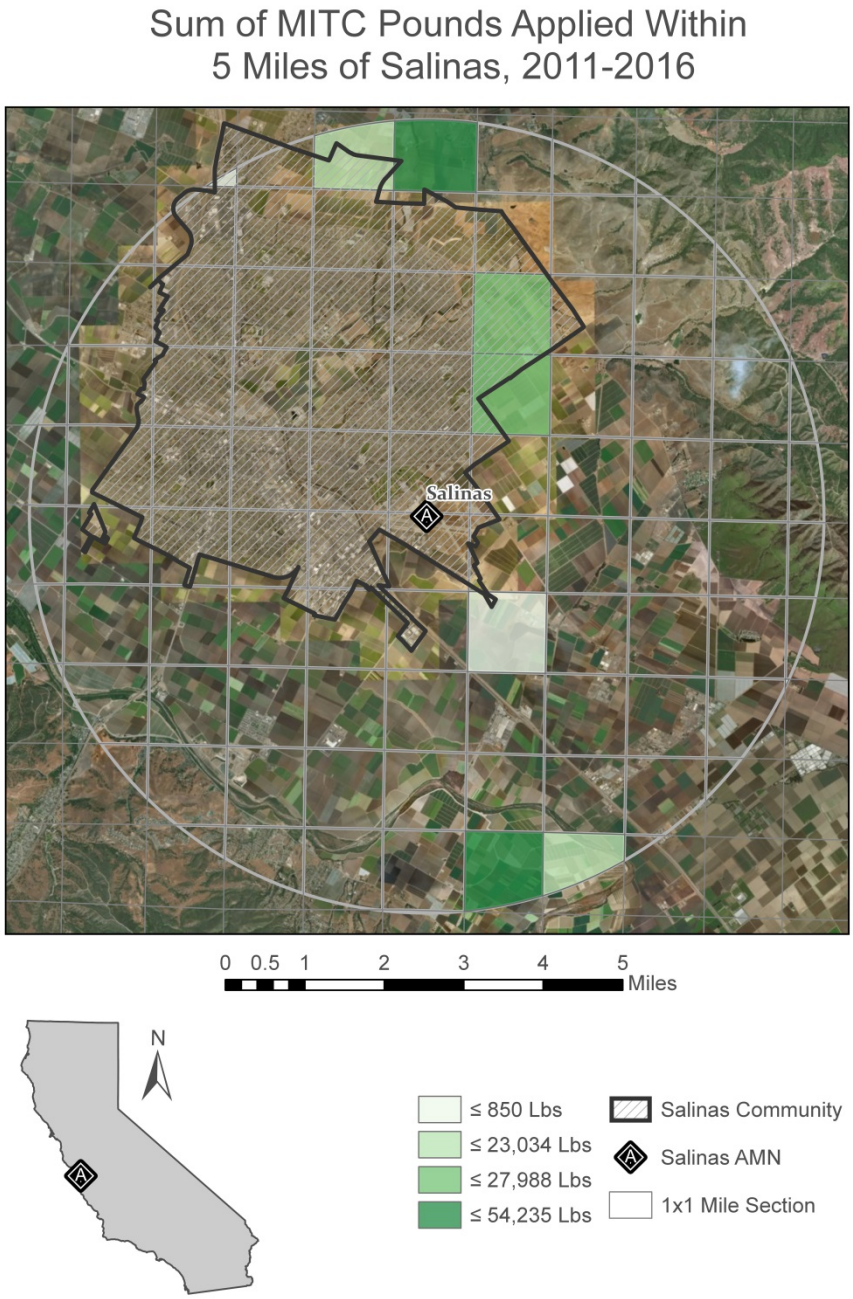


Figure 5. Sum of MITC pounds applied within 5 miles of Salinas, 2011-2016.

Table 43. Annual adjusted pound sum of reported pesticide use of 31 active ingredients within a 5-mi radius of the Shafter Air sampling site location.

Shafter							
Active Ingredient	2011	2012	2013	2014	2015	2016	SUM
1,3-D*	84,111	82,759	92,766	98,026	90,877	146,907	595,449
MITC*	47,878	27,667	24,410	11,581	10,300	–	121,838
CHLORPYRIFOS*	16,685	13,871	23,648	11,817	14,469	4,786	85,276
CHLOROTHALONIL	3,211	5,583	9,772	18,100	6,096	12,857	55,622
OXYFLUORFEN	7,299	10,063	9,111	6,395	6,853	9,711	49,434
ORYZALIN	8,869	9,532	8,689	1,092	2,886	269	31,340
METHYL BROMIDE*	915	9,096	167	18,127	–	–	28,307
CHLOROPICRIN*	304	404	–	16,158	–	8,757	25,623
IPRODIONE	8,245	2,473	1,496	629	1,677	3,322	17,845
EPTC	1,724	3,121	3,415	2,920	2,513	1,445	15,140
PROPARGITE	300	–	6,893	1,834	–	443	9,471
S-METOLACHLOR	732	1,403	1,531	1,114	932	882	6,596
DIAZINON*	782	2,381	947	–	–	–	4,112
DIURON	894	247	521	546	446	686	3,342
ACEPHATE	104	781	581	530	458	665	3,122
DIMETHOATE	379	378	622	726	613	267	2,985
PHOSMET	1,407	–	806	450	–	–	2,664
NORFLURAZON	67	282	113	287	625	227	1,603
TRIFLURALIN	328	419	430	396	6	–	1,582
PERMETHRIN	822	257	185	200	54	30	1,551
MALATHION	215	766	176	2	<1	117	1,279
METHIDATHION	148	1,015	–	–	–	–	1,163
SIMAZINE	81	236	72	33	141	330	896
DEF	456	29	–	–	7	8	500
DDVP	–	110	–	57	–	–	168
CYPERMETHRIN	26	17	29	7	26	17	122
CHLORTHAL-DIMETHYL	–	–	–	28	–	–	28
BENSULIDE	–	–	–	<1	–	–	<1
DICOFOL	–	–	–	–	–	–	–
ENDOSULFAN	–	–	–	–	–	–	–
OXYDEMETON METHYL	–	–	–	–	–	–	–

* Data was queried from the PUR database on 01-19-2018 and was subjected to the additional Air Program QC procedures described above and in Craig (2017). Non-asterisked AIs were queried on 3-1-2018 and are displayed as retrieved from PUR database.

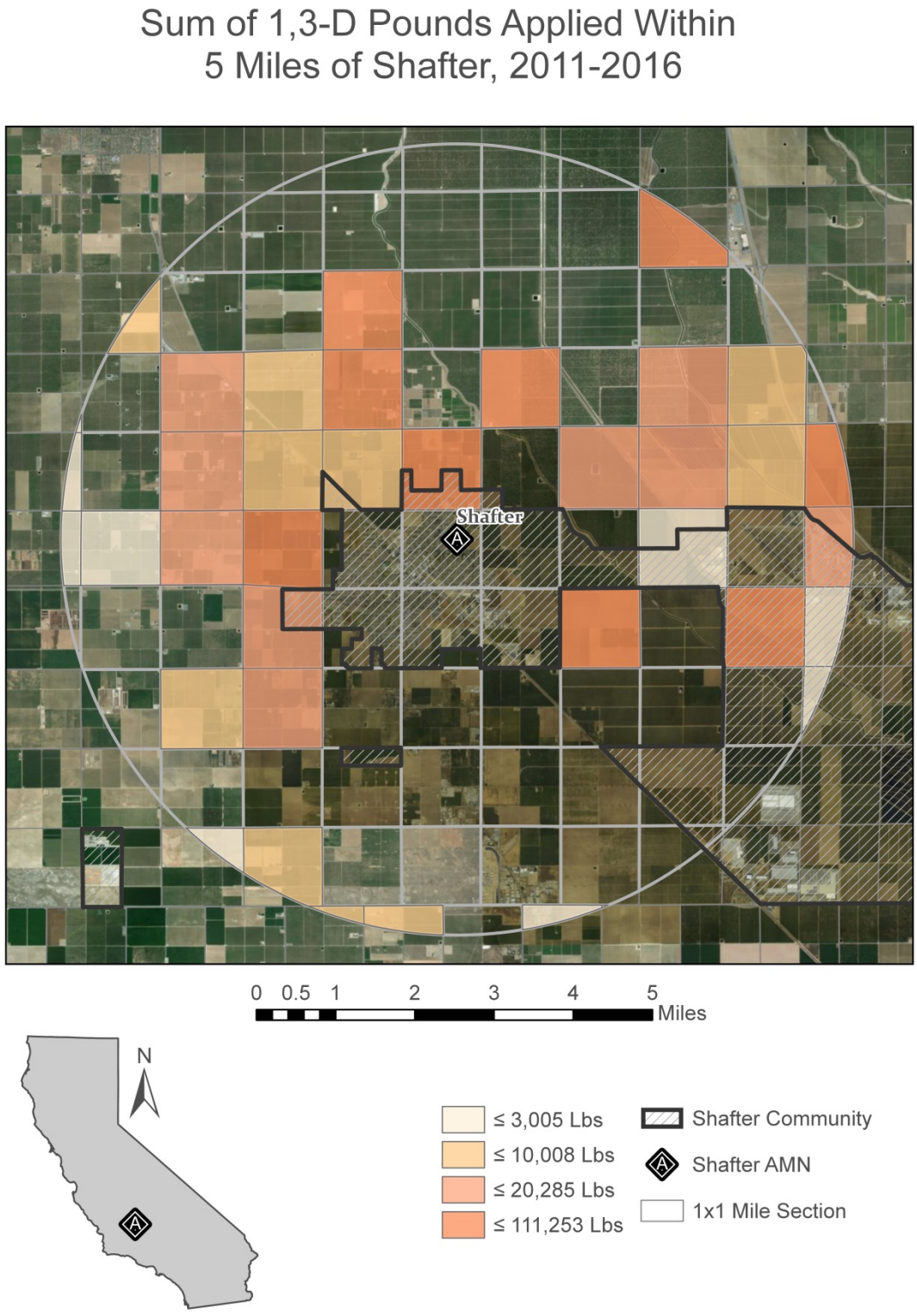


Figure 6. Sum of 1,3-dichloropropene pounds applied within 5 miles of Shafter, 2011-2016.

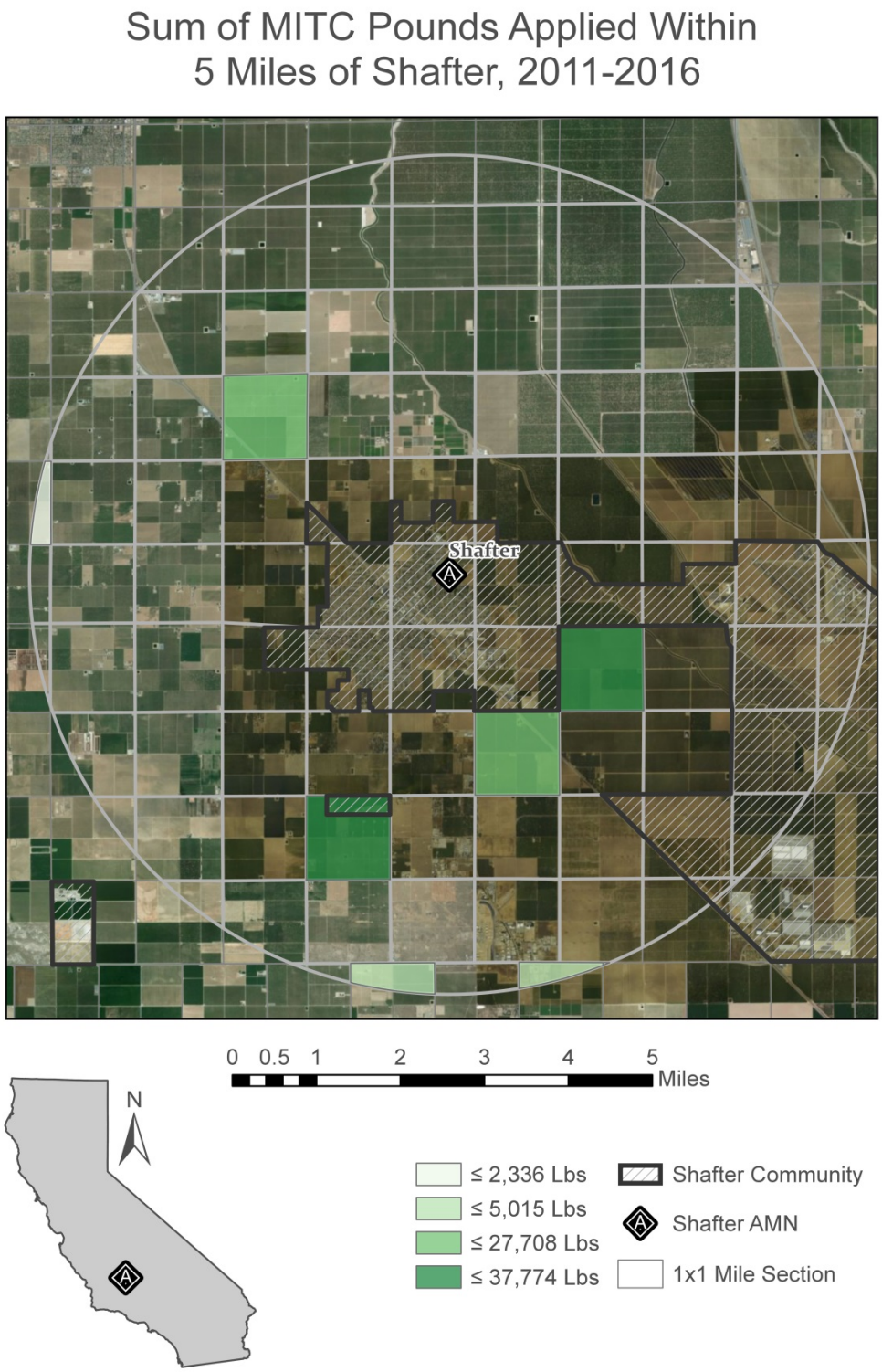


Figure 7. Sum of MITC pounds applied within 5 miles of Shafter, 2011-2016.

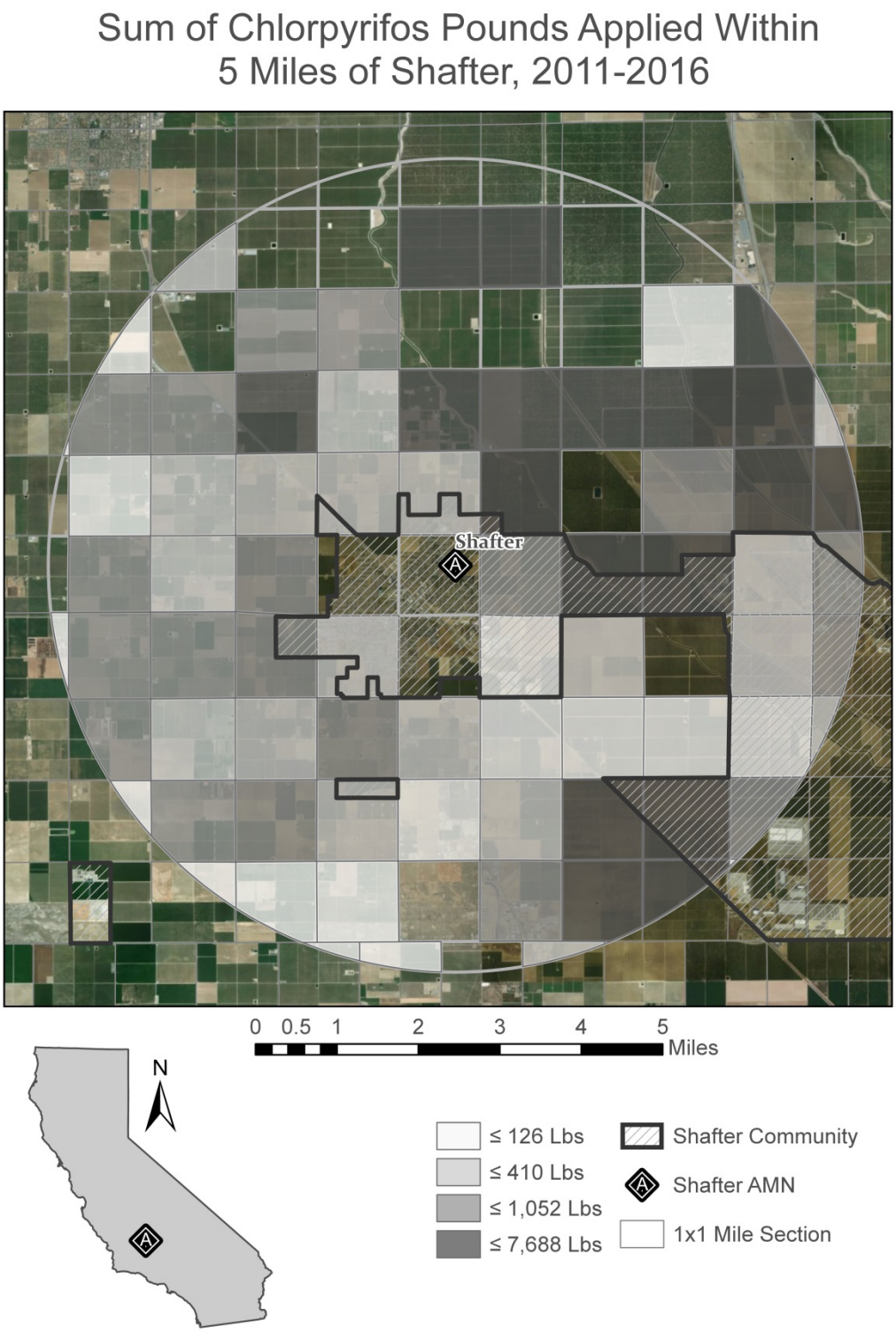


Figure 8. Sum of chlorpyrifos pounds applied within 5 miles of Shafter, 2011-2016.

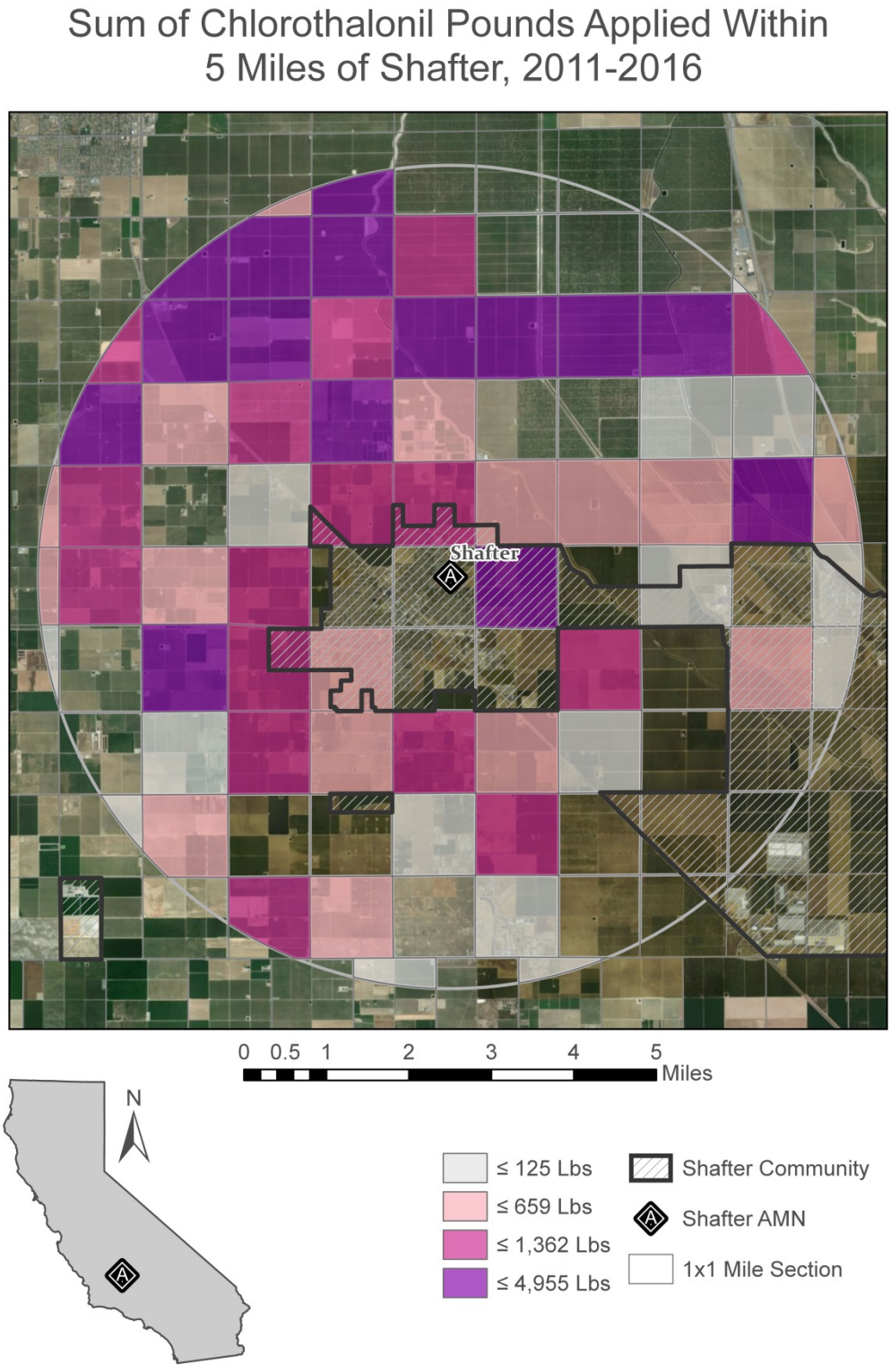


Figure 9. Sum of chlorothalonil pounds applied within 5 miles of Shafter, 2011-2016.

Table 44. Annual adjusted pound sum of reported pesticide use of 31 active ingredients within a 5-mi radius of the Ripon sampling site location.

Ripon							
Active Ingredient	2011	2012	2013	2014	2015	2016	SUM
MITC*	266,145	267,526	304,358	264,243	281,197	260,010	1,643,478
1,3-D*	177,719	200,760	140,478	182,565	192,259	162,944	1,056,725
METHYL BROMIDE*	93,039	100,291	103,382	146,458	32,915	61,042	537,127
CHLOROPICRIN*	42,245	53,069	61,137	90,630	28,003	41,182	316,266
CHLOROTHALONIL	10,444	10,736	8,283	7,518	5,200	5,820	48,004
OXYFLUORFEN	5,313	4,580	5,547	5,204	4,395	6,195	31,236
ORYZALIN	6,020	5,851	4,808	3,016	3,952	2,577	26,226
CHLORPYRIFOS*	4,500	5,109	5,001	5,555	3,449	989	24,601
BENSULIDE	4,365	3,900	4,318	3,074	4,310	4,178	24,147
IPRODIONE	4,600	2,763	3,638	4,119	3,216	4,199	22,536
MALATHION	761	1,964	1,453	2,456	715	750	8,100
PHOSMET	2,366	2,331	1,126	1,606	3	–	7,434
SIMAZINE	1,547	1,095	561	845	322	1,357	5,730
CHLORTHAL-DIMETHYL	397	579	623	695	1,221	1,390	4,907
PERMETHRIN	1,389	776	991	643	348	424	4,573
PROPARGITE	1,032	903	696	854	548	135	4,170
S-METOLACHLOR	197	82	753	433	633	748	2,848
DIMETHOATE	416	307	368	530	611	458	2,689
TRIFLURALIN	104	113	1,330	1,016	84	29	2,679
DIAZINON*	370	397	519	332	503	342	2,463
EPTC	11	209	119	773	904	–	2,018
DIURON	581	257	212	122	480	295	1,949
ENDOSULFAN	270	291	265	70	118	–	1,014
NORFLURAZON	224	157	5	16	13	181	597
CYPERMETHRIN	5	1	16	46	102	213	382
ACEPHATE	–	11	40	<1	161	134	348
DDVP	–	20	8	58	26	–	113
DEF	–	–	–	–	–	–	–
DICOFOL	–	–	–	–	–	–	–
METHIDATHION	–	–	–	–	–	–	–
OXYDEMETON METHYL	–	–	–	–	–	–	–

* Data was queried from the PUR database on 01-19-2018 and was subjected to the additional Air Program QC procedures described above and in Craig (2017). Non-asterisked AIs were queried on 3-1-2018 and are displayed as retrieved from PUR database.

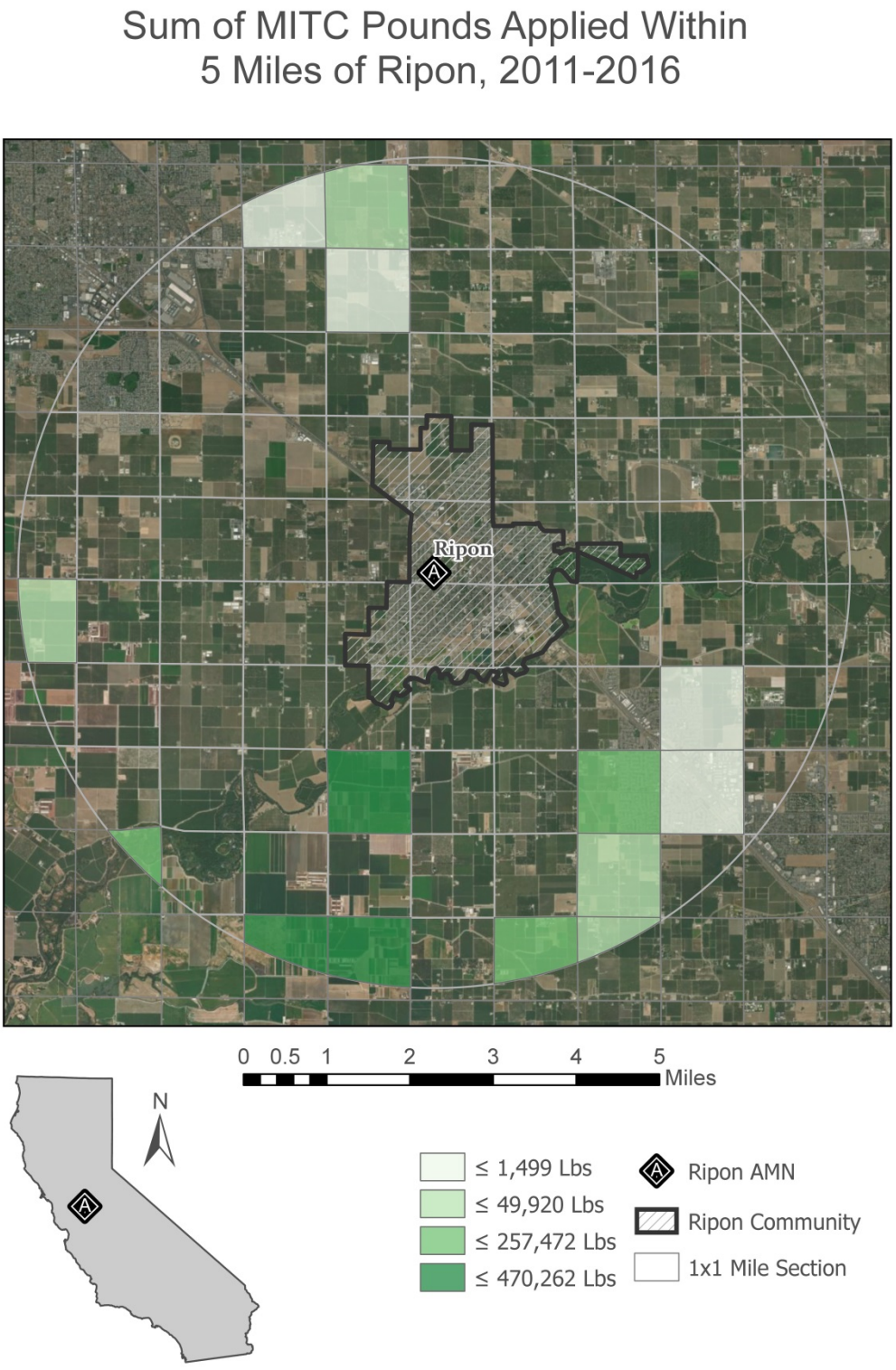


Figure 10. Sum of MITC pounds applied within 5 miles of Ripon, 2011-2016.

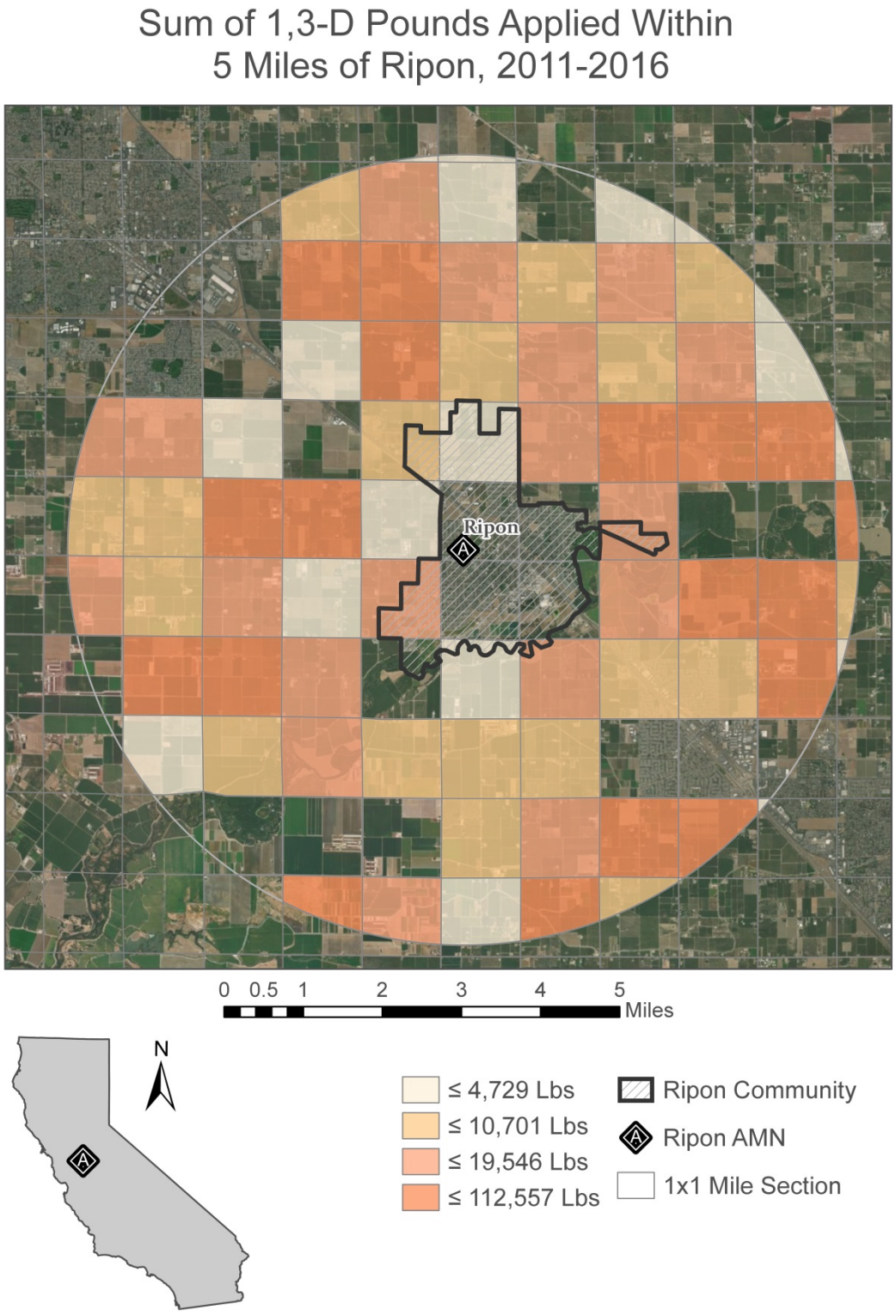


Figure 11. Sum of 1,3-dichloropropene pounds applied within 5 miles of Ripon, 2011-2016.

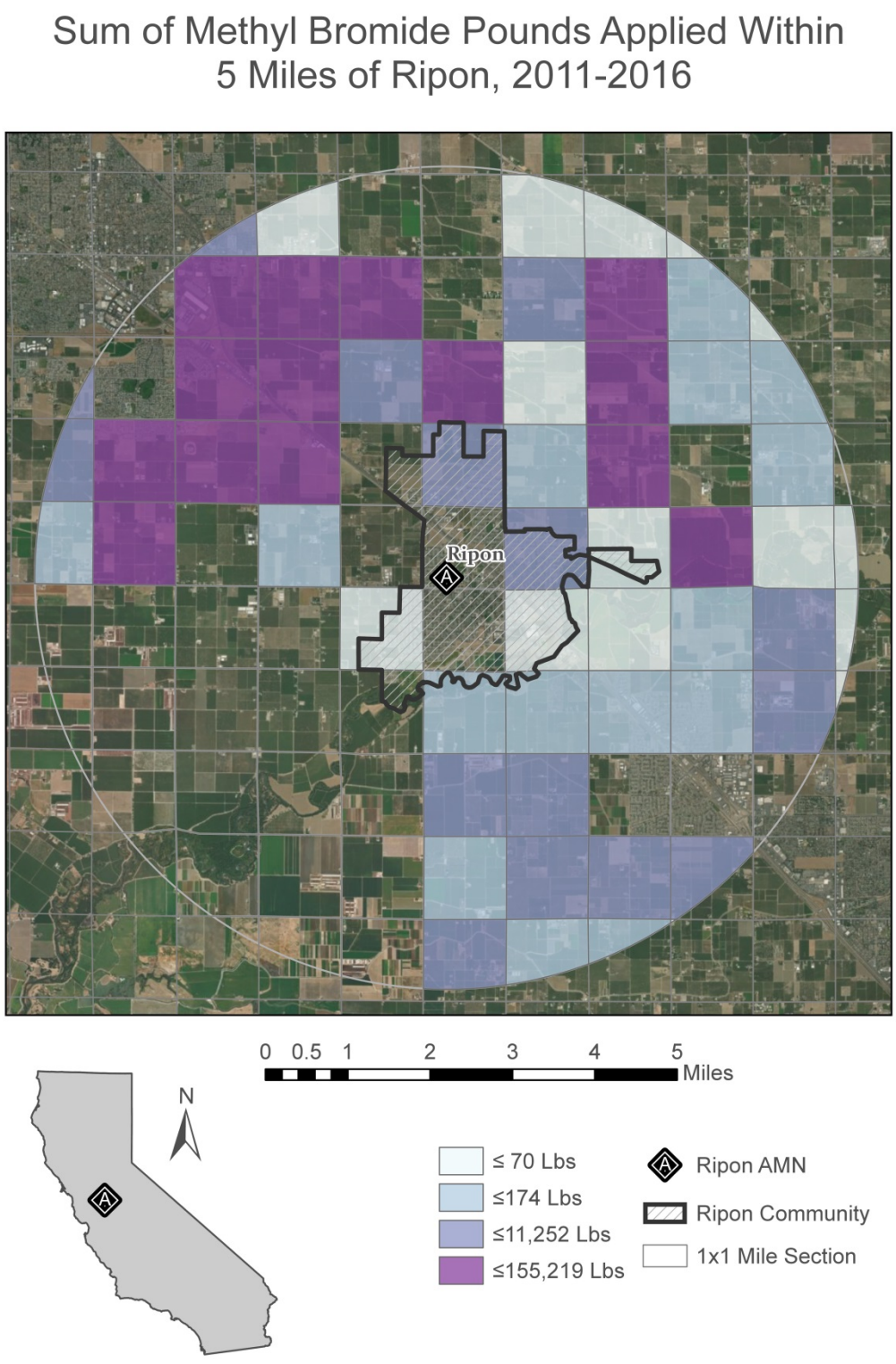


Figure 12. Sum of methyl bromide pounds applied within 5 miles of Ripon, 2011-2016.

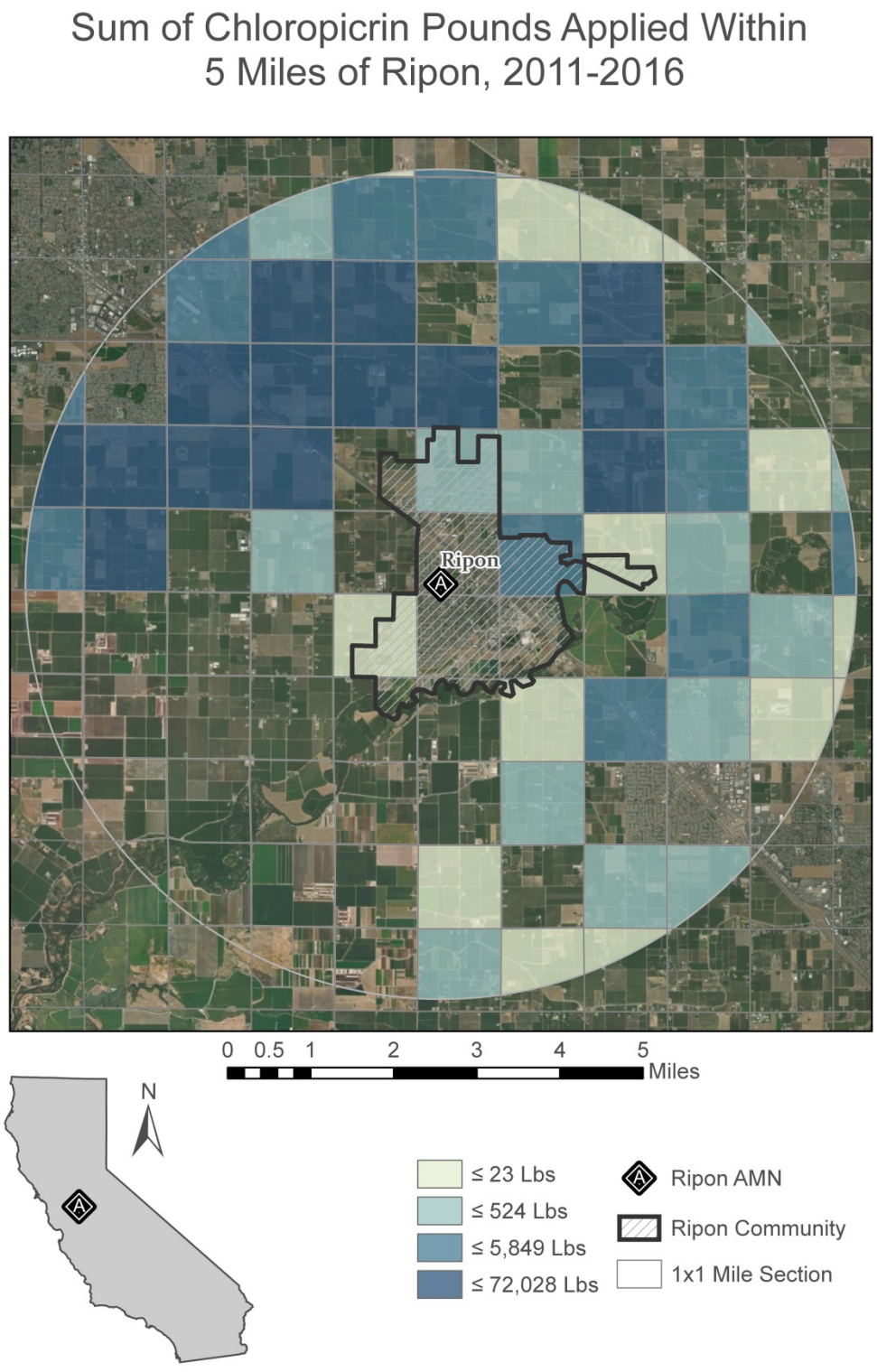


Figure 13. Sum of chloropicrin pounds applied within 5 miles of Ripon, 2011-2016.

Section 5:

Air Concentrations and Reported Agricultural Use of Selected Pesticides

Introduction

This section presents data on reported pesticide use over time relative to measured air concentrations over time at each of the three AMN locations by examining them visually, through figures. However, one cannot tell from a visual inspection alone whether observed trends are statistically significant. In Sections 6, 7, and 10 we provide multiple statistical analyses to better address this question.

The pesticides included in this section were chosen due to the high percentage of consistent quantifiable detections. They include the fumigants 1,3-D, chloropicrin, MBr, and MITC as well as the organophosphates chlorpyrifos and diazinon. Throughout the 2011 – 2016, these pesticides had the highest number of quantifiable detections of all pesticides included in the AMN.

Methodology

Air Concentrations

For this section, ambient air monitoring results are plotted as rolling 4-week averages. Similarly, reported use data is aggregated as rolling 4-week averages. Display of measured air concentrations in a rolling 4-week average time period was selected to allow for a standard metric that was easy to compile in order to compare to reported use values. All figures plot pesticide use data on the primary axis and pesticide concentration data on the secondary axis over the course of the study. Concentration data is in the foreground, use data is in the background. The datasets consist of 48 points for concentration and for use in 2011 and 52 points for both for the rest of the years.

Use Information

The PUR database was queried at a spatial scale covering a 5-mi radius of each of the three sampling site locations from February 1, 2011, to December 31, 2016. The PUR database provides location information in the form of PLSS 1 mi^2 sections. The query included sections on the basis of any part of their 1 mi^2 area

falling within the 5-mi radius from the sampling site location. The collected use data was then plotted against measured AMN air concentrations collected between February 1, 2011, and December 31, 2016.

Limitations

Reported concentrations are "adjusted concentrations", that is, in the case of NDs, concentrations are reported as half of the MDL. Thus, there are no data points where concentrations are zero. Additionally, reporting limits for 1,3-D and MBr changed three times throughout the study due to improved laboratory analytical methods.

The following summaries are the results of this analysis organized by sampling site and then chemical.

Comparisons by community

Note: In the following sections, all sampling occurred from February 1, 2011, through December 31, 2016, within a 5-ml radius of the sampling site location.

Salinas

1,3-D

Figure 14 charts the measured concentration of 1,3-D versus use reported for the Salinas sampling site. On June 20, 2011, the reporting limit for 1,3-D was decreased from 2,270 ng/m^3 to 227 ng/m^3 and then further decreased to 22.7 ng/m^3 on October 24, 2013. Applications show a cyclical annual pattern of high and no use. Peak use occurred during mid-August to early December in 2011 and 2012. Applications started earlier the following years. In 2013 to 2015, peak use generally occurred from late June and early July to late November. Use significantly dropped beginning in 2015 and by 2016 applications began earlier than previous years.

Detection patterns generally followed application patterns, although the higher reporting limits from the beginning of the study and up to October 24, 2013, somewhat obscure this (Figure 14). However, in 2014 most applications were not detected.

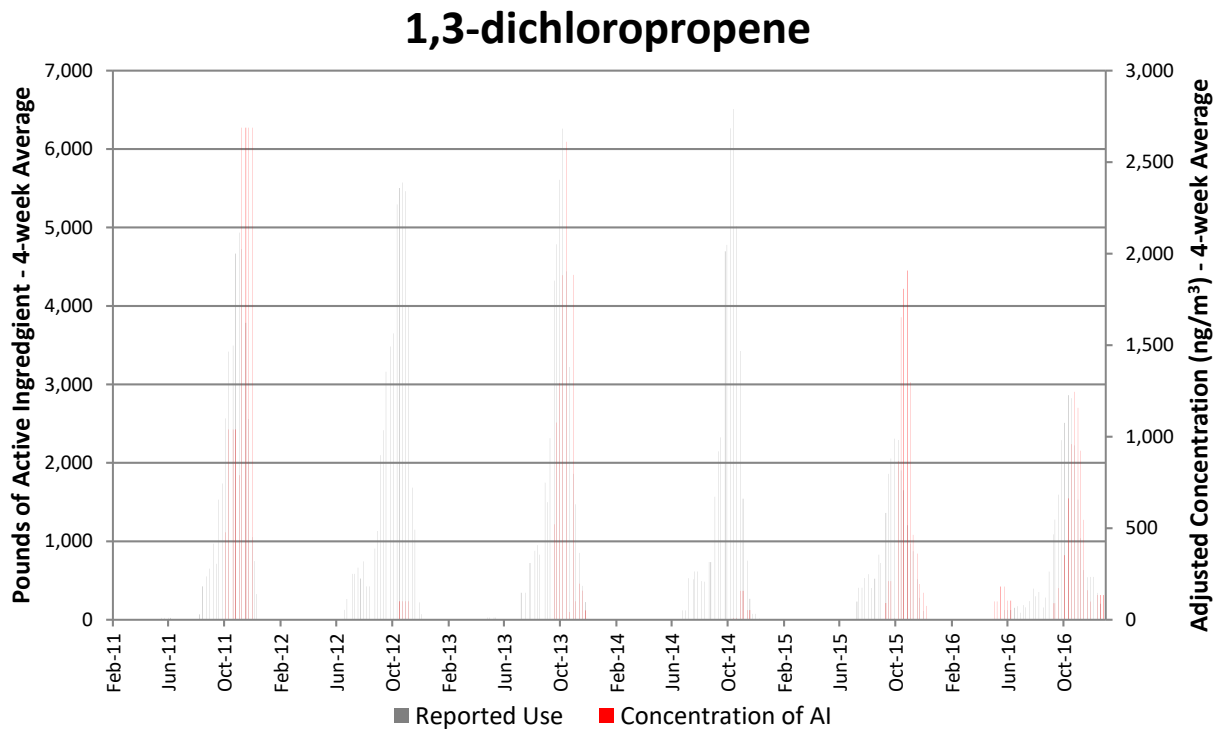


Figure 14. Concentration versus use for 1,3-dichloropropene in Salinas between February 1, 2011 and December 31, 2016.

Chloropicrin

Figure 15 charts the measured concentration of chloropicrin versus use reported for the Salinas sampling site. The peak application period generally occurred between early July and late November each year. The first and second week of October routinely had the highest use of chloropicrin every year.

Detections often coincided with chloropicrin use except in 2012 when no detections above the MDL occurred during the peak use period. The LOQ for chloropicrin was 111 ng/m^3. In the analysis of chloropicrin use for the Ripon site, two records were flagged for application rates above 110% the allowed maximum. Both records were retained and corrected as mentioned earlier.

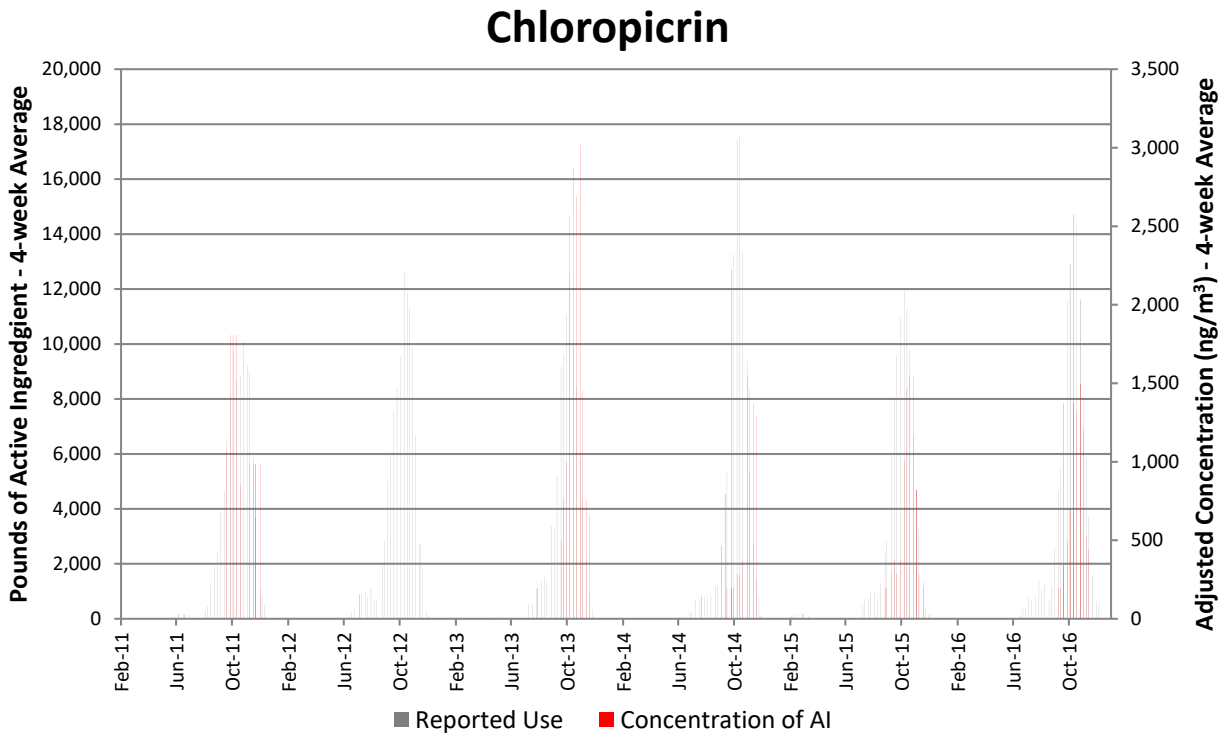


Figure 15. Concentration versus use for chloropicrin in Salinas between February 1, 2011 and December 31, 2016.

Chlorpyrifos

Figure 16 charts the measured concentration of chlorpyrifos versus use reported for the Salinas sampling site. Concentration data includes detections for both chlorpyrifos and its OA breakdown product. The reporting limit for chlorpyrifos was 2.5 ng/m^3 and 1.45 ng/m^3 for its OA. Chlorpyrifos use around the Salinas site was variable for the first half of the study period. Beginning in February of 2011, use was at about half of its maximum and peaked for 2011 between May and March. Use continued to drop after this peak and by the beginning of October 2011 had almost ceased. Use picked up again in November 2011 and continued through the end of August 2012.

Use of chlorpyrifos picked up again by late October 2012 and continued through the end of August 2013. Afterwards, use became sporadic, with virtually no applications between May and November 2014. There was minimal use throughout 2015 and applications ceased by 2016.

Detections of chlorpyrifos and its OA in Salinas were not generally consistent with its use. During the peak application period in 2011, detections of chlorpyrifos and its OA occurred infrequently. However, by

November 2011 and through April 2012, detections were relatively frequent for chlorpyrifos. Detections ceased in 2012 after April, but picked up again briefly in late January and early February of 2013. The last remaining detections greater than the reporting limit occurred in March 2014, which corresponds to the lack of chlorpyrifos use in the area. Overall, detections were greater for chlorpyrifos compared to its OA breakdown product.

In the analysis of chlorpyrifos use within five miles of the monitoring site in Salinas, one record was flagged for an application rate above 110% the allowed maximum. The amount applied was corrected to 110% the allowed maximum and the record retained.

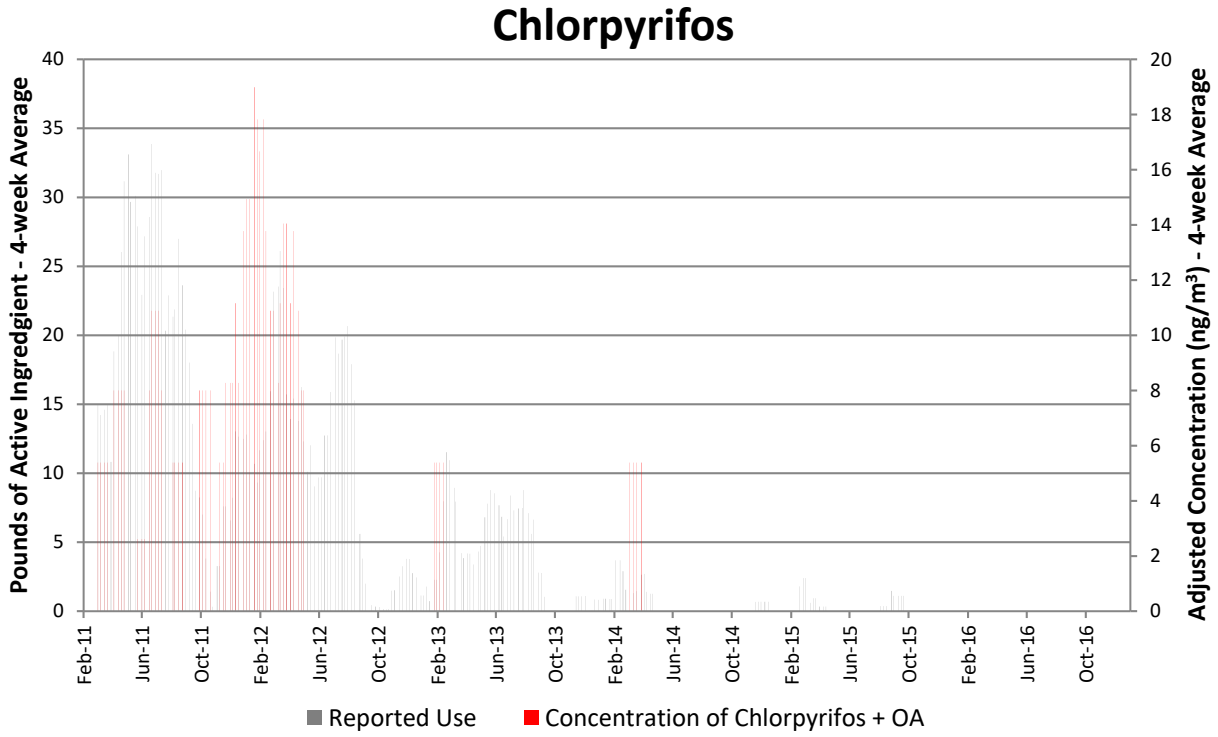


Figure 16. Concentration versus use for chlorpyrifos in Salinas, California between February 1, 2011 and December 31, 2016.

Diazinon

Figure 17 charts the measured concentration of diazinon versus use reported for the Salinas sampling site. Concentration data includes detections for both diazinon and its OA. The LOQ for diazinon was 0.6 ng/m^3 and 1.05 ng/m^3 for its OA. The greatest number of diazinon applications occurred from early March to early

September 2011. Applications greatly decreased after 2011 with the second greatest period of use occurring in early February to early July 2012. Afterwards, use of diazinon became sporadic.

Detections of diazinon and its OA did correlate with applications in 2011 but detections were not common throughout the study period. Also, the highest measured concentrations occurred during a brief period (mid-November to early December 2013) during which there was no reported applications within 5-mi of the sampling site.

For the Salinas sampling site, one record was flagged for an application rate above 110% the allowed maximum. The amount applied was corrected to 110% the allowed maximum and the record retained.

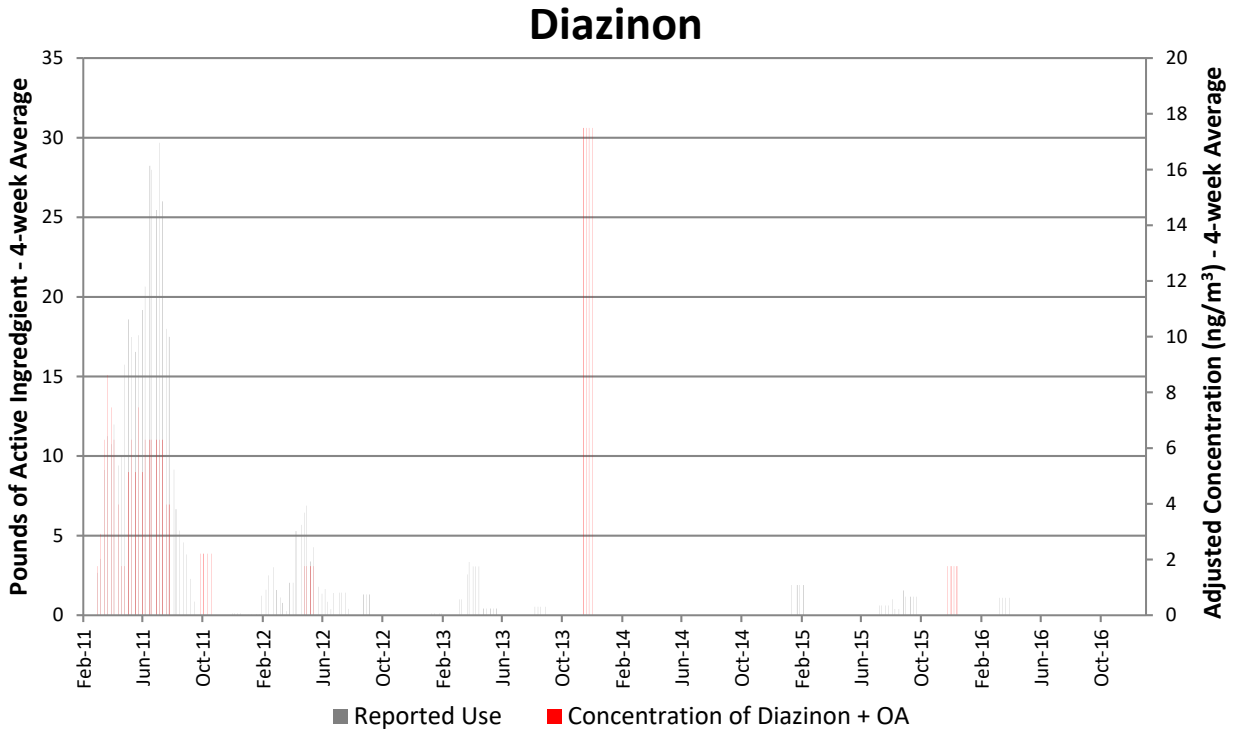


Figure 17. Concentration versus use for diazinon in Salinas, California between February 1, 2011 and December 31, 2016.

MeBr

Figure 18 charts the measured concentration of MeBr versus use reported for the Salinas sampling site. The MDL for MeBr was reduced twice from its original reporting level of 1,980 ng/m^3; on June 20, 2011 the reporting limit was decreased to 198 ng/m^3 and on October 16, 2013 the reporting limit was reduced again

to 19.8 ng/m^3. Applications of MeBr showed a cyclical pattern beginning in August and ending by November each year. However, use periods narrowed each subsequent year. In 2011, use began in early August and ended in mid-November. By 2016, use did not begin until mid-September and ended by late October.

Detections generally trended with use throughout the study except during peak application periods in 2013 and 2015. There were also periods of detections with no reported use of MeBr within 5-mi of the sampling site in Salinas. In June and December of 2012 and again in June through July of 2015 detections occurred despite no reported use of MeBr. A possible reason for these lower concentrations of MeBr where there were no reported applications can be due to MeBr use in commodity applications, which are on a monthly basis and at a county-level resolution instead of on a section level like agricultural applications.

In the analysis of MeBr around the Salinas site, one record was flagged for an application rate above 110% the allowed maximum. The amount applied was corrected to 110% the allowed maximum and the record retained. Also, three additional records were flagged for an application greater than 44 acres but were retained and plotted in figure 6.

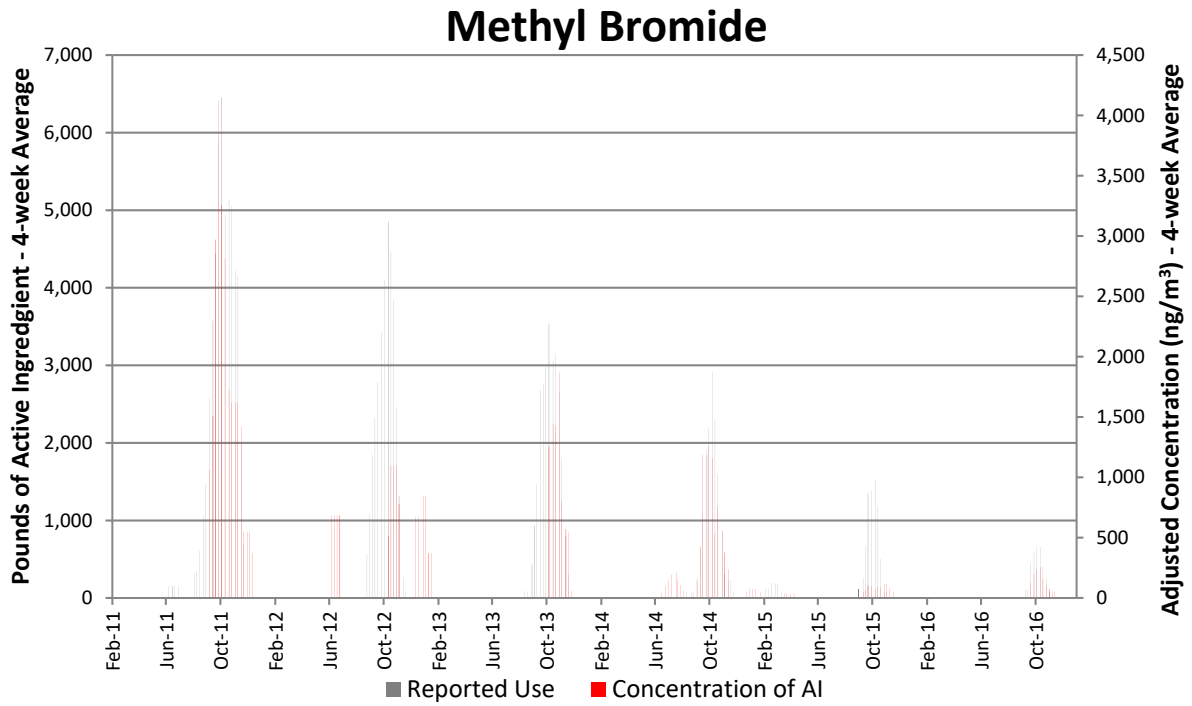


Figure 18. Concentration versus use for methyl bromide in Salinas between February 1, 2011 and December 31, 2016.

MITC

Figure 19 charts the measured concentration of MITC versus use reported around the Salinas sampling site. The MDL remained constant at 2.8 ng/m^3 throughout the study. MITC applications were confined to a use period of mid or late October to mid-November between 2011 and 2016 (although use did occur slightly earlier in 2014 and 2015). Use consistently trended upwards each consecutive year. From 2011 to 2014, detections correlated with use (2011 through 2013 use data obscured by concentration data). However, detections ceased to correlate with use within five miles of the monitoring site by 2015. One MITC use record was flagged for an application rate above 110% the allowed maximum. The amount applied was corrected to 110% the allowed maximum and the record retained.

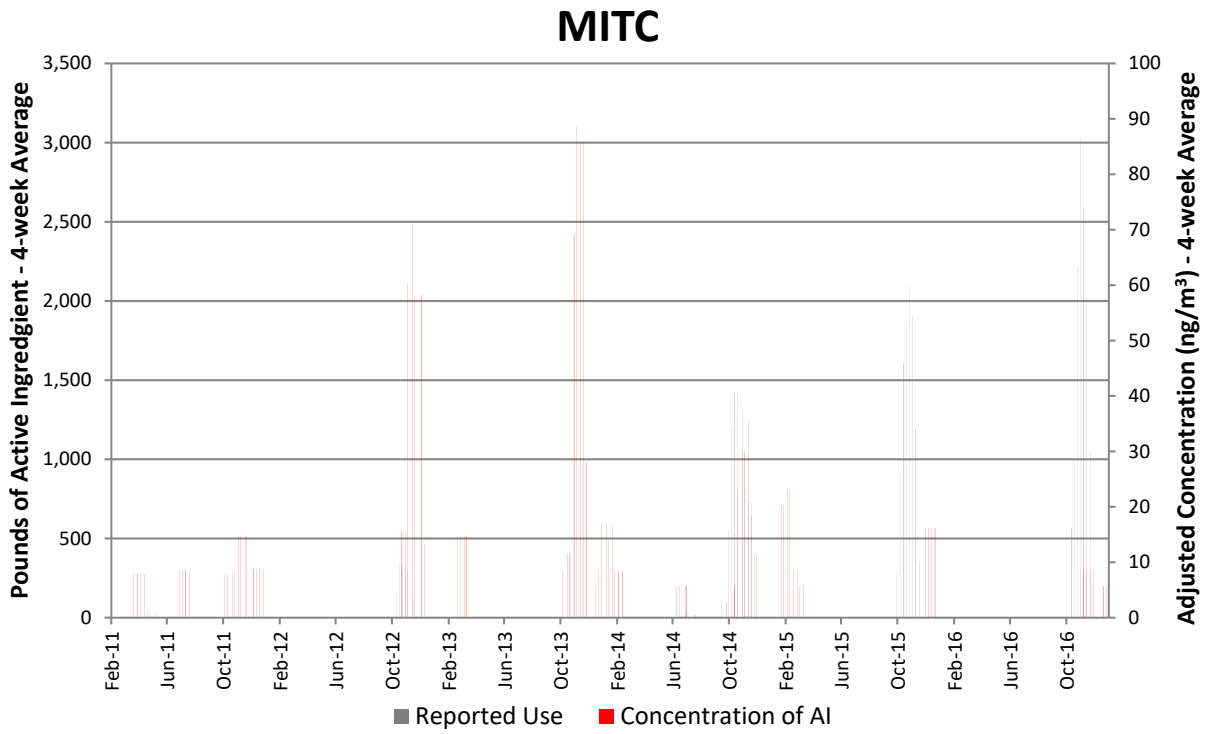


Figure 19. Concentration versus use for MITC in Salinas between February 1, 2011 and December 31, 2016.

Shafter

1,3-D

Figure 20 charts the measured concentration of 1,3-D versus use reported around the Shafter sampling site. On June 20, 2011, the reporting limit for 1,3-D was decreased from 2,270 ng/m^3 to 227 ng/m^3 and then further decreased to 22.7 ng/m^3 on October 24, 2013. Use of 1,3-D occurred throughout the study with varying amounts of 1,3-D applied. The only time period which 1,3-D use ceased for an extended period was approximately late spring to mid-summer or late summer. Peak use generally occurred in the fall to early winter.

The detections with the greatest magnitude occurred between late November 2013 and late January 2014; use was not particularly high at that time, however. Detections briefly matched use well in November 2016.

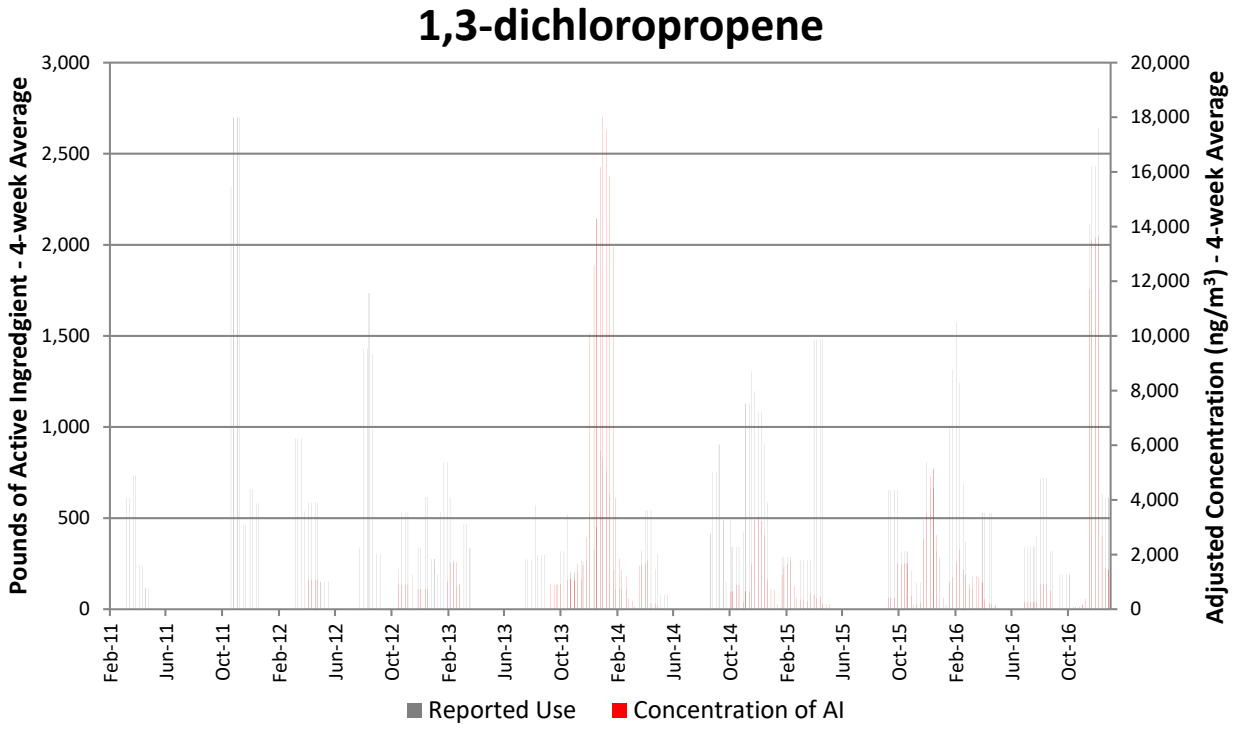


Figure 20. Concentration versus use for 1,3-dichloropropene in Shafter between February 1, 2011 and December 31, 2016.

Chloropicrin

Figure 21 charts the measured concentration of chloropicrin versus use reported around the Shafter sampling site. There was very little use of chloropicrin around the Shafter site during the study. Relatively

small amounts were applied between 2011 and 2013. In 2014, applications occurred briefly between late November and late December. Applications between late November and late December again occurred in 2016. No chloropicrin was detected between 2011 and 2016 at the Shafter site.

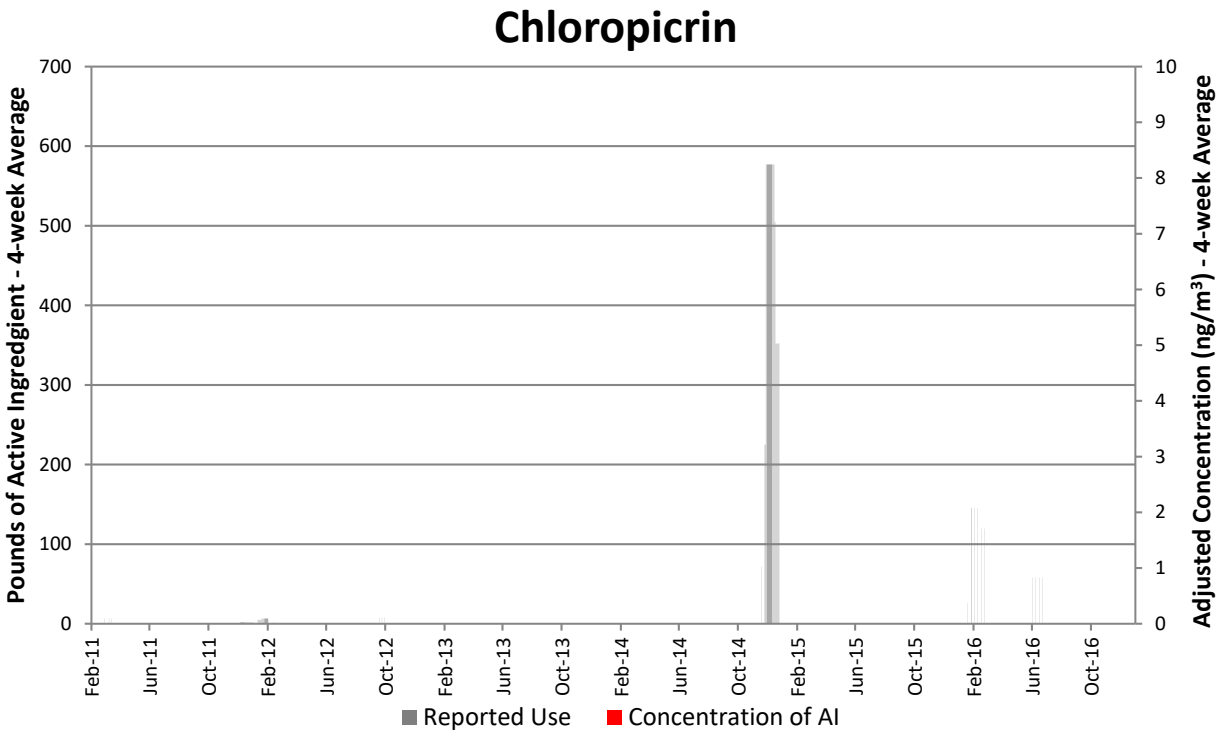


Figure 21. Concentration versus use for chloropicrin in Shafter between February 1, 2011 and December 31, 2016.

Chlorpyrifos

Figure 22 charts the measured concentration of chlorpyrifos versus use reported around the Shafter sampling site. Concentration data includes detections for both chlorpyrifos and its OA. The reporting limit for chlorpyrifos was 2.5 ng/m^3 and 1.45 ng/m^3 for its OA. The vast majority of chlorpyrifos + OA detections were at ND and Trace levels. Peak use routinely occurred in late December or early January to late January or early February every year. Between 2011 and 2013 there were reduced amounts of chlorpyrifos applied between July and August. There was a downward trend in chlorpyrifos use after its peak in 2013. After the early months of January 2016, use became minimal relative to the prior years.

Detections generally followed use patterns, although there were detections of chlorpyrifos and its OA with no reported use around Shafter monitoring site during July 2015. The number of detections was greater for chlorpyrifos than for its OA.

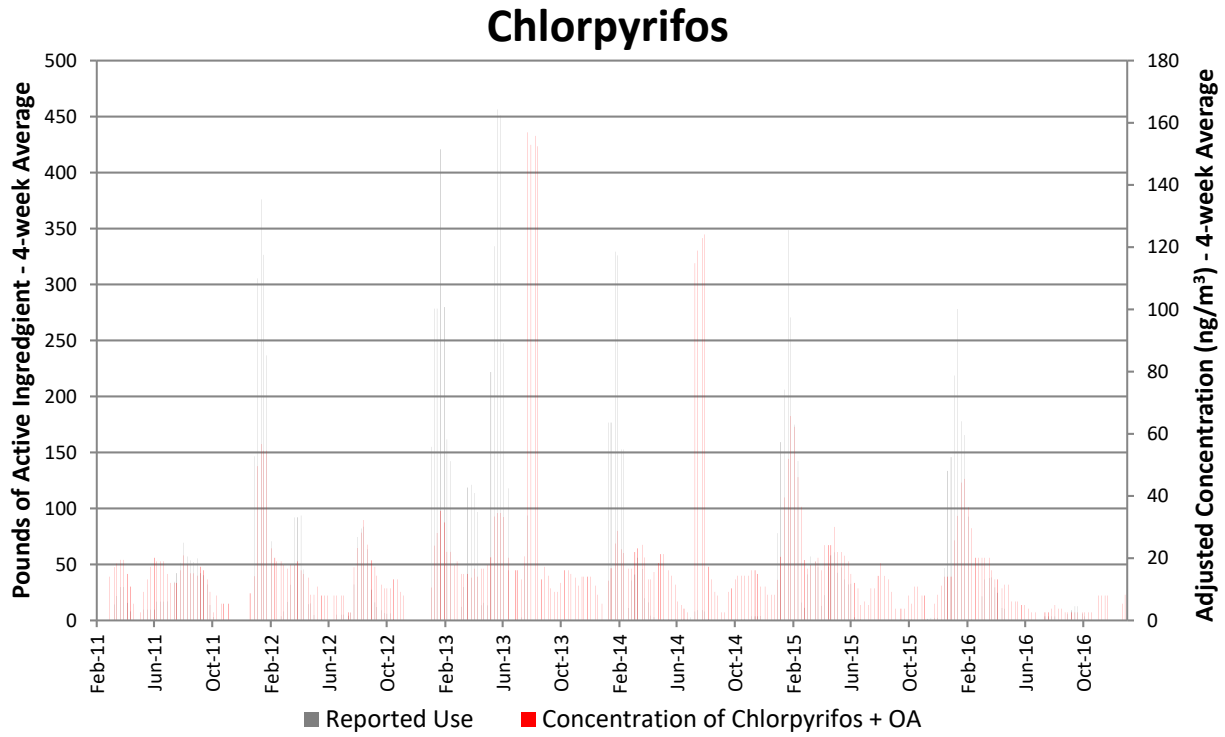


Figure 22. Concentration versus use for chlorpyrifos in Shafter between February 1, 2011 and December 31, 2016.

Diazinon

Figure 23 charts the measured concentration of diazinon versus use reported around the Shafter sampling site. Concentration data includes detections for both diazinon and its OA. The reporting limit for diazinon was 0.6 ng/m^3 and 1.05 ng/m^3 for its OA. From 2011 to 2016, diazinon was not applied around the Shafter monitoring site. In 2011 and 2013, applications were limited, from late October to mid-November. During these brief periods of application, detections correlated well with use. However, there were a small number of detections that did occur without reported use of diazinon in 2011 and 2016.

For diazinon use around the Shafter site, nine records were flagged for an application rate above 110% the allowed maximum. The amounts applied were corrected to 110% the allowed maximum and the records retained.

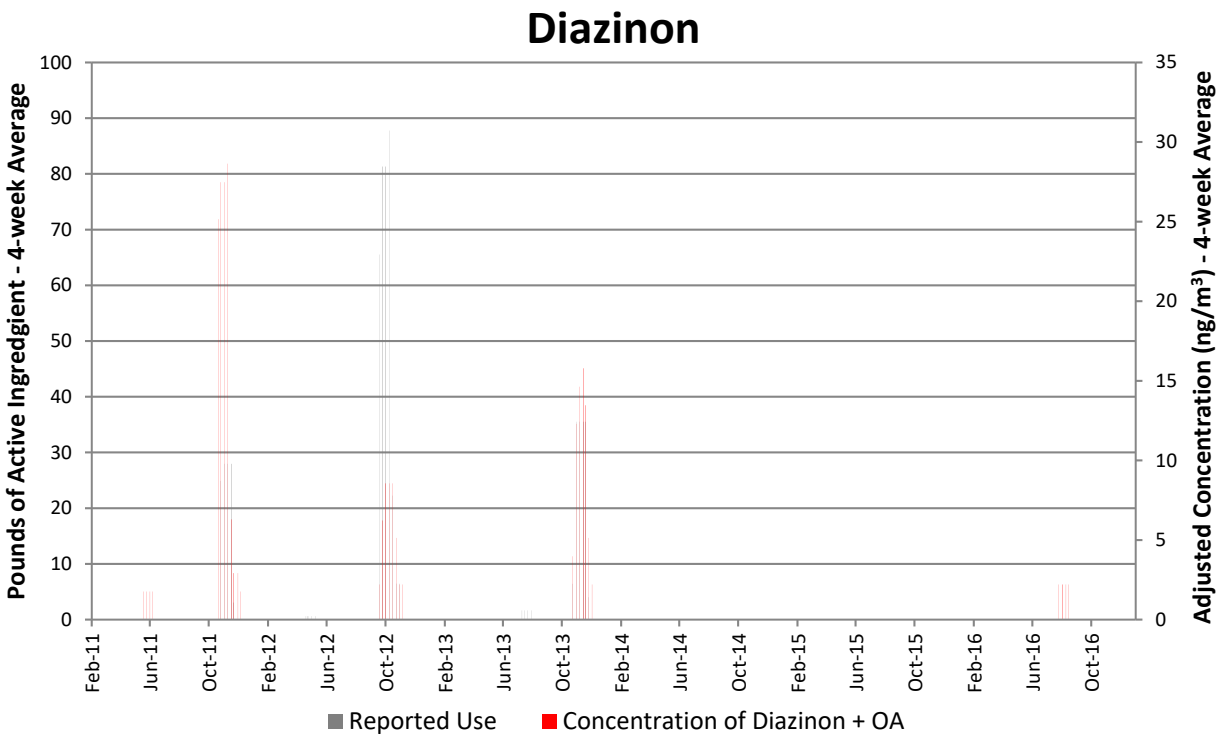


Figure 23. Concentration versus use for diazinon in Shafter between February 1, 2011 and December 31, 2016.

MeBr

Figure 24 charts the measured concentration of MeBr versus use reported around the Shafter sampling site. Reporting limits for MeBr were reduced twice from its initial reporting level of 1,980 ng/m^3; on June 20, 2011, the reporting limit was decreased to 198 ng/m^3 and on October 16, 2013 the reporting limit was reduced to 19.8 ng/m^3. Use of MeBr around the Shafter monitoring site was not common throughout the study. Relatively high use occurred from spring to early summer during the years where use was reported. Detections did not have a strong correlation to use except in 2012. Minor detections without reported use occurred later in the study.

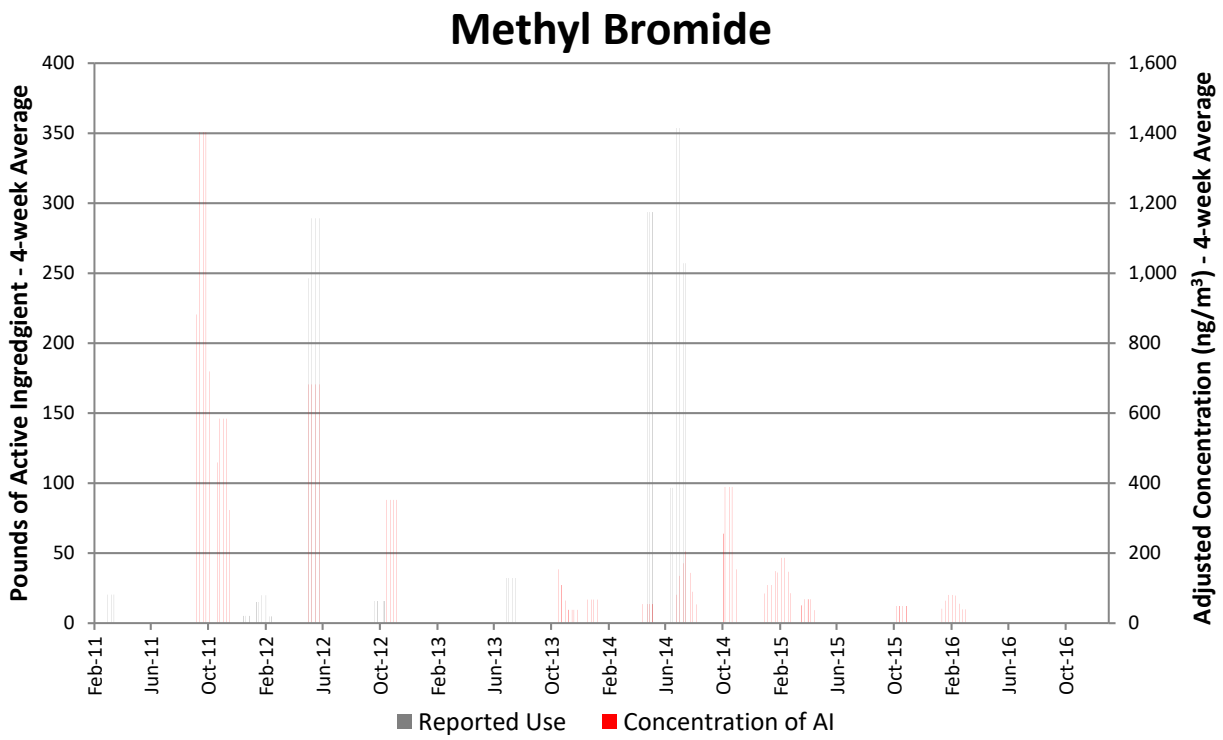


Figure 24. Concentration versus use for methyl bromide in Shafter between February 1, 2011 and December 31, 2016.

MITC

Figure 25 charts the measured concentration of MITC versus use reported around the Shafter sampling site. The reporting limit remained constant at 2.8 ng/m^3 throughout the study. Applications of MITC generally occurred February to March, August, and November to December. Use tended to decrease over the study period, with no applications around the Shafter monitoring site in 2016.

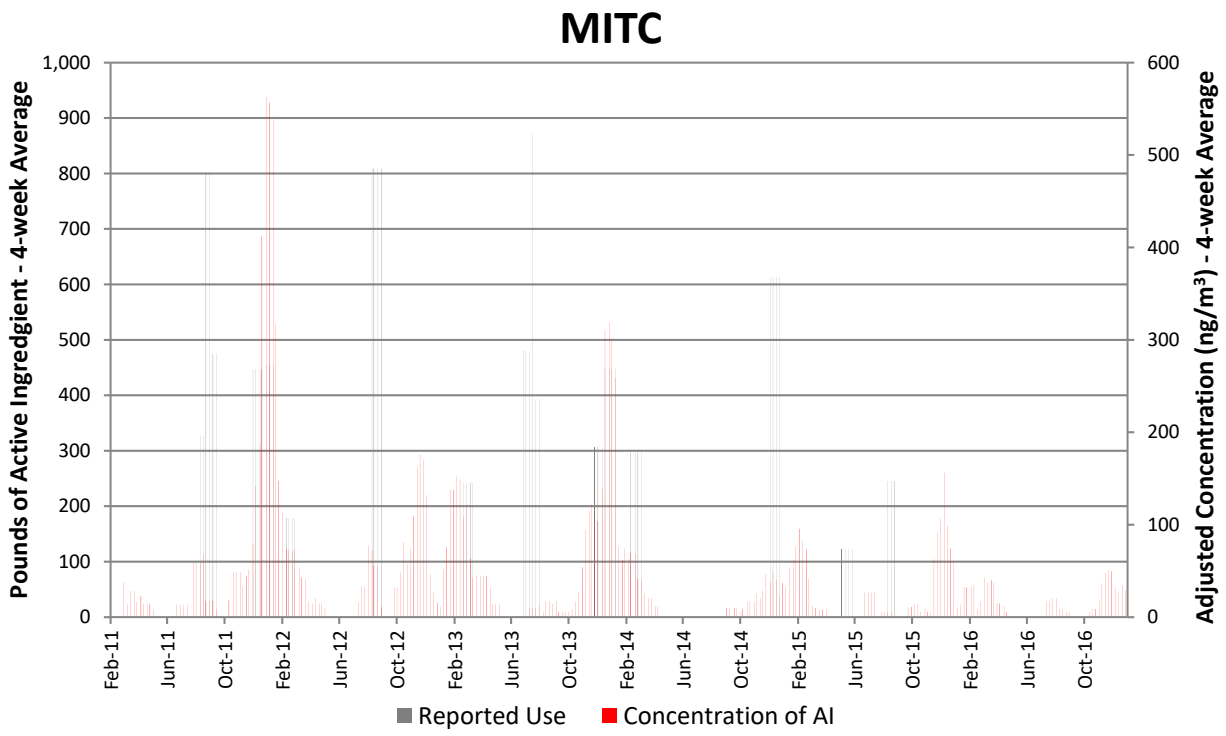


Figure 25. Concentration versus use for MITC in Shafter between February 1, 2011 and December 31, 2016.

Ripon

1,3-D

Figure 26 charts the measured concentration of 1,3-D versus use reported around the Ripon sampling site. On June 20, 2011, the reporting limit for 1,3-D was decreased from 2,270 ng/m^3 to 227 ng/m^3 and then further decreased to 22.7 ng/m^3 on October 24, 2013. Applications show an alternating pattern of high use and little to no use every year. Peak use consistently occurred during the second half of November and the first half of December. Peak detections occurred during November 2012 and January 2013 and did not occur again until November 2015 and January 2016.

For the 1,3-D use data around the Ripon monitoring site, two records were flagged: one for an application rate above 110% the allowed maximum, and one for reporting an incorrect application method. Both records were corrected and retained as mentioned earlier.

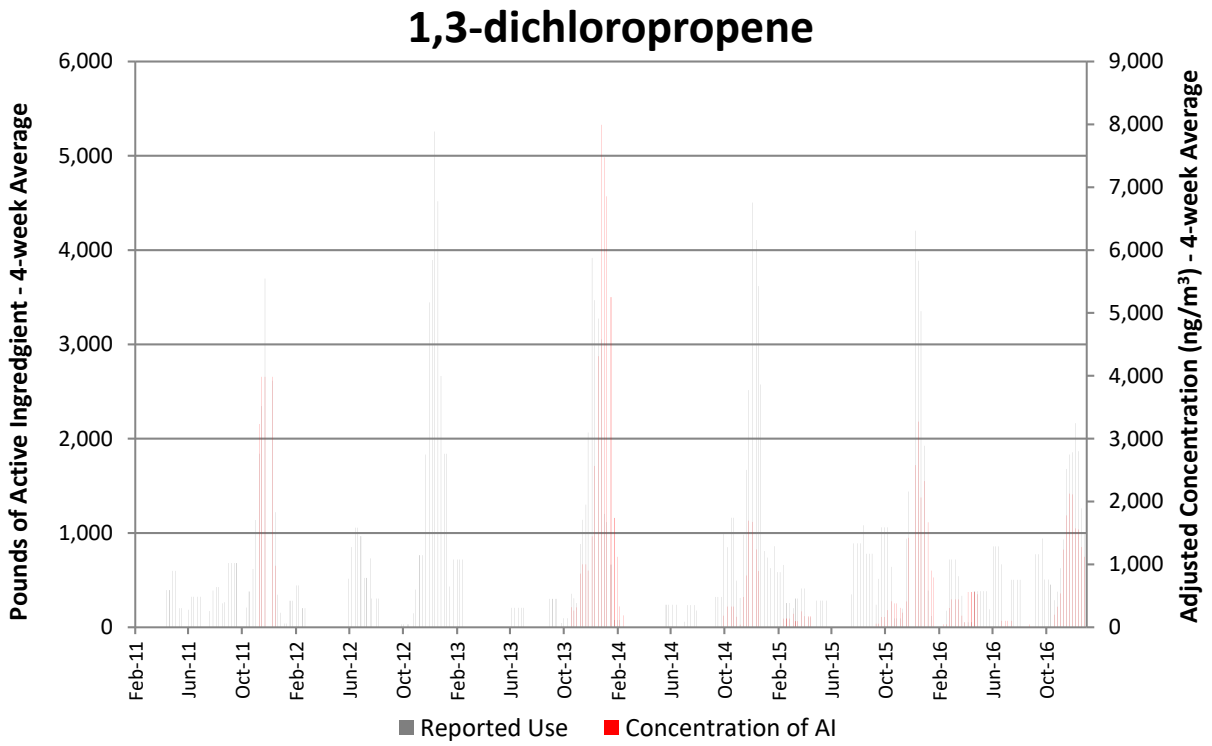


Figure 26. Concentration versus use for 1,3-dichloropropene in Ripon between February 1, 2011 and December 31, 2016.

Chloropicrin

Figure 27 charts the measured concentration of chloropicrin versus use reported around the Ripon sampling site. Applications fluctuated between a high use period and moderate use period every year. Peak applications generally occurred between the middle of March and the end of May every year. Another period of chloropicrin application, albeit relatively shorter, occurred mid-November to mid-December each year. Use of chloropicrin appears to steadily increase from 2011 to a peak in 2014, then decreased considerably in 2015 and thereafter.

Peak periods of detections occurred between the end of March and the beginning of April and continued until the first week of May for 2013 and 2014. Aside from these two instances of peak detections, the detection of chloropicrin at the sampling site in Ripon was rare. A small peak in detections during December 2016 coincides with a small use period during the same time. The reporting limit for chloropicrin was 111 ng/m^3.

In the analysis of chloropicrin use around the Ripon monitoring site, one record was flagged for reporting an incorrect application method, no correction to the data was made and the record was retained for use in this section.

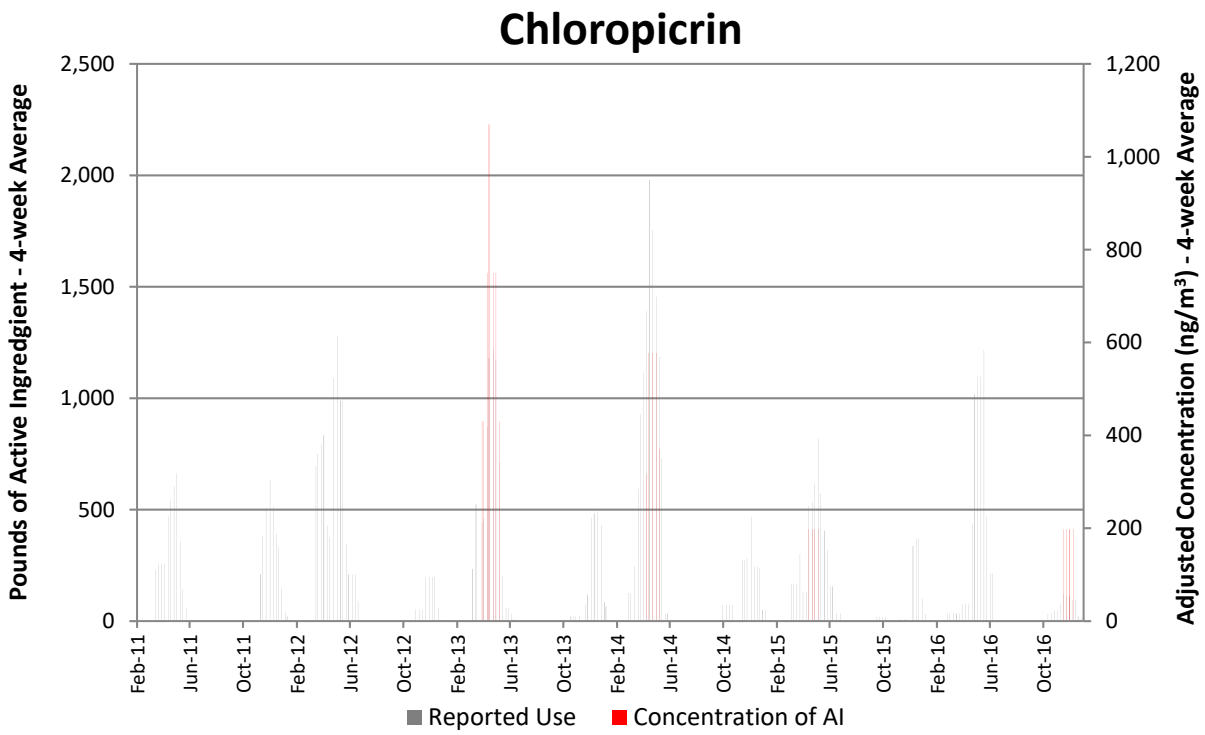


Figure 27. Concentration versus use for chloropicrin in Ripon between February 1, 2011 and December 31, 2016.

Chlorpyrifos

Figure 28 charts the measured concentration of chlorpyrifos versus use reported around the Ripon sampling site. Concentration data includes detections for both chlorpyrifos and its OA. The reporting limit for chlorpyrifos was 2.5 ng/m^3 and 1.45 ng/m^3 for its OA. Use of chlorpyrifos in Ripon roughly followed the pattern of use, which began in early May and ended by the last week of August 2011 to 2013. By 2014, chlorpyrifos use began early with applications occurring in February and continuing to the end of August. Overall use markedly decreased in 2015 compared to the previous use periods and then decreased even more in 2016 when applications occurred only in June and July.

There were detections of chlorpyrifos and its OA with no reported use within five miles of the monitoring site in Ripon. From 2011 to 2016, detections were greater for chlorpyrifos compared to its OA.

In the analysis of chlorpyrifos use around the Ripon monitoring site, one record was flagged for an application rate above 110% the allowed maximum. The amount applied was corrected to 110% the allowed maximum and the record retained.

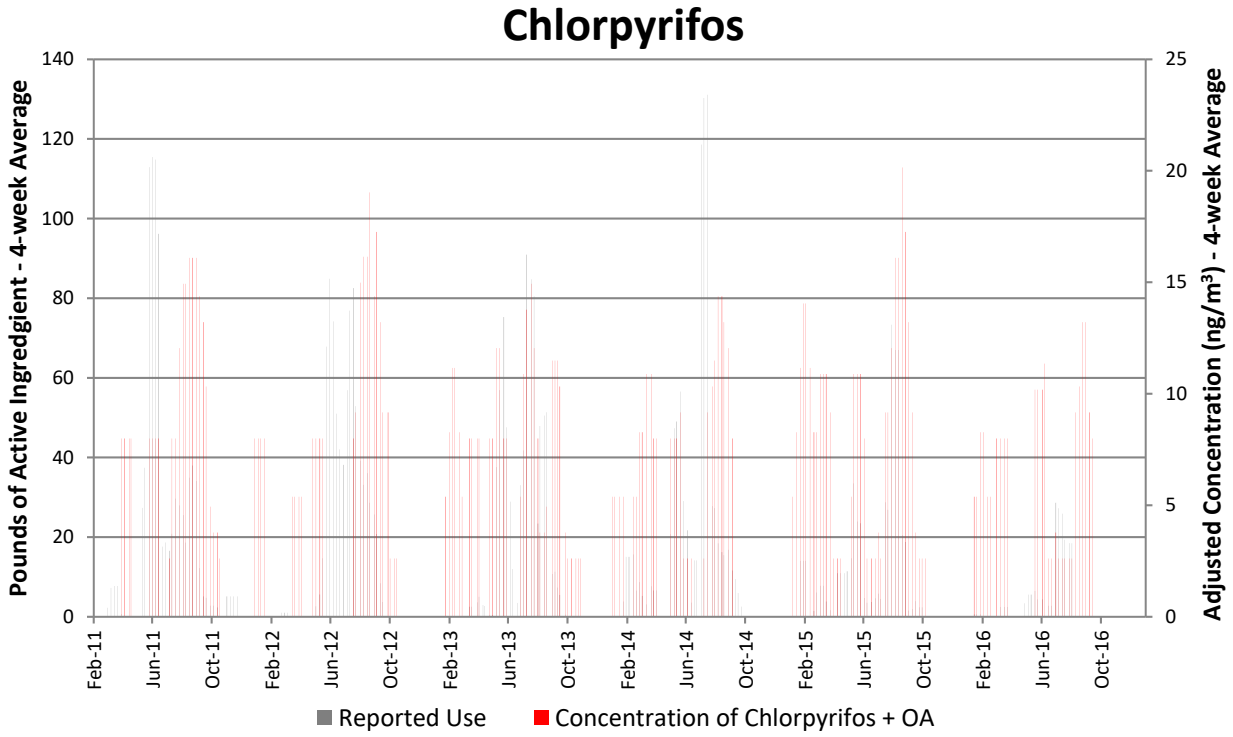


Figure 28. Concentration versus use for chlorpyrifos in Ripon between February 1, 2011 and December 31, 2016.

Diazinon

Figure 29 charts the measured concentration of diazinon versus use reported around the Ripon sampling site. Concentration data includes detections for both diazinon and its OA. The reporting limit for diazinon was 0.6 ng/m^3 and 1.05 ng/m^3 for its OA. Applications trended to be greatest during January and February for most years, particularly in 2013, 2015, and 2016. Applications were also carried out in June and July each year but not at the amounts observed during the winter months. Use continued to increase from 2011 to 2013 but dropped sharply in 2014. Use began to increase the following year and remained roughly stable into 2016. Overall, detections of diazinon were not common. The strongest correlation of detections to use occurred in February of 2013 where diazinon was detected at a greater concentration than its OA.

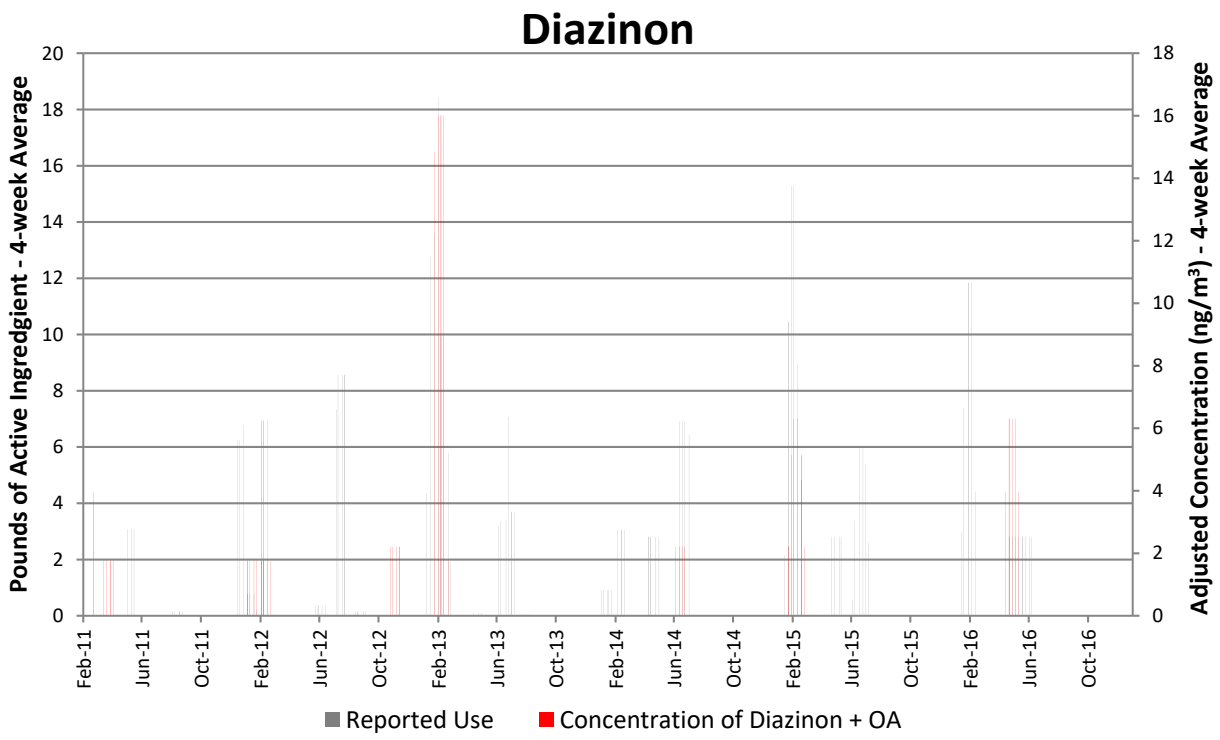


Figure 29. Concentration versus use for diazinon in Ripon between February 1, 2011 and December 31, 2016.

MeBr

Figure 30 charts the measured concentration of MeBr versus use reported around the Ripon sampling site. The reporting limits for MeBr were reduced twice from its initial reporting level of 1,980 ng/m^3; on June 20, 2011 the reporting limit was decreased to 198 ng/m^3 and on October 16, 2013 the reporting limit was reduced again to 19.8 ng/m^3. Use of MeBr followed a pattern of peak applications beginning mid to late March and ending between May and early June throughout the study period. Additional applications tended to occur in September to October and then again in November to December. Detections often did not follow the same pattern as use, except for peak use periods in 2014 and 2016.

Eight records were flagged for application rates above 110% the allowed maximum; the records were adjusted and retained. Three records were flagged for a combination of reporting an incorrect application method, reporting applications greater than 44 acres, or both. These records were retained for use in this section.

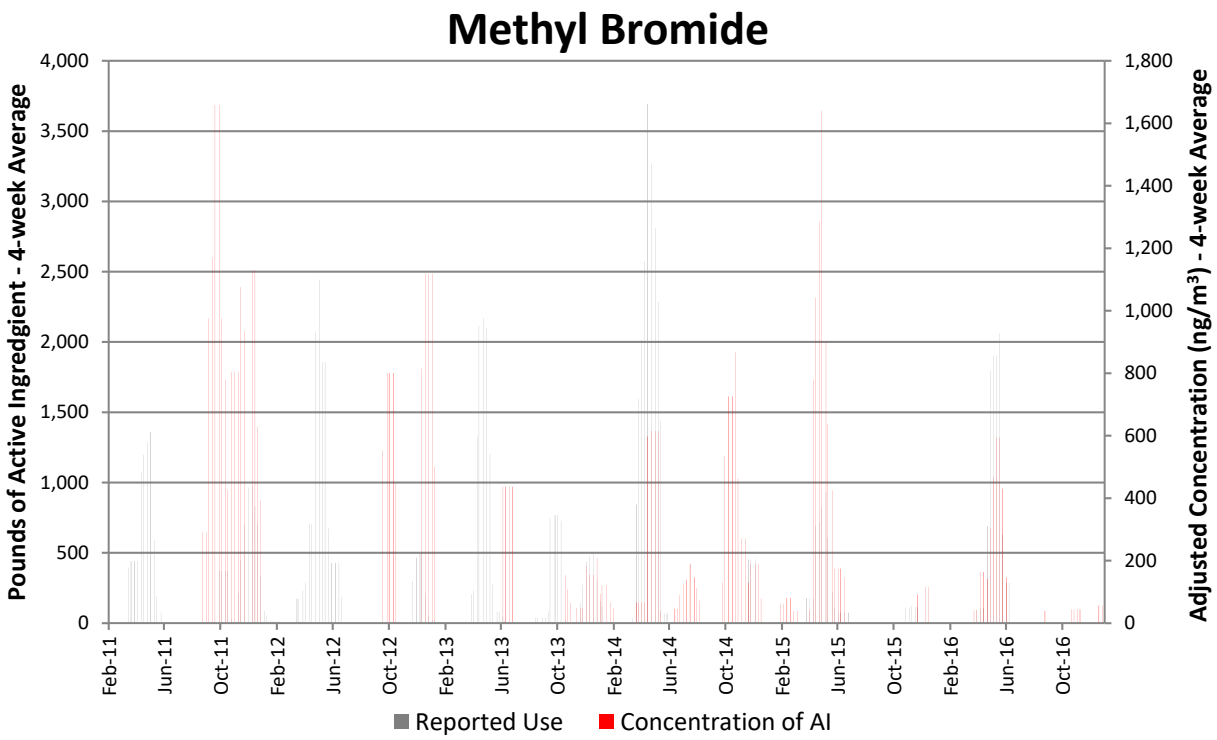


Figure 30. Concentration versus use for methyl bromide in Ripon, California between February 1, 2011 and December 31, 2016.

MITC

Figure 31 charts the measured concentration of methyl bromide versus use reported around the Ripon sampling site. The reporting limit remained constant at 2.8 ng/m^3 throughout the study. MITC use followed a pattern of nearly year-round applications but with significantly reduced use every late fall to early winter (approximately November to February) with peak use occurring at about the same time of the year and in similar amounts (over 2,000 lbs of AI averaged in August). Detections often did not trend with use; the detections that did occur were generally during the late fall and early winter (opposite of use trends).

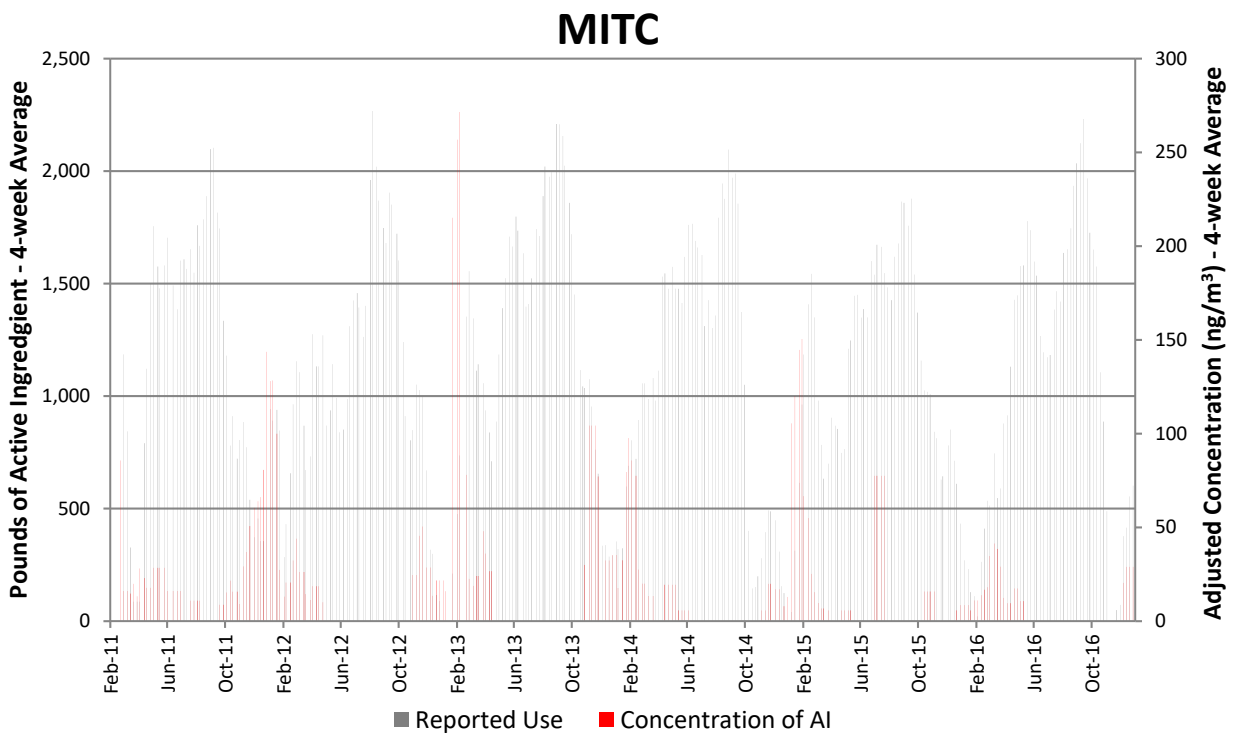


Figure 31. Concentration versus use for MITC in Ripon between February 1, 2011 and December 31, 2016.

Conclusion

The purpose of this section was to present a simple visual display of both the reported agricultural use and the measured pesticide air concentrations over time for 2011-2016. This section's intent was not to statistically assess the data; however, Section 6 does present statistically analyses results of pesticide concentrations and pesticide use, allowing us to evaluate this relationship further. Sections 7 and 10 also present results from advanced statistical analyses of the measured air concentration data and reported use data.

Section 6:

Simple Linear Regression Analysis of Selected Pesticides and Their Use

Introduction

DPR is interested in evaluating possible relationships between measured air concentrations and reported pesticide use for subchronic and chronic time periods over the years 2011 - 2016 at the sampling sites of Ripon, Salinas, and Shafter. To test whether a relationship exists between two quantitative variables a simple linear regression model was applied. The dependent variable for this analysis was pesticide air concentrations expressed in ng/m^3 and the independent variable was reported agricultural use in lbs of AI. The model can be represented using the equation:

$$\hat{y}=b_0+b_1x_i$$

Using this linear model, $\hat{y}$ is the response variable representing the estimated average air concentration of a subchronic period (4 or 13 weeks) or a chronic period (one year). The variable b_0 is identified as the y intercept when x is equal to zero and b_1x_i as the slope of the line for every increase or decrease in $\hat{y}$.

A selection of six pesticides and two degradates are included in this report's section analysis: 1,3-D (cis and trans isomers), chloropicrin, chlorpyrifos and its OA, diazinon and its OA, MeBr, and MITC. These pesticides were selected because they had greater counts of quantifiable detections and were characterized as high use fumigants or organophosphates.

Methods

Considerations for Changes in Laboratory Detection Limits

Through the course of the AMN, the laboratory methods underwent modifications that resulted in changes to the MDL. To address these changes, DPR parsed the data to compare pesticide use and air concentrations only for time periods where a detection limit remained unchanged. For this section analysis, 1,3-D and MeBr data from February 1, 2011 to June 19, 2011, was not used. The first interval used for both 1,3-D and MeBr analysis was between June 20, 2011, and October 14, 2013; the second time interval was October 15, 2013 through December 31, 2016. For chloropicrin, the LOQ was lowered once; therefore, DPR's analysis on this AI begins on June 18, 2013. These deviations limit how the data can be evaluated on the same scale.

For the entirety of the AMN (2011 - 2016), chlorpyrifos and its OA, diazinon and its OA, and MITC had laboratory detection limits that remained unchanged.

Comparing Air Concentration and Pesticide Data

For this evaluation, a week is defined as starting on Sunday and ending on a Saturday. The sample start date was used as the criteria to define the sample in a given week. Per standard DPR practice, reported ND concentrations were replaced with a value of one half of the MDL (adjusted concentration) and reported trace detections were replaced with a value equal to the midpoint between the LOQ and MDL. Pounds of AIs were obtained from the PUR database by using the proportion method outlined in Section 4 of this report. Briefly, a 5-mi radius around each of the three sampling sites was overlaid onto a county section map layer in ArcGIS and section ID numbers were extracted. A proportion value was assigned to each section depending on the actual portion of that section that was within the specified distance from the site location (Figure 32). Each record of lbs of AI was then multiplied by the proportion factor to yield the adjusted pounds (Adj. Lbs). Next, the week number was extracted from the application date and then the Adj. Lbs were summed by week. PUR data with no application date, but a reporting year were not included in this analysis. If no pesticide use within 5 miles of the sampling site location was reported for a specified week, zero values were applied. PUR data and air monitoring results were matched by week number. Multiple air samples falling within the same week were averaged as one air concentration for that week.

Concentrations of chlorpyrifos and its OA were summed to obtain a total chlorpyrifos concentration for each week using the adjusted concentration. Similarly, concentrations of diazinon and its OA were also summed and the total diazinon concentration was used for this analysis. Additionally, the isomers of 1,3-D (cis and trans) were combined as a sum to calculate the total 1,3-D in a sample and the adjusted concentration was used for the analysis.

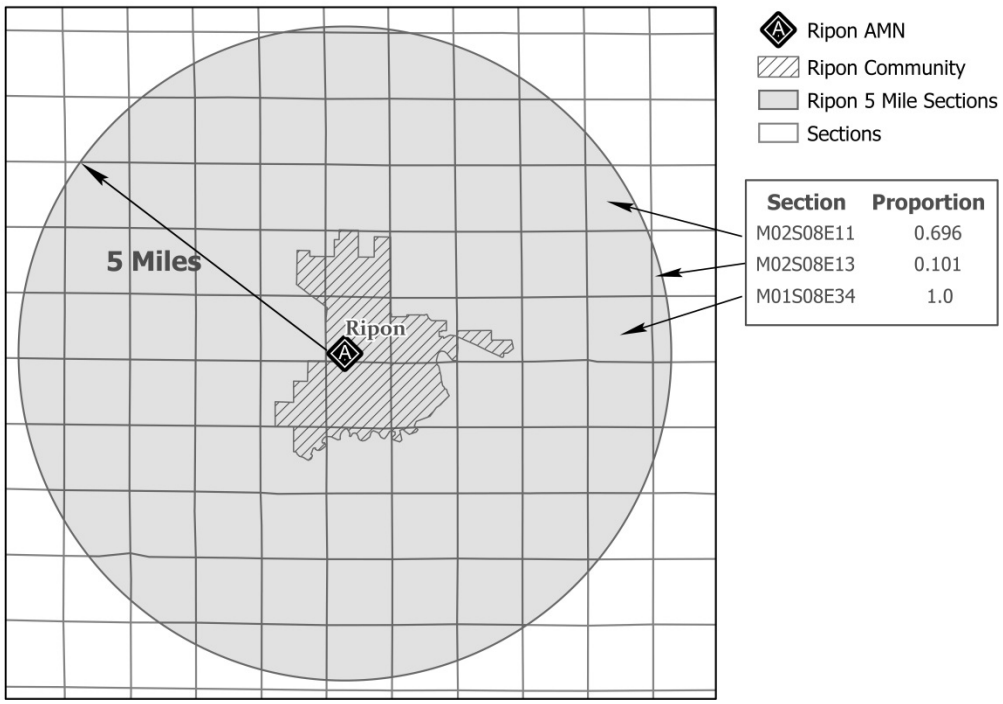


Figure 32. A graphical representation of DPR's proportion method to assign use amounts of applications in sections not entirely included inside of the assigned 5-mile distance from an AMN sampler location.

Linear Regression

A linear regression was applied to the six AIs at the three sampling sites. Regression results are presented and those that are statistically significant are noted. The models represent the best fit linear equations using the sampling data and reported pesticide use (Adj. Lbs). An alpha level of 0.05 was used for all regression analysis. In addition, the r^2 and standard error are reported. Regression analysis was computed for subchronic and chronic time periods. Historically, AIs with NDs > 90% have been omitted from inclusion in linear regression analysis, but they are included in this section for the selected six AIs at the three sampling site locations.

Subchronic Period

For most pesticides included in the AMN, DPR uses a standard 28-day period to represent subchronic concentrations. The average of consecutive 4-weeks of measured air concentrations was generated and each 4-week average was used to represent a subchronic concentration. The same averaging method was applied to the reported pesticide use within 5-mi from the three sampling site locations.

However, for two of the AIs (1,3-D and chloropicrin), DPR has established 90-day periods (13 weeks) to represent a subchronic timeframe for these AIs rather than the 28-day period used for other AIs in the AMN. As previously detailed, the 90-day time periods for these two AIs were derived based on two separate 90-day inhalation exposure studies used to calculate a seasonal reference concentration (RfC) for these AIs. The RfC value was derived after adjusting for differences in breathing and exposure duration between the experimentally exposed rats and children exposed under ambient conditions, and by applying a default uncertainty factor of 100 (Rubin 2016).

Treatment of Gaps in Sampling Data

Unforeseen circumstances in the field or laboratory (e.g., primary samples were lost and make-up samples were not possible); resulted in some weeks having incomplete monitoring data. To achieve this analysis, various ways of looking at the data for subchronic time period were examined. The number of gaps in the data determined whether a time step was included. Two scenarios were considered to determine if an interval was to be included in the subchronic regression models: (1) only include complete sets of 13 weeks, and (2) allow intervals of 12 weeks (i.e., allow up to 1 missing AMN week). Any time step interval less than 12 weeks was omitted from the regression analysis. In the latter scenario, pesticide use was averaged for the entire 13 weeks and air concentrations averaged for 12 weeks. Both scenarios are presented in this section. For the following AIs, a minimum of three weeks of data was required to be included in the subchronic regression model: chlorpyrifos, chlorpyrifos OA, diazinon, diazinon OA, methyl bromide and MITC. These special cases generally occurred in the interval preceding a detection limit change, in the last interval in 2016, or if there was a gap in air monitoring data.

Chronic Time Period

In this analysis, one year of averaged adjusted air concentration data corresponds to a chronic time period. The mean was comprised of the concentrations of the weekly samples and summarized for each year. Although the AMN began in February 2011, this 11-month sampling year was still included in the annual regression analysis for the following AIs: MITC, chlorpyrifos, chlorpyrifos OA, diazinon, and diazinon OA. MDL changes for 1,3-D, chloropicrin, and MeBr, prevented the use of several sampling years in this analysis (2011, 2012, and 2013); therefore, only the years 2014, 2015, and 2016 are included in the chronic time period regression analysis for these AIs. The weekly summaries of pesticide use within the 5-mi radius were averaged in the same manner. A linear regression for all six AIs per site was calculated.

Analysis Limitations

The scope of this regression analysis was limited to comparing reported pesticide use data in the 5-mi radii from sampling site locations. The model does not take into account any commodity, research exemption or other applications absent of a reported section (Meridian Township Range and Section; MTRS). It is possible that these applications, which are only required to be reported at the county level, may be a contributing factor in some measured air concentrations at a sampling site location. However, since these types of applications do not have greater spatial resolution, it was not possible to include them in this analysis.

For this analysis, there were no time-lags, data transformations, or other data adjustments made prior to linear regression analysis.

Analysis Results

Ripon

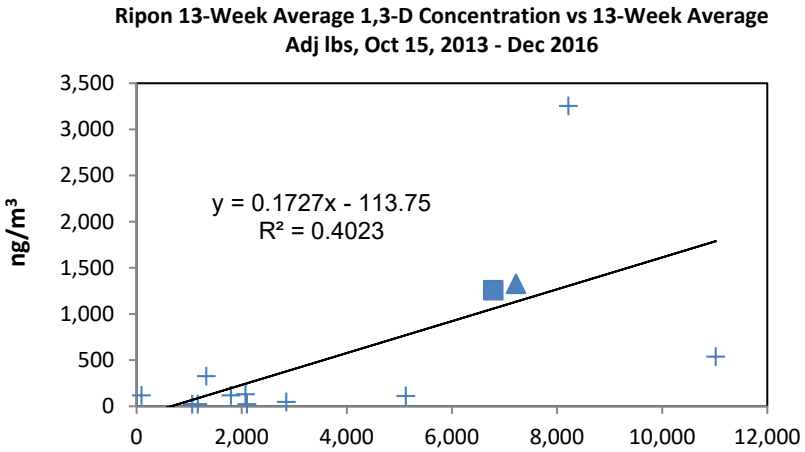
1,3-D

Within a 5-mi radius of the Ripon sampling site there were 250 reported applications of 1,3-D for 2011-2016, 126 of which occurred between 2014-2016. Untarped fumigant applications were the most common reported method of application in the 5-mi radius.

1,3-D subchronic concentrations when the MDL was equal to 454 ng/m^3 (June 20, 2011 to October 14, 2013), resulted in eight of the nine 13-week intervals having no detectable concentrations, even though 1,3-D use was reported during that time. A linear regression was applied, but it was not significant ($p>0.05$).

Subchronic concentrations for 1,3-D at the Ripon sampling site were statistically significant ($p<0.05$) for data between October 15, 2013 and December 31, 2016 when the dataset included the two 12 week intervals of 1,3-D concentrations (Figure 33). One of the 12-week intervals was produced from a gap in data for week 49 in 2015 (triangle symbol) and the second 12-week interval was a result of a sampling conclusion at the site at the end of 2016 (square symbol) (Figure 33). The peak subchronic concentration for 1,3-D was 3,253 ng/m^3. The coefficient of determination indicated a moderate positive relationship which may explain approximately 40% of the variation in 1,3-D subchronic concentrations. When applying a linear regression to the dataset with complete 13 week intervals, the r^2 dropped from 0.40 to 0.33 and was no longer statistically significant ($p=0.06$).

Analysis of chronic concentrations of 1,3-D were limited to years 2014-2016 and a linear regression model yielded a low r^2 of 0.001 and poorly correlated with no statistical significance. Chronic concentrations for the three years fell between 302 to 389 ng/m^3 per year.



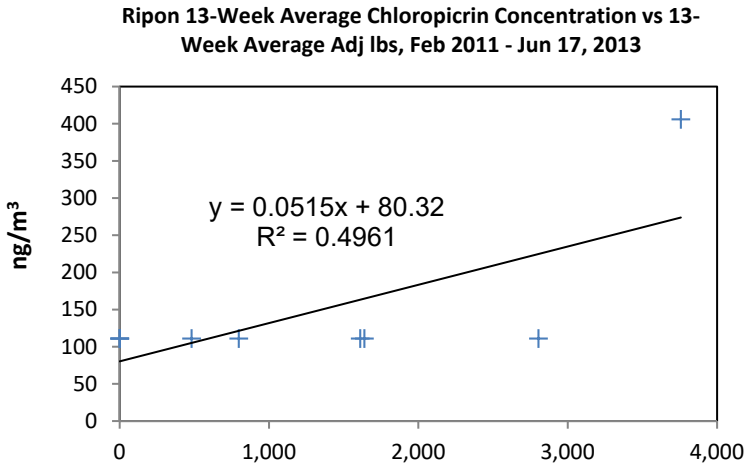
Regression Statistics	
Multiple R	0.634
R Square	0.402
Adjusted R Square	0.348
Standard Error	747.916
Observations	13

Figure 33. Ripon 13-week average 1,3-D concentration vs 13-week average Adj. Lbs, Oct 15, 2013 - Dec 2016

Chloropicrin

Within 5 miles of the Ripon sampling site, there were a total of 338 reported chloropicrin applications that occurred between February 1, 2011, and December 31, 2016. A total of 137 reported applications occurred in 2014 and 2016 and were included in the comparison between chronic concentrations and annual average use of chloropicrin. The linear regression model did not determine statistically significant results for data from 2014 to 2016 (Figure 34). The poor relationship may be influenced by the number of NDs and the dataset having only two quantifiable detections from 2011 to 2016.

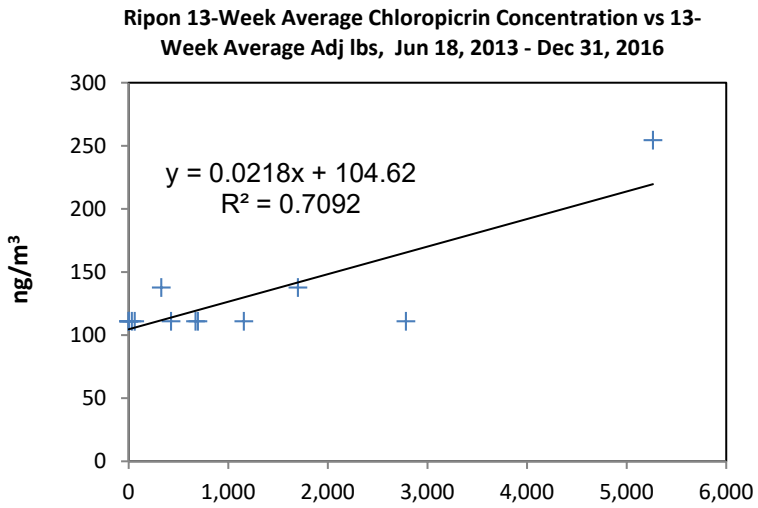
During the period February 1, 2011, to June 17, 2013, there were nine 13-week time steps included in the subchronic regression analysis. The last time step was excluded since it was composed of only 7-weeks and did not meet the minimum criteria of 12 weeks. Eight of the nine observations were all ND concentrations. The peak subchronic concentration was 405 ng/m^3 when the average Adj. Lbs were 3,757 lbs. The reporting p-value for chloropicrin data was statistically significant at $p < 0.05$.



Regression Statistics	
Multiple R	0.704
R Square	0.496
Adjusted R Square	0.424
Standard Error	74.601
Observations	9

Figure 34. Ripon 13-week average chloropicrin concentration vs 13- week average Adj. Lbs, Feb 2011 - Jun 17, 2013

During the time period when the chloropicrin LOQ was equal to 694 ng/m^3 (June 18, 2013, to December 31, 2016), the subchronic linear regression model produced a coefficient of determination of 0.709 at the Ripon sampling site and results were statistically significant ($p < 0.001$) (Figure 35). There were 14 observations included in the analysis and during this time frame the highest subchronic concentration of chloropicrin equaled 254 ng/m^3.



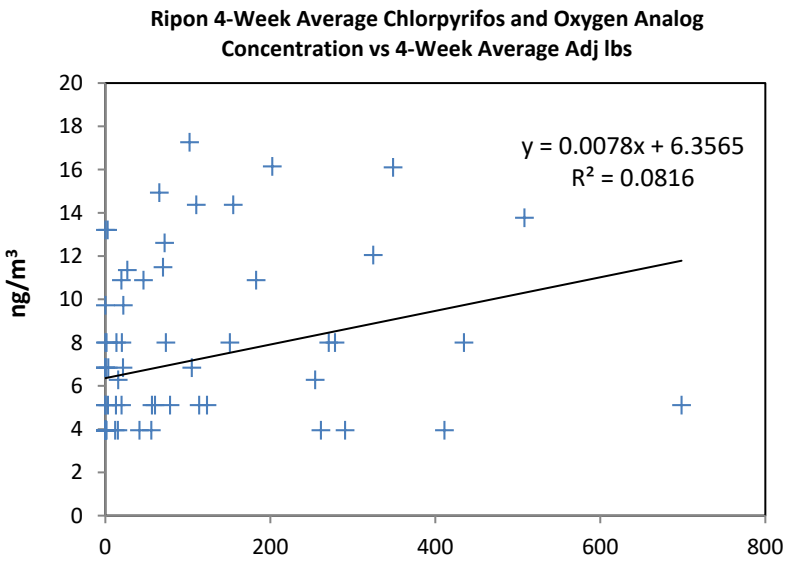
Regression Statistics	
Multiple R	0.842
R Square	0.709
Adjusted R Square	0.685
Standard Error	21.605
Observations	14

Figure 35. Ripon 13-week average chloropicrin concentration vs 13- week average Adj. Lbs, Jun 18, 2013 - Dec 31, 2016

Chlorpyrifos and Chlorpyrifos OA

Chlorpyrifos and chlorpyrifos OA produced poor relationships in Ripon for the chronic regression. Although the subchronic coefficient of determinations were low (r^2 = 0.08), the result was statistically significant

($p<0.05$) (Figure 36). Results may likely be greatly influenced by the large number of NDs at this site for both chlorpyrifos and its OA. During 2011 - 2016, there were 627 applications made within 5-miles from the sampling site location.

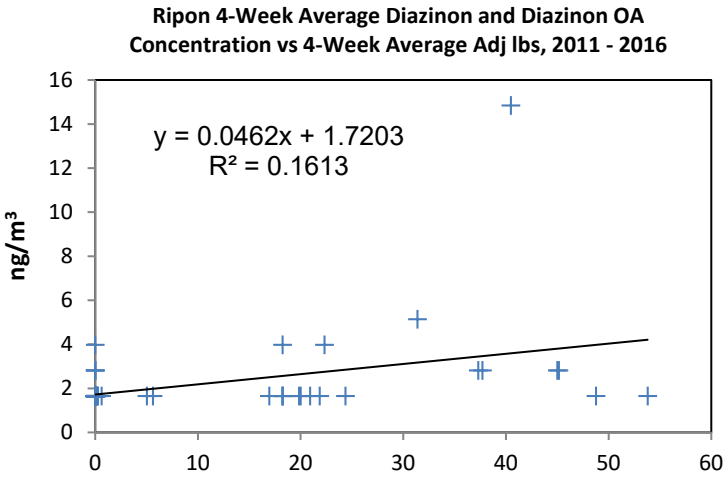


Regression Statistics	
Multiple R	0.285
R Square	0.081
Adjusted R Square	0.069
Standard Error	3.603
Observations	77

Figure 36. Ripon 4-week average chlorpyrifos and oxygen analog concentration vs 4-week average Adj. Lbs

Diazinon and Diazinon OA

In Ripon, subchronic concentrations of diazinon and its OA in Ripon ranged from 1.65 to 14.84 ng/m^3. The r^2 was low, accounting for 16% of the variation in subchronic air concentrations using 4-week averages of Adj. Lbs of diazinon. Although, the coefficient of determination was low, the result was significant ($p < 0.00029$). Pesticide use for diazinon during 2011-2016 was characterized as low (2,463 Adj. Lbs) within the 5-mi radius of the sampling site locations. The count of diazinon applications made from February 1, 2011, to December 31 2016 was 68. It is likely that since use was minimal near the Ripon sampling site, the results were poorly correlated (Figure 37). The fit of the linear regression may have been poor since there was only one quantifiable detection of diazinon and none for its OA.



Regression Statistics	
Multiple R	0.401
R Square	0.161
Adjusted R Square	0.150
Standard Error	1.491
Observations	77

Figure 37. Ripon 4-week average diazinon and diazinon OA concentration vs 4-week average Adj. Lbs, 2011 - 2016

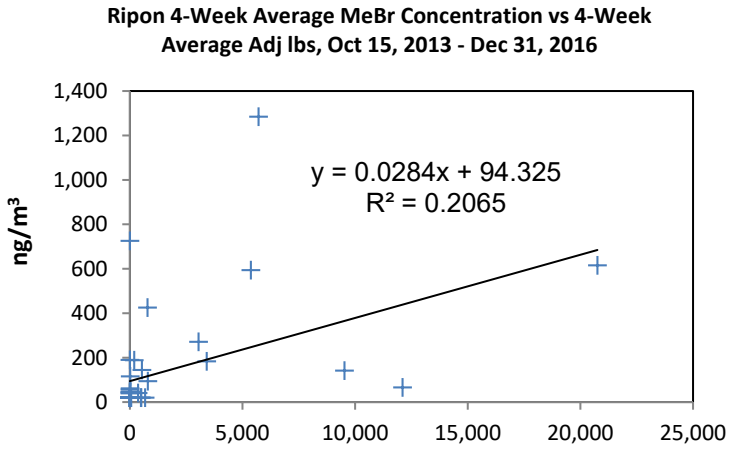
In Ripon, chronic concentrations of diazinon and its OA were summed and ranged from 1.74 to 2.75 ng/m^3 for years 2011 to 2016. The linear regression for chronic concentrations versus annual Adj. Lbs failed to produce results that were statistically significant ($p > 0.05$).

MeBr

A linear regression was attempted for data between June 20, 2011, and October 14, 2015 when the MDL equaled 396 ng/m^3, but this also resulted in a poor correlation (data not shown). During this period, the maximum subchronic concentration for MeBr was 1,179 ng/m^3, but coincided with a data gap for this time step (3-week average). The second highest concentration was 1,118 ng/m^3 .

Between October 15, 2013 and December 31, 2016 when the MDL equaled 39.6 ng/m^3, 212 agricultural applications of MeBr were reported and included in the subchronic linear regression (Figure 38). A maximum subchronic concentration for MeBr was determined to be 1,285 ng/m^3 during this time frame. The model presented a positive relationship ($r^2 = 0.20$) and yielded statistically significant results with a p-value of 0.0025 indicating a positive relationship of measured air concentrations with reported use during this time frame at this sampling site location.

Chronic concentrations of MeBr were compared to annual averages of reported agriculture applications for years 2014 to 2016. However, the linear regression, failed to produce significant results (p = 0.82) (Figure 38). During this time 154 MeBr applications within 5-miles of the Ripon sampling site were reported.

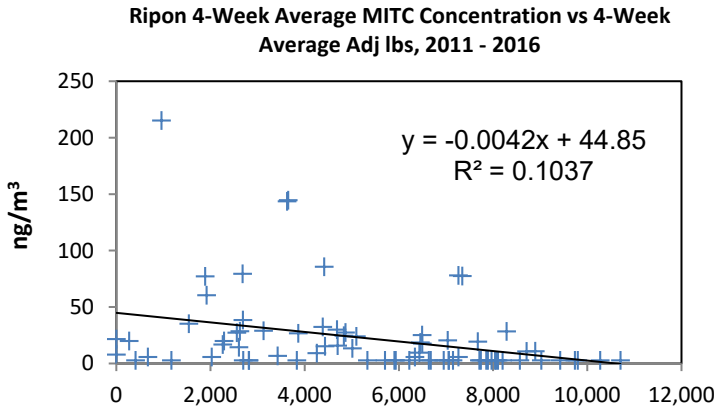


Regression Statistics	
Multiple R	0.454
R Square	0.206
Adjusted R Square	0.186
Standard Error	225.457
Observations	42

Figure 38. Ripon 4-week average MeBr concentration vs 4-week average Adj. Lbs, Oct 15, 2013 - Dec 31, 2016

MITC

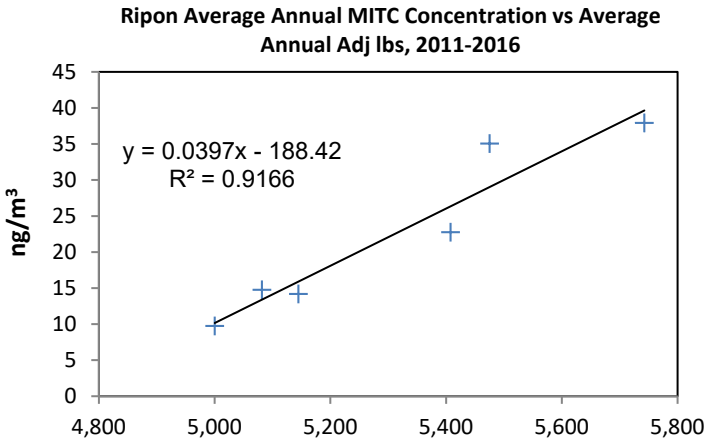
Subchronic concentrations of MITC yielded an r^2 of 0.10 when compared to 4-week averages of MITC-generating products at the Ripon sampling site (Figure 39). MITC subchronic concentrations were between 2.8 and 215 ng/m^3 for 2011 - 2016. The linear regression was statistically significant with a reporting p-value below 0.005 (Figure 39). Out of the 77 observations of 4-week intervals, only two intervals reported no MITC applications within 5 miles of the Ripon sampling site.



Regression Statistics	
Multiple R	0.3221
R Square	0.1037
Adjusted R Square	0.0918
Standard Error	34.6757
Observations	77

Figure 39. Ripon 4-week average MITC concentration vs 4-week average Adj. Lbs, 2011 - 2016

Results between MITC chronic concentrations and annual MITC-generating product applications presented a good fit at the Ripon sampling site. Comparing annual MITC concentrations to annual Adj. Lbs of MITC products from 2011 to 2016, the model yielded a positive linear relationship and an r^2 of 0.9166 (Figure 40). Resultant p-values were less than 0.005, showing statistical significance in the linear model. The average annual MITC concentration highest in 2013 (38 ng/m^3) and the lowest average annual concentration was 10 ng/m^3 in 2016. Since DPR began collecting sampling data in Ripon there were 13,826 applications of combined MITC-generating products (Basmid G, K-Pam HL and Vapam) within the 5-mi radius from the sampling site location.



Regression Statistics	
Multiple R	0.957
R Square	0.917
Adjusted R Square	0.896
Standard Error	3.785
Observations	6

Figure 40. Ripon average annual MITC concentration vs average annual Adj. Lbs, 2011-2016

Salinas

1,3-D

The Salinas area is a high-use region for 1,3-D. Between 2011 and 2016, there were 617 reported applications within a 5-mi radius of the Salinas sampling site. The highest use for 1,3-D tended to occur in the later months of the year. Among the last three years of monitoring at Salinas, 346 applications of 1,3-D were reported. Chronic concentrations of 1,3-D plotted against weekly average Adj. Lbs yielded an r^2 of 0.98, but a p-value greater than 0.05, which suggests the data is not statistically significant. Chronic concentrations for 2014-2016 ranged from 33 to 200 ng/m^3.

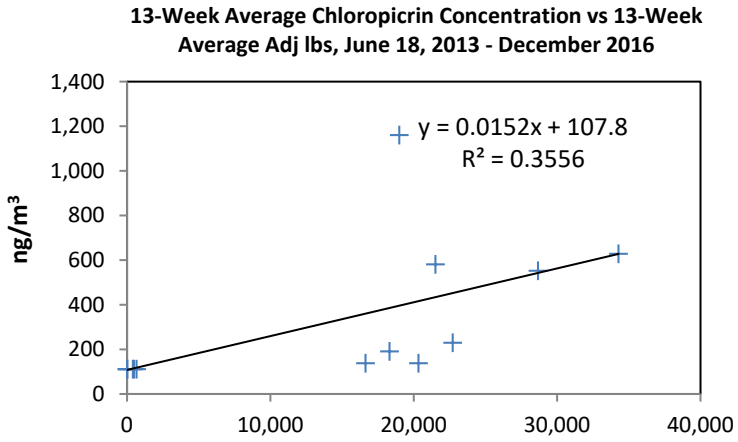
The 1,3-D data for Salinas was further complicated by gaps in weekly data, which limited the number of intervals with a minimum of 12-weeks that could be used in the subchronic regression analysis. The subchronic concentrations of 1,3-D data between June 20, 2011, and October 14, 2013, was highest at 1,235 ng/m^3. No relationship was shown using the linear regression model between applied 1,3-D and subchronic average concentrations of 1,3-D. The same was true for 1,3-D concentration and use data after October 15, 2013. Concentrations of 1,3-D ranged from 22.7 to 464 ng/m^3. It is worth noting that tarpaulins

are used in the Salinas region when applying 1,3-D in order to lower air emissions, therefore, this mitigation procedures affected the correlation of use data with measured air concentrations.

Section 7 of this report further explores 1,3-D air concentrations and use data by incorporating several additional variables to explain the use-concentration relationship. The additional variables explored in this section include: refined estimates of the proportion of mass emitted from fumigated fields depending on application method (e.g., use of tarpaulins during applications), flux profiles (fumigant mass emitted from a field over time), meteorological data, and spatial data (including distance and direction of a fumigation from a monitoring site). All of these variables were applied to the model using a relatively simple pollutant dispersion function to approximate the relative impact of an application in accordance with meteorological conditions, application method, and distance from an air monitoring station.

Chloropicrin

Chronic concentrations of chloropicrin for 2014-2016 ranged from 228 to 253 ng/m^3. During the same time frame, weekly averages of pesticide use ranged from 10,460 to 12,892 Adj. Lbs. There was no statistical significance when applying a linear regression for the chronic time period for chloropicrin (Figure 41). During the sampling period (2011-2016), 1,228 chloropicrin applications were made within a 5-mi radius of the Salinas sampling site. Analysis of subchronic chloropicrin concentrations were best correlated with reported use for the period October 18, 2013, to December 31, 2016. Using this dataset in our model, the coefficient of determination was 0.35 with a p-value of 0.024. During this period, a peak subchronic concentration was measured at 1,160.7 ng/m^3.

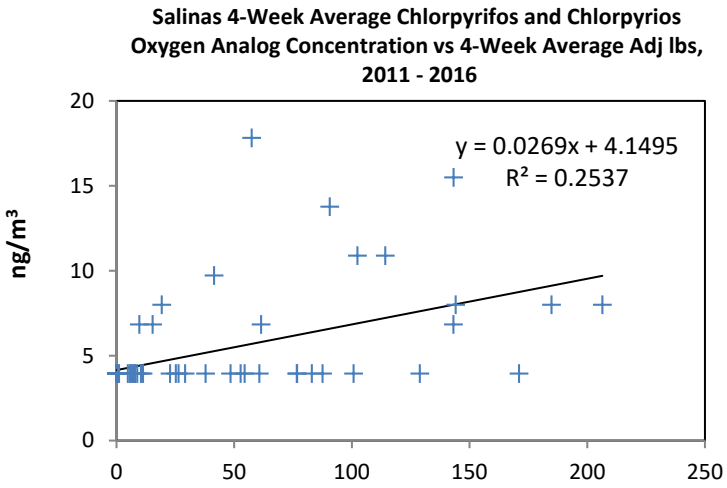


Regression Statistics	
Multiple R	0.596
R Square	0.356
Adjusted R Square	0.302
Standard Error	261.606
Observations	14

Figure 41. 13-week average chloropicrin concentration vs 13-week average Adj. Lbs, June 18, 2013 - December 2016

Chlorpyrifos and Chlorpyrifos OA

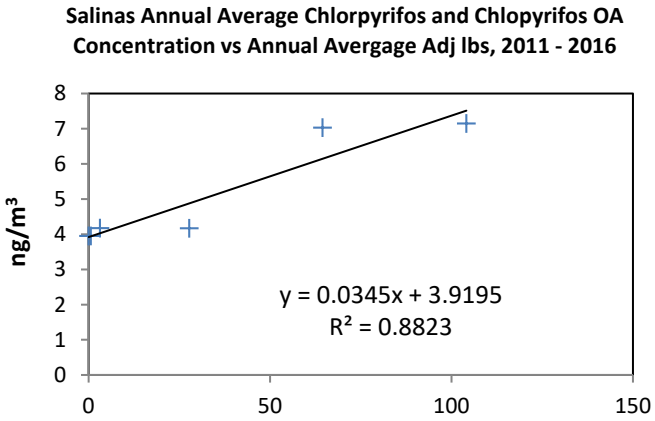
Chlorpyrifos and chlorpyrifos OA subchronic concentrations measured at the Salinas sampling site peaked at 17.82 ng/m^3. The r^2 between 4-week averaged air concentrations and 4-week averages of applied chlorpyrifos Adj. Lbs was 0.25 (Figure 42). The 77 observations in the linear regression presented a highly significant p-value of <0.000005.



Regression Statistics	
Multiple R	0.504
R Square	0.254
Adjusted R Square	0.244
Standard Error	2.365
Observations	77

Figure 42. Salinas 4-week average chlorpyrifos and chlorpyrifos OA concentration vs 4-week average Adj. Lbs, 2011 -2016

The linear regression model results for chronic concentrations of chlorpyrifos summed with its OA and the annual chlorpyrifos use were of statistical significance ($p < 0.01$). The coefficient of determination was 0.882 for 2011-2016 (Figure 43). The range of chronic concentrations was between 3.95 and 7.15 ng/m^3 depending on the sampling year. Use data show that a total of 814 chlorpyrifos applications were made within a 5-mi radius from the Salinas sampling site, for a 6-year sum of 10,529 Adj. Lbs. Most applications occurred prior to 2015 and the number of applications dropped to zero in 2016.

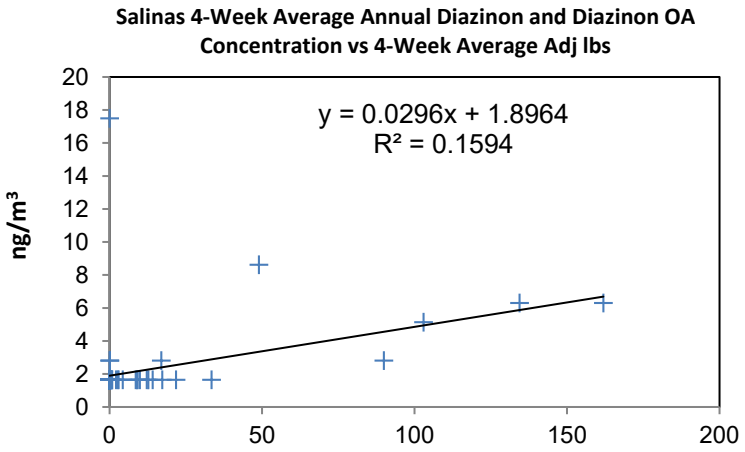


Regression Statistics	
Multiple R	0.939
R Square	0.882
Adjusted R Square	0.852
Standard Error	0.601
Observations	6

Figure 43. Salinas annual average chlorpyrifos and chlorpyrifos OA concentration vs annual average Adj. Lbs, 2011 -2016

Diazinon and Diazinon OA

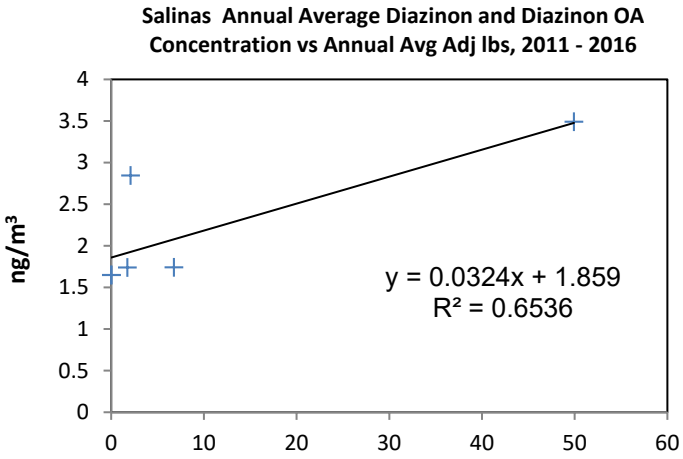
Approximately 16% of subchronic concentrations of diazinon and its OA are explained using the simple linear regression model (Figure 44). Subchronic concentrations of diazinon and its OA ranged from 1.7 to 18 ng/m^3. The peak was not associated with any reported applications within 5 miles of the sampling site. The linear regression included 77 observations; the results are statistically significant (p-value = 0.0003.



Regression Statistics	
Multiple R	0.399
R Square	0.159
Adjusted R Square	0.148
Standard Error	1.950
Observations	77

Figure 44. Salinas 4-week average annual diazinon and diazinon OA concentration vs 4-week average Adj. Lbs, 2011 -2016

Salinas' diazinon and diazinon OA chronic concentrations ranged between 1.7 and 3.5 ng/m^3 for the sampling years 2011-2016. In the 5-mi radius of the Salinas sampling site, a total of 458 applications of diazinon occurred during 2011-2016. The 6-year sum of applied diazinon was 2,818 lbs. Air monitoring results captured one quantifiable detection for diazinon and its OA at the Salinas sampling site. Chronic concentrations of diazinon and its OA when compared to Adj. Lbs of diazinon yielded an r^2 of 0.65, but it was not significant as it was just over the threshold of what is considered statistically significant (p=0.05) (Figure 45).

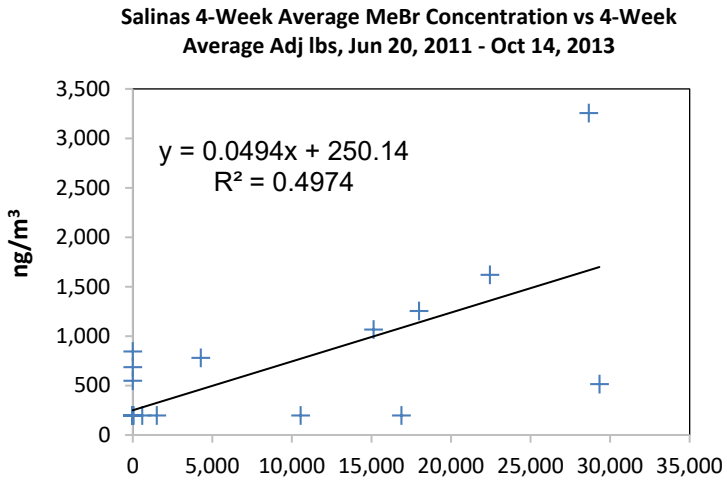


Regression Statistics	
Multiple R	0.808
R Square	0.654
Adjusted R Square	0.567
Standard Error	0.519
Observations	6

Figure 45. Salinas annual average diazinon and diazinon OA concentration vs annual Adj. Lbs, 2011 – 2016.

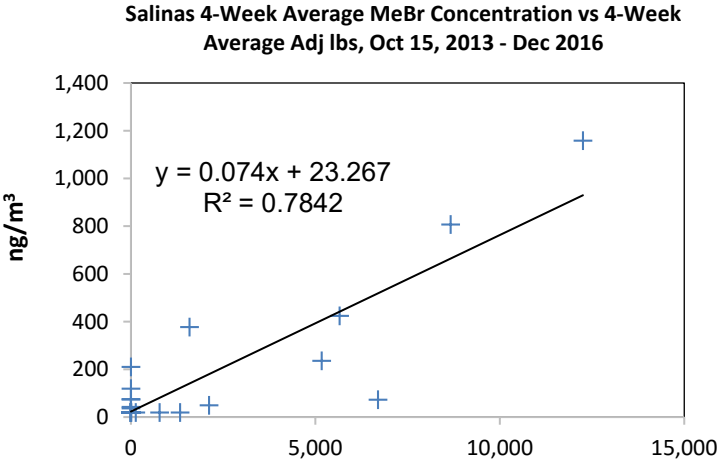
MeBr

Linear regressions for subchronic concentrations were divided into two groups: one from June 20, 2011 to October 14, 2013, and a second one from October 15, 2013 through December 31, 2016. Results for both sets were statistically significant ($p<0.0001$). During the time when MeBr's MDL equaled 396 ng/m^3 (06/20/2011 to 10/14/2013), the maximum subchronic concentration was 3,244 ng/m^3. The linear model produced a moderately correlated relationship between the 4-week averages of MeBr concentrations and Adj. Lbs (Figure 46). The coefficient of determination was slightly stronger at 0.78 during the period when the MDL equaled 39.6 ng/m^3 (10/15/2013 to 12/31/2016; Figure 47). The highest subchronic concentration for MeBr during this time was 1,158 ng/m^3.



Regression Statistics	
Multiple R	0.705
R Square	0.497
Adjusted R Square	0.479
Standard Error	468.644
Observations	29

Figure 46. Salinas 4-week average MeBr concentration vs 4-week average Adj. Lbs, Jun 20, 2011 - Oct 14, 2013



Regression Statistics	
Multiple R	0.885
R Square	0.784
Adjusted R Square	0.778
Standard Error	104.722
Observations	42

Figure 47. Salinas 4-week average MeBr concentration vs 4-week average Adj. Lbs, Oct 15, 2013 - Dec 2016

For the years 2014-2016, chronic concentrations of MeBr ranged from 35 to 186 ng/m^3. An analysis of the Salinas data for chronic MeBr concentrations failed to prove statistically significant for 2014-2016. Since DPR began sampling at Salinas, 396 applications occurred within the 5-mile radius of the sampling site location.

MITC

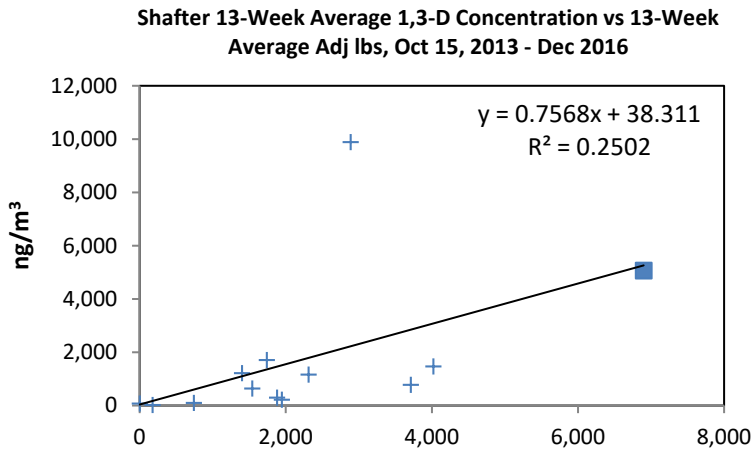
At the Salinas sampling site, subchronic concentrations of MITC ranged from 2.8 to 89 ng/m^3. A linear regression model for subchronic concentrations did not yield reliable results; therefore, DPR was not able to characterize the MITC air monitoring data with its use (data not shown). Chronic concentrations of MITC from 2011-2016 ranged from 3.5 to 12 ng/m^3. The linear regression model did not result in a statistically significant dataset ($p = 0.16$). From 2011-2016 at the Salinas sampling site, there were a total of 77 records of applications of MITC- generating products within 5-mi of the sampling site location

Shafter

1,3-D

Subchronic 1,3-D concentrations in the intervals during June 20, 2011 to October 14, 2013 did not meet the minimum requirements set forth in this section for use in a linear regression model. During the time period of October 15, 2013, to December 31, 2016 when the MDL = 45.4 ng/m^3, we saw a moderate relationship ($r^2 = 0.25$), but results were not statistically significant ($p > 0.05$) (Figure 48). Though the results were not a good fit, the maximum subchronic concentration during this time was 9,884 ng/m^3.

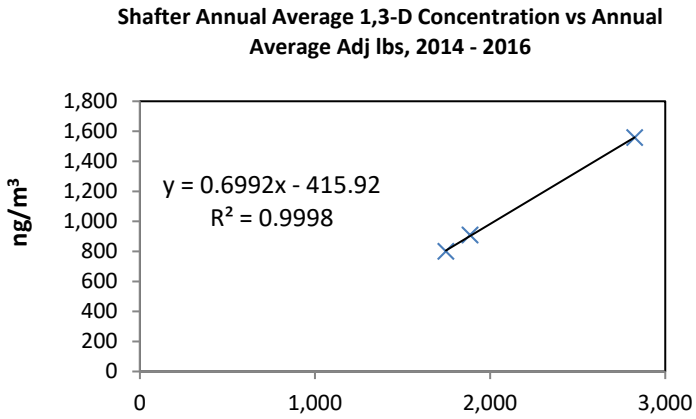
As mentioned earlier, Section 7 of this report further explores 1,3-D air concentrations and use data by incorporating additional variables to explain the use-concentration relationship..



Regression Statistics	
Multiple R	0.500
R Square	0.250
Adjusted R Square	0.182
Standard Error	2518.169
Observations	13

Figure 48. Shafter 13-week average 1,3-D concentration vs 13-week average Adj. Lbs, Oct 15, 2013 - Dec 2016

Following the second change to detection limits (MDL= 45.4ng/m^3), a very strong positive relationship (r^2 = 0.9998) between 1,3-D's average annual concentration and annual Adj. Lbs from 2014 to 2016 (Figure 49). These results were measured as statistically significant ($p < 0.05$). During this time period, all of the 58 applications that occurred within 5 miles of the Shafter sampling site consisted of the 1,3-D product Telone II using the field fumigation method code 1206: untarped/deep/broadcast. 1,3-D applications occurred on almond, carrot, grape and potato crops. The consistency of application method and pesticide product may contribute, in large part, to the strong coefficient of determination. In this regression, the standard error in three years of 1,3-D data was 9.15 and provided a good fit between Shafter chronic concentrations and annual adjusted use data.



Regression Statistics	
Multiple R	0.999
R Square	0.999
Adjusted R Square	0.999
Standard Error	9.158
Observations	3

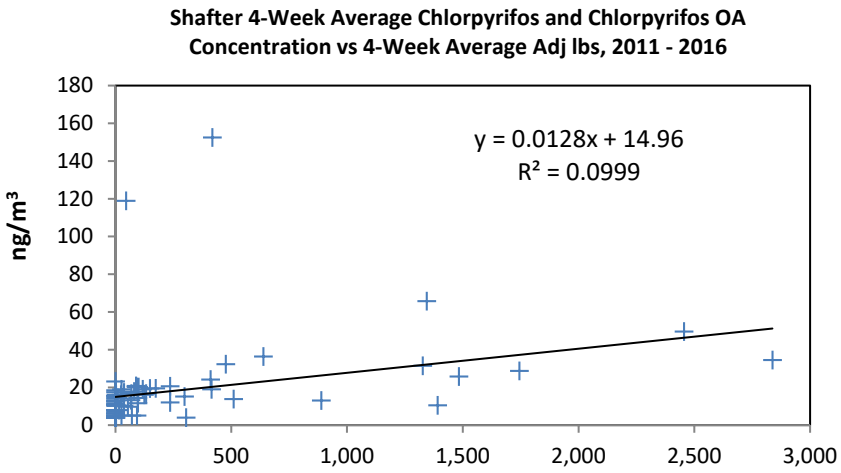
Figure 49. Shafter annual average 1,3-D concentration vs annual average Adj. Lbs, 2014 - 2016

Chloropicrin

In Shafter, data did not meet the minimum criteria for a linear regression model for subchronic and chronic intervals. DPR has not detected chloropicrin in the air at the Shafter sampling site from 2011 to 2016. Through the course of 2011-2016, a total of 25,623 Adj. Lbs of chloropicrin were applied within 5-mi of the Shafter sampling site via 22 unique applications.

Chlorpyrifos and its Oxygen Analog

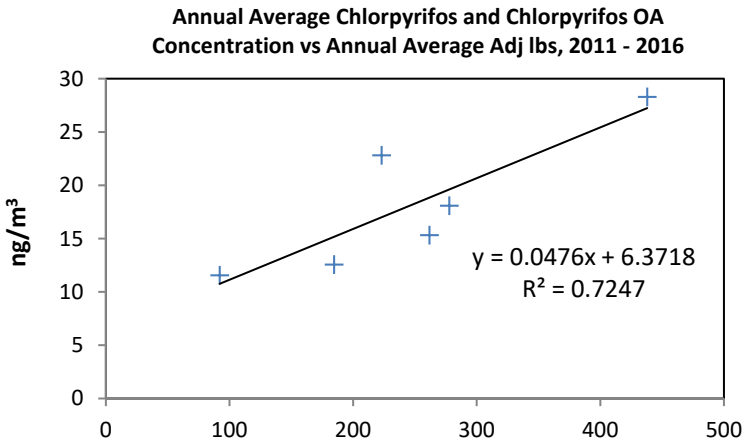
Regression analysis for subchronic concentrations of chlorpyrifos and its OA at the Shafter sampling site were statistically significant ($p < 0.01$) and presented a low r^2, explaining 9% of the variation in our linear model (Figure 50). The highest subchronic concentration for chlorpyrifos and its OA was 152 ng/m^3.



Regression Statistics	
Multiple R	0.316
R Square	0.099
Adjusted R Square	0.087
Standard Error	21.080
Observations	77

Figure 50. Annual average chlorpyrifos and chlorpyrifos OA concentration vs annual average Adj. Lbs, 2011 - 2016

When using the linear regression model at the Shafter sampling site, results for chronic concentrations of chlorpyrifos and its OA plotted against annual average Adj. Lbs correlated well with 72% of variation explained. Chronic concentrations of chlorpyrifos and its OA at the Shafter sampling site ranged from 12 to 29 ng/m^3. The six 1-year observations were statistically significant ($p < 0.05$) (Figure 51). Since DPR began sampling at Shafter, there have been a total of 735 records of chlorpyrifos applications made within the 5-mi radius of the sampling site.

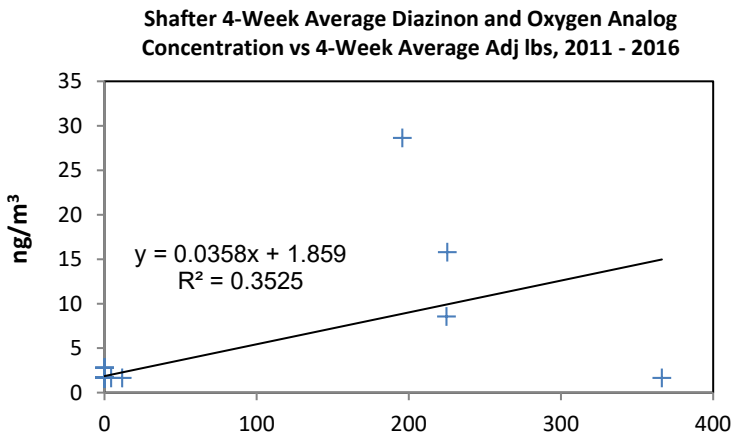


Regression Statistics	
Multiple R	0.851
R Square	0.725
Adjusted R Square	0.656
Standard Error	3.775
Observations	6

Figure 51. Annual average chlorpyrifos and chlorpyrifos OA concentration vs annual average Adj. Lbs, 2011 - 2016

Diazinon and Diazinon Oxygen Analog

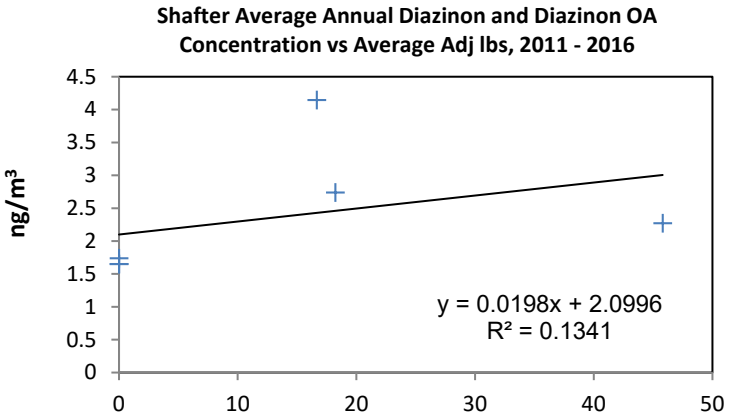
The regressional analysis for subchronic concentrations of diazinon and its OA compared with diazinon use within 5 miles of the sampling site, yielded a positive correlation (r^2 = 0.35) (Figure 52). Results were considered statistically significant ($p < 0.01$) with a standard error of 2.87. Subchronic concentrations ranged from 1.7 to 29 ng/m^3 .



Regression Statistics	
Multiple R	0.593
R Square	0.352
Adjusted R Square	0.343
Standard Error	2.875
Observations	76

Figure 52. Shafter 4-week average diazinon and its oxygen analog concentration vs 4-week average Adj. Lbs, 2011 – 2016.

Regression analysis on chronic concentrations of diazinon and its OA demonstrated a poor relationship (r^2= 0.134) at the Shafter sampling site and results were not statistically significant (Figure 53). Diazinon was not applied frequently near the Shafter sampling site and only comprised of 28 applications amounting to 4,112 Adj. Lbs between years 2011 and 2013. Diazinon was not applied within 5-mi of the Shafter site during the years 2014 to 2016.

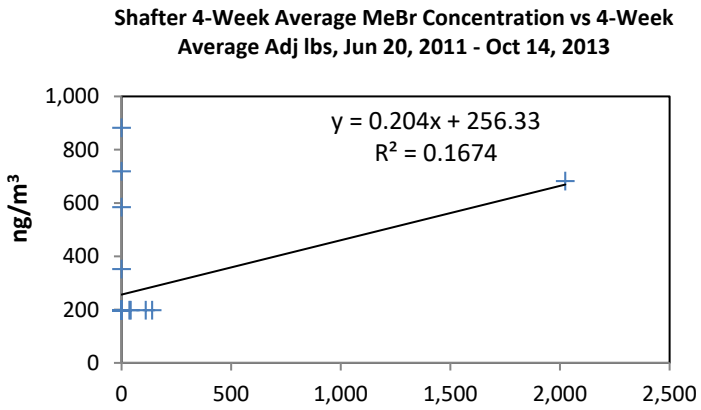


Regression Statistics	
Multiple R	0.3662
R Square	0.1341
Adjusted R Square	-0.0824
Standard Error	1.0118
Observations	6

Figure 53. Shafter average annual diazinon and diazinon OA concentration vs average Adj. Lbs, 2011 – 2016.

MeBr

Subchronic concentrations of MeBr were generally not associated with reported agricultural applications within the 5-mi radius of the sampling site. Between June 20, 2011 and October 14, 2013, a total of 11 reported applications were used to correlate with subchronic concentrations. The peak subchronic concentration was 882 ng/m^3; however, there were no reported applications within 5-mi of the sampling site during time period. The coefficient of determination during this period was 0.16, indicating a small relationship exists in the data (Figure 54). Results were statistically significant ($p<0.05$). MeBr is used in commodity fumigations, which could be influencing measured air concentrations in Shafter. Subchronic concentrations after October 15, 2013 ranged from 20 to 390 ng/m^3 and were poorly correlated ($r^2 = 0.01$).



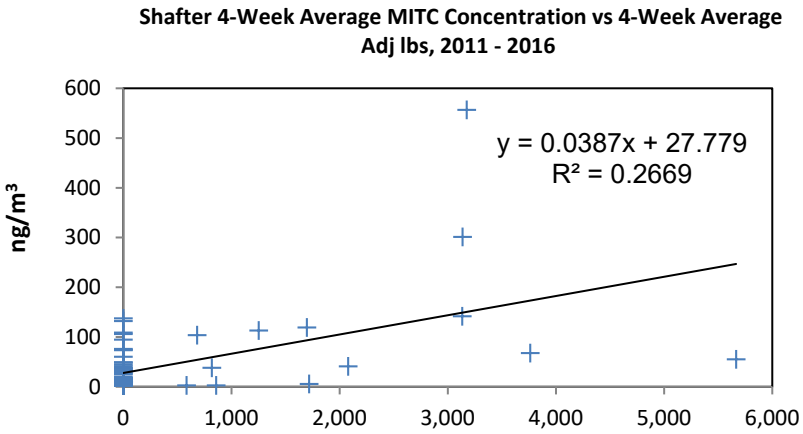
Regression Statistics	
Multiple R	0.409
R Square	0.167
Adjusted R Square	0.138
Standard Error	170.804
Observations	30

Figure 54. Shafter 4-week average MeBr vs 4-week average Adj. Lbs, 2011 - 2016

Due to the number of laboratory changes for MeBr detection limits, complete datasets of annual concentrations of MeBr were limited to the final three years (2014-2016), and the Shafter sampling site results were not statistically significant. For these years, chronic concentrations of MeBr in Shafter ranged from 26 to 70 ng/m^3. The last year of reported agriculture use of MeBr within a 5-mi radius of the sampling site occurred in 2014.

MITC

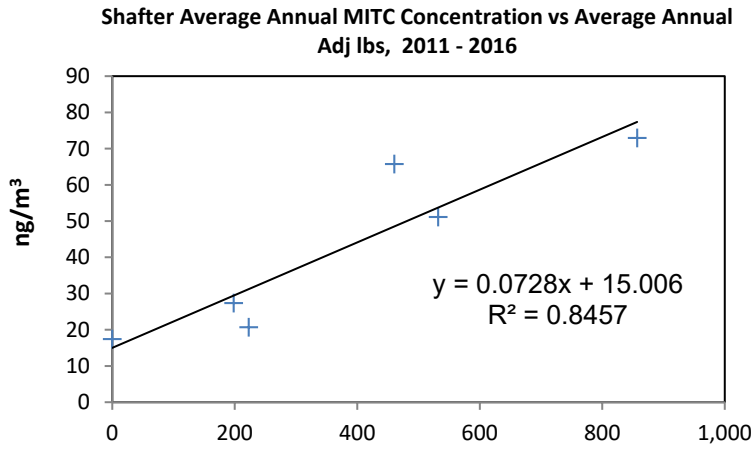
MITC data summarized by subchronic intervals using the linear model estimated 26% of relationship using measured MITC concentrations and reported use within 5 miles of the sampling site location (Figure 55). The p-value for the 77 subchronic concentrations was statistically significant ($p < 0.000001$). Subchronic MITC concentrations ranged from 2.8 to 556 ng/m^3 and the maximum MITC subchronic concentration was not associated with the highest amounts of MITC-generating products used within 5 miles of the sampling site location.



Regression Statistics	
Multiple R	0.516
R Square	0.266
Adjusted R Square	0.257
Standard Error	65.915
Observations	77

Figure 55. Shafter 4-week average MITC concentration vs 4-week average Adj. Lbs, 2011 - 2016

MITC annual concentrations at the Shafter sampling site were plotted against the average annual MITC use resulting in 84% of explained variability ($r^2 = 0.8457$) during years 2011 to 2016 (Figure 56). The data was considered statistically significant ($p < 0.01$). From 2011 to 2016, there were a total of 28 applications made within a 5-mi radius of the sampling site location. Annual concentrations ranged from 18 to 73 ng/m^3 coinciding with the lowest amount of reported pesticide use in 2016 and the highest in 2011, respectively.



Regression Statistics	
Multiple R	0.919
R Square	0.845
Adjusted R Square	0.807
Standard Error	10.533
Observations	6

Figure 56. Shafter average annual MITC concentration vs average annual Adj. Lbs, 2011 – 2016.

Conclusions

Model results showed a weak positive relationship between pesticide use and measured concentrations for most of the pesticides analyzed at all three sampling locations for subchronic time periods. While, for chronic time periods, only data from the Shafter sampling location showed any statistically significant relationship between use and concentrations for all pesticides analyzed with the exception of MeBr and diazinon. Several factors contributed to the difficulty of correlating subchronic and chronic concentrations with reported use data: the large number of non-detections, weeks with no reported use but with detected concentrations, and multiple changes to laboratory analytical methods that resulted in decreasing detection limits.

Section 7:

Application of Emission Ratios, Gaussian Plume Functions, and Meteorological Data in the Analysis of Use-Concentration Relationships of 1,3-Dichloropropene

Introduction

1,3-D, also known as Telone, is a widely-used fumigant in California agriculture. The fumigant is usually applied as a mixture in equal parts of two geometric isomers, cis-1,3-D and trans-1,3-D. Applied as a liquid via shank injection or drip irrigation, the substance quickly volatilizes and re-dissolves into an aqueous film that surrounds soil particles (DPR 2015). A proportion of the applied fumigant will volatilize from the soil surface in the days and weeks following application, resulting in off-site transport and possible human exposure via inhalation (DPR 2015). Volatilized 1,3-D will eventually degrade or be removed by photooxidation, reaction with ozone, or wet deposition (Vidrio 2012).

Long-term air monitoring performed by the DPR's AMN includes the sampling of both isomers of 1,3-D. As part of the AMN, a 24-hr air sample of 1,3-D was collected on a random day each week at each of three monitoring stations located in major agricultural areas throughout the state. Two studies have previously examined whether a predictable relationship exists between the amount of fumigant applied in an area and ambient air concentrations over either 24-hr (Brown 2016) or annual (Tao 2016) timescales. Those studies applied application adjustment factors to account for differences in the proportion of 1,3-D emitted from a field based on application method, application season, and the region of application. Both studies, as well as the previous section of this report, found that linear regression could not adequately explain the relationship between 1,3-D use and concentration over any of the timescales tested.

In this section, we take another look at whether it is possible to explain ambient 1,3-D concentrations using pesticide use data contained within the PUR database. In contrast to past studies, this approach takes into account several additional variables to explain the use-concentration relationship. Additional variables include refined estimates of the proportion of mass emitted from fumigated fields depending on application method (called 'emission ratios', or 'ERs'), flux profiles (fumigant mass emitted from a field over time), meteorological data, and spatial data (including distance and direction of a fumigation from a monitoring site). Rather than applying these data as variables in a multiple linear regression, these variables are implemented into a function that attempts to estimate air concentration based on use data and environmental conditions, which is then compared to measured air concentration data using regression

methods. The process uses a relatively simple pollutant dispersion function to approximate the relative impact of an application in accordance with meteorological conditions, application method, and distance from an air sampling location.

Methods

Data Sources

Air Concentration and 1,3-Dichloropropene Use Data

PUR data was retrieved from the PUR database on September 27, 2017; it included application records submitted for the period 2011-2016. The dataset was reviewed for completeness (via two independent queries of the PUR) and was screened for potential errors prior to analysis (Craig 2017). Although there are likely uncorrected errors in the dataset, they cannot be readily identified or corrected at this time. Therefore, we proceed with the assumption that the importance of any errors is diminished when the data is assessed on a multi-week timescale rather than a daily timescale due to the 'averaging' of symmetrically-distributed errors.

The PUR dataset was evaluated for completeness of the 'fumigation field method' ('FFM') code prior to analysis. A FFM code is a 4-digit code used in pesticide use reporting that designates a specific set of application practices used in a given fumigation (see DPR 2017b for a complete list of method codes and their descriptions). Use of this field is necessary in order to apply the correct ER to PUR records to estimate the mass of 1,3-D (Adj. Lbs) emitted from a given field. We evaluated completeness of this field within 10 miles of each sampling site location and summarize the data (Table 45). The reporting rate was very poor across all sites in 2011, but rose sharply in 2012. Reporting rates from 2013 and beyond were approximately 95% or greater across all sites and we consider these datasets adequate for analysis. Where an FFM code was missing, a substitution for the missing value was chosen according to the most common method (by count) reported within 10 miles of a given site.

Table 45. Method reporting rate summarized by year and site, as a percentage of record count for 1,3-D applications occurring within 10 miles of each sampling site location.

FFM Code Reporting Rate by Year, within 10 mi of Site						
Site	2011	2012	2013	2014	2015	2016
Salinas	2.9%	81.5%	96.3%	99.1%	94.7%	99.7%
Ripon	62.5%	93.6%	97.4%	94.6%	100.0%	100.0%
Shafter	19.0%	86.2%	100.0%	100.0%	100.0%	100.0%

Analysis of measured air concentration data was complicated by three changes in the MDL between 2011-2016: the MDL for each isomer of 1,3-D was first lowered from 4,540 ng/m^3 to 454.0 ng/m^3 in early 2011 and lowered again from 454.0 ng/m^3 to 45.4 ng/m^3 in late 2013. Data collected during the two highest MDLs (4,540 ng/m^3 to 454.0 ng/m^3) was not considered in this analysis due to the high detection limit relative to seasonal subchronic concentrations (in Ripon and Salinas), low rates of detection, and low FFM code reporting rates for the period of 2011-2012.

Spatial Data

ArcGIS (version 10.5) was used to identify the PLSS township-sections falling within 10 miles of each sampling site location. PLSS township-sections were selected around each sampling site location in a 10-mi radius and were then exported into a separate shapefile. The distance and direction to each PLSS section from a given sampling site location was then determined using a custom Python function. The resulting output included a list of all PLSS sections contained within 10 miles of each AMN site, paired with the straight-line distance from the sampling site location to the use section centroid (x) and direction of each section's centroid from the respective sampling site location (dir_{site}). Proximate to Shafter, where field level data was available, we obtained 'exact' distances for fields within 3,000 m of the sampling site. The same process was not possible for Ripon and Salinas, where field level data is not readily available.

1,3-D Flux Data

A series of simulations performed in HYDRUS (Brown and Spurlock 2018 [draft document]) were used to produce estimates of ERs and flux profiles for 16 of the 18 approved 1,3-D application methods (Table 46). ERs describe the cumulative amount of 1,3-D emitted in a post-fumigation period of 7 days (for untarped or polyethylene [PE] tarped applications) or 11 days (for Totally Impermeable Film [TIF] applications). ER is calculated as the ratio of emitted 1,3-D to the initial amount of applied 1,3-D. The ER and SD of the ER estimate for each method are summarized in Table 46, where SD provides an estimate of variation around the ER estimate. Flux profiles are a time series summarizing the total flux occurring over 6-h discrete periods

covering the span of the 11 days following the end of application and are used here to estimate the proportion of cumulative emission that is lost during each discrete 6-h period. That proportion is further divided by 6 to obtain an estimate of the hourly proportion of total mass lost over each hour of 11 days post-fumigation. In the software R, flux profiles and ER were joined to individual records on the basis of FFM code to be used in calculation of the estimated mass of fumigant lost per hour from a given field ('hourly Adj. Lbs').

Table 46. HYDRUS-estimated mean ERs for 1,3-D application methods from Brown and Spurlock (2018).

FFM Code	Method Description	Emission Ratios (ER)	Standard Deviation (SD)
1201	1,3-D - Nontarp/Shallow/Broadcast	0.541	0.090
1202	1,3-D - Tarp/Shallow/Broadcast	0.424	0.123
1203	1,3-D - Tarp/Shallow/Bed	0.523	0.123
1204	1,3-D - Shallow Untarped w/ 3x Irrigation	0.443	0.104
1205	1,3-D - Tarp/Shallow/Bed w/ 3x Irrigation	0.497	0.119
1206	1,3-D - Nontarp/Deep/Broadcast	0.323	0.127
1207	1,3-D - Tarp/Deep/Broadcast	0.26	0.137
1208	1,3-D - Tarp/Deep/Bed	0.389	0.148
1209	1,3-D - Tarp/Chemigation/Bed	0.575	0.114
1210	1,3-D - Nontarp/Deep/Strip	0.316	0.135
1242	1,3-D - TIF/Shallow/Broadcast - 60% credit	0.123	0.039
1243	1,3-D - TIF/Shallow/Bed - 60% credit	0.242	0.097
1245	1,3-D - TIF/Shallow/Bed w/ 3x Irrigation - 60% credit	0.192	0.060
1247	1,3-D - TIF/Deep/Broadcast - 60% credit	0.085	0.044
1248	1,3-D - TIF/Deep/Bed - 60% credit	0.231	0.110
1259	1,3-D - TIF/Chemigation/Bed - 60% credit	0.246	0.062

Meteorological Data

Hourly meteorological data was retrieved for each site through the California Irrigation Management Information System (CIMIS). The sites were initially selected based on the nearest CIMIS station to a given sampling site location unless geographic features (e.g., hills) were such that the site did not appear to be representative of the weather around the sampling site location.

Hourly stability and mixing height data was processed using the DPR-developed computer program MetProc (Luo 2017). Stability classes were calculated with use of CIMIS data using the "σ_A" method, which uses the SD in wind direction, wind speed, and a night/day classification to determine stability class (U.S.

EPA 2000). For the Shafter analysis, data was collected from CIMIS station #182 (Delano), NOAA data from Meadows Field Airport (WBAN ID 23155), and NOAA upper air data from Vandenberg Air Force Base. For the Ripon analysis, data was collected from CIMIS station #71 (Modesto), NOAA data from the Stockton Metropolitan Airport (WBAN ID 23237), and upper air data from Oakland International Airport. For the Salinas analysis, data was collected from CIMIS station #214 (Salinas South II), NOAA data from the Salinas Municipal Airport (WBAN ID 23233), and upper air data from Oakland International Airport. Missing or invalid periods of the combined CIMIS and NOAA data were filled via linear interpolation, as recommended by the U.S. EPA (2000).

Modeling Methods

Gaussian Plume Function

Gaussian plume functions (GPFs) are typically used to predict downwind concentrations from a steady-state emission source. These functions serve as the basis for the US EPA recommended air dispersion models AERMOD and ISCST3 for estimation of downwind concentrations from a steady-state point source. When accurately parameterized and applied to ideal conditions of uniform meteorology and flat terrain, these models provide very good accuracy within a short distance (<1 km) of a ground-level source, and are accurate to a factor of 2 within 10 km of the source (Collett & Oduyemi 1997). U.S. EPA currently recommends that this class of models be applied at distances no greater than 50 km (US EPA 2016).

The model is applied here to weight 1,3-D applications near the sampling site location to a greater degree than those distant from the sampling site to produce a more accurate estimate of ambient concentrations based on use data. The function is calculated using hourly time steps with hourly meteorological data and estimates of hourly flux data.

A GPF (EQ 1-3) was used to produce an analytical solution of time-averaged downwind air concentration based on the hourly flux estimate from each field (Green et al. 1980).

$$\chi(x, y, Q, H) = \frac{Q}{\pi u \sigma_y \sigma_z}\left\{\exp\left(-\frac{y^2}{2{\sigma_y}^2}\right)\right\}\left\{\exp\left(-\frac{-(z-h)^2}{2{\sigma_z}^2}\right) + \exp\left(-\frac{-(z+h)^2}{2{\sigma_z}^2}\right)\right\} \quad (1)$$

$$\sigma_z(x) = \frac{Lx}{[1 + (x/a)]^q} \quad (2)$$

$$\sigma_y(x) = \frac{Kx}{[1 + (x/a)]^p} \quad (3)$$

Where x is the distance (m) between a given location and the PLSS section of a given fumigant application, Q is the estimated hourly flux from a fumigant application as determined by hourly adjusted pounds (Adj. Lbs/h) converted to units of ng/s, u is average daily wind speed (in m/s), y is lateral displacement from the plume centerline (m), z is the vertical displacement from the plume centerline (m), and h is the effective plume height (m). L, K, α , p, and q are dispersion coefficients determined by atmospheric stability class.

We assumed ground-level plume height (h = 0 m) and a receptor height of z = 2 m based on the height of the air intake line at sampling site locations. Lateral displacement from the plume centerline at the sampling site (y) used a simple geometric calculation for a triangle, taking into account the absolute difference in angle between wind 'from' direction (dir_{wind}) and dir_{site} and the distance between application site and AMN site, x. Where $|dir_{wind} - dir_{site}| > 90°$, we set the cross-wind distance to 1E10 m to indicate an effectively infinite crosswind distance.

Mixing heights (z_{mix}) are generally lower in the winter than in the summer months, which limits dispersion in the upward direction and may increase ground-level concentrations, particularly in valleys where z_{mix} may fall below the height of the surrounding mountains and limit lateral dispersion. These effects were approximated by the replacement of the last expression of EQ 1 with the reflection function $S(z_r)$ described by Yamartino (1977):

$$X(x, Q, z_r) = \frac{Q}{\pi u \sigma_y \sigma_z}\left\{\exp\left(-\frac{y^2}{2{\sigma_y}^2}\right)\right\} S(z_r) \quad (4)$$

where

- for $\sigma_z/z_{mix} \leq 0.63$

$$S(z_r) = \sum_{j=0,\pm1}\left\{\exp\left[-\frac{1}{2}\left(\frac{z_r + 2j\, z_i - h_e}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z_r + 2j\, z_i + h_e}{\sigma_z}\right)^2\right]\right. \quad (5)$$

- for $0.63 < \sigma_z/z_{mix} \leq 1.08$

$$S(z_r) = \frac{\sqrt{2\pi}\sigma_z}{z_i}\,(1 - \beta)\left[1 + \beta^2 + 2\beta\cos\left(\pi\frac{z_r}{z_i}\right)\cos\left(\pi\frac{h_e}{z_i}\right)\right] \quad (6)$$

$$\beta = \exp\left[-\frac{1}{2}\left(\frac{\pi\sigma_z}{z_i}\right)^2\right] \quad (7)$$

- and for $\sigma_z/z_{mix} > 1.08$

$$S(z_r) = \frac{\sqrt{2\pi}\sigma_z}{z_i} \quad (8)$$

Using the above equations, a fumigated field was idealized as a steady-state point source with constant flux over each hour. Dispersion coefficients were those estimated using the formulation proposed by Green et al. (1980). Coefficients were selected from a lookup table (Table 47) based on hourly stability class. The resulting curves are shown in Figure 57.

Table 47. Stability-class dependent coefficients used in computation of EQs 2-3, adapted from Green (1980).

Stability Class	K	α (m)	p	L	q
A	0.25	927	0.189	0.102	-1.918
B	0.202	370	0.162	0.0962	-1.01
C	0.134	283	0.134	0.0722	0.102
D	0.0787	707	0.135	0.0475	0.465
E	0.0566	1070	0.137	0.0335	0.624
F	0.037	1170	0.134	0.022	0.7

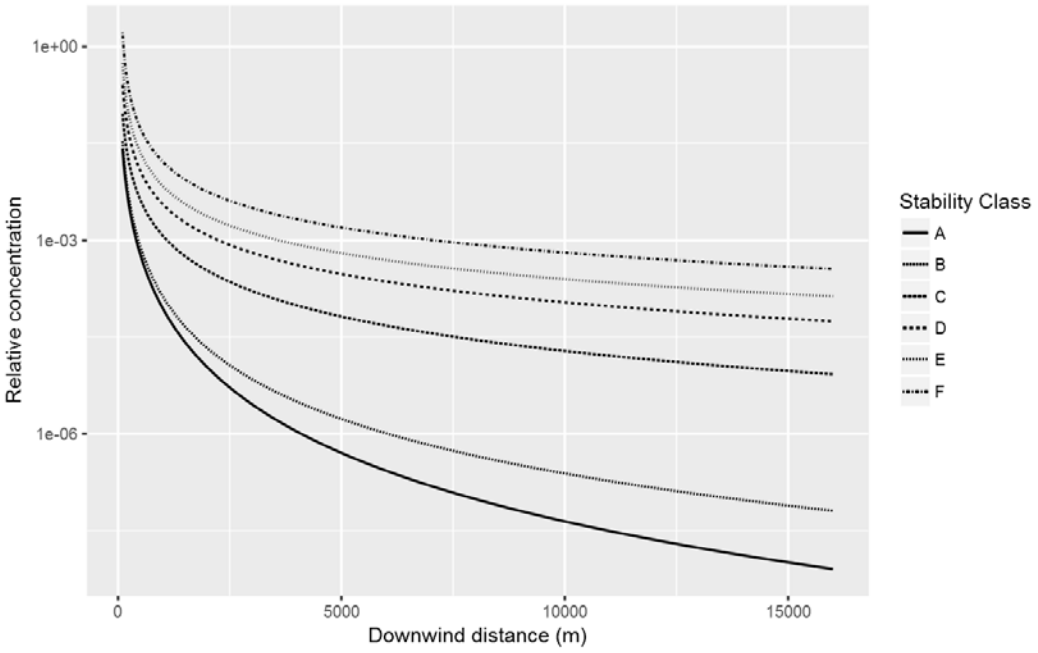


Figure 57. Assumed relationship between emission and downwind concentration at a 2 m receptor height as a function of downwind distance at fixed wind speed and emission rate from EQ. 4, displayed by stability class at distances of up to 16km (10mi) downwind.

Ambient Concentration Estimation Procedure

Example data and code used to perform the data preparation process using R is provided in Appendix B. As a summary, the following actions are performed:

1) Hourly wind speed and stability data is joined to each PUR record for the day of application as well as 11 days post-application (11 d or 264 h total).
2) The denominator of the GPF is calculated for each PUR record on an hourly basis, using inputs of hourly wind speed (m/s), downwind distance (m) between the PLSS section of fumigation and the AMN location, crosswind distance (m) between the plume centerline and sampling site location, mixing height (m), and hourly stability class (A-F) to determine the set of coefficients to be used for a given hour.
3) The mass of 1,3-D applied as part of an application reported in the PUR is multiplied by an ER corresponding to the FFM code reported for that application. The value is scaled by the relative proportion of mass lost during a given hour based on flux profile estimates, and a unit conversion is used to change to units of kg/h.

4) The value calculated in step 3 is input as the flux parameter in the GPF and reflection terms are applied based on hourly stability class and mixing height values. The output from the GPF is then saved into a new column.
5) The process is repeated for each of the 264 h following each application. The hourly GPF output is then grouped by day and averaged within each day to obtain the estimated downwind concentration resulting from that application on a given day.

The resulting output provides an estimate of air concentration at a downwind sampling site due to a single application. The process above is repeated for all PUR records within radius of a given AMN location. Once the process has been completed for all PUR records, the output is summarized by day to produce an estimate 1,3-D air concentration for a given day based on all nearby applications.

Statistical Analysis

Estimated air concentrations and measured air concentrations were each summarized into discrete 90-day period averaged bins based on time steps described in Table 48. The dataset was then used as an input into ordinary least squares (OLS) regression. The results of the regression will vary to some degree based on the selection of the time steps; in this case, time steps were selected in order to coincide 1 to 2 days prior to the date of the first air sample retrieved at the 45.4 ng/m^3 MDL (late 2013) and subsequent 90-day periods were defined as the 90-day period immediately following the previous 90-day period (i.e. there were no gaps between 90-day periods). We did not evaluate the effect of different start dates on the outcome of the regression. Discrete 90-day periods covered the time period leading up to the end of 2016, but any remainders beyond the last complete 90-day period were not included in the analysis, resulting in some results from December 2016 that were not included in the final dataset. The starting date of each 90-day period is summarized in Table 48.

Table 48. Starting date of each 90-day period used in the regressions. Starting dates were selected to begin 1 to 2 days prior to the collection date for the first sample to meet the 45.4 ng/m^3 MDL.

Time step	Ripon	Salinas	Shafter
1	10/17/2013	9/16/2013	10/15/2013
2	1/15/2014	12/15/2013	1/13/2014
3	4/15/2014	3/15/2014	4/13/2014
4	7/14/2014	6/13/2014	7/12/2014
5	10/12/2014	9/11/2014	10/10/2014
6	1/10/2015	12/10/2014	1/8/2015
7	4/10/2015	3/10/2015	4/8/2015
8	7/9/2015	6/8/2015	7/7/2015
9	10/7/2015	9/6/2015	10/5/2015
10	1/5/2016	12/5/2015	1/3/2016
11	4/4/2016	3/4/2016	4/2/2016
12	7/3/2016	6/2/2016	7/1/2016
13	10/1/2016	8/31/2016	9/29/2016
End date	12/30/2016	11/29/2016	12/28/2016

Statistical analysis was performed in R (version 3.4.4). Diagnostic plots were used to visually assess patterns in the residuals and to ensure that assumptions of linear regression were adequately met. The Breusch-Pagan test was used as a simple test of heteroscedasticity in the residuals. Where residuals showed evidence of heteroscedasticity or non-linear patterns, we considered transformation of independent or dependent variables as dictated by patterns in the residuals. Regressions were performed for each of the three individual sites, and an additional regression using aggregated data from all three sampling sites was also considered.

Results

We found evidence of a positive relationship between predicted and measured 1,3-D concentrations at all three sampling locations (Figure 58). The predicted concentrations exceeded measured concentration by approximately an order of magnitude, but produced fits with the measured data that were approximately linear. Goodness-of-fit measures varied substantially by site, with R^2 values of 0.50 at Shafter, 0.79 at Salinas, and 0.93 at Ripon.

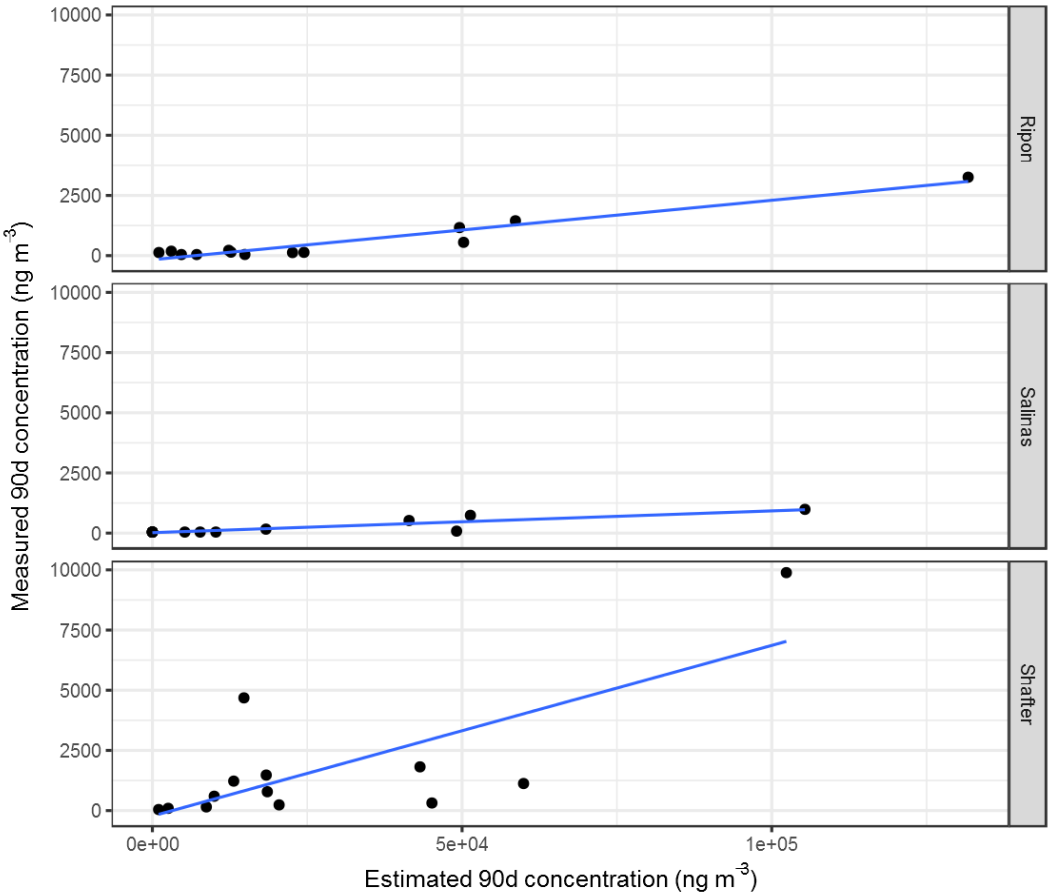


Figure 58. Linear regressions of predicted vs measured subchronic 1,3-D concentration for each of three AMN sites with discrete 90-day periods, data covering the period of late 2013 to December 2016, using a 10-mile domain.

Residuals were generally well-behaved with the most notable issues being influential points (i.e., an outlier that greatly affects the slope of the regression line) in the case of Ripon and Shafter regressions. We observed possible patterns in the scale-location plot of the Shafter site which suggested heteroscedasticity in the residuals, although all three regressions passed the Breusch-Pagan test against heteroscedasticity ($p > 0.05$). The Shafter and Salinas models did show presence of a heavy-tailed distribution in the residuals; although a normal distribution of the residuals is not a strict requirement for OLS regression (according to the Gauss-Markov theorem), the resulting confidence intervals should be treated with caution. Therefore we concluded that the assumptions of OLS regression were adequately met, noting that influential points may exhibit an outsize effect on the slope coefficients of the Shafter and Ripon regressions.

The value of slope coefficients varied by site, indicating the presence of some site- or region-specific variables for which we were unable to account. The slope between predicted and measured concentration at Shafter was approximately 3 times greater at Ripon, and 8 times greater than Salinas. The difference

appears to result from a greater increased in measured 1,3-D air concentrations per unit mass applied at Shafter as compared to the other two locations (Table 49), a relationship for which the model is unable to fully account.

Table 49. Summary of regression results using measured 90-day mean 1,3-D air concentration as the response variable.

Model	Coefficients	Estimate	S.E.	t-value	p	adj. R^2
Ripon, measured 90 d conc. 1,3-D	(Intercept)	-1.68e+02	9.23e+01	-1.823	0.095	0.926
	Est. 90d conc	2.47e-02	2.01e-03	12.297	<0.001	
Salinas, measured 90 d conc. 1,3-D	(Intercept)	1.94e+01	5.05e+01	0.384	0.708	0.787
	Est. 90d conc	9.05e-03	1.34e-03	6.733	<0.001	
Shafter, measured 90 d conc. 1,3-D	(Intercept)	-2.27e+02	7.61e+02	-0.298	0.771	0.503
	Est. 90d conc	7.10e-02	1.96e-02	3.623	0.004	
All sites, measured 90 d conc. 1,3-D	(Intercept)	-1.97e+01	3.07e+02	-0.064	0.950	0.317
	Est. 90d conc	3.23e-02	7.49e-03	4.313	<0.001	

Discussion

Sources of Unexplained Variation

The coefficient of the Shafter regression was 3 to 8 times greater than the estimated coefficients at the Ripon and Salinas sites, respectively. This pattern is consistent with past observations using a larger monitoring dataset (containing several additional monitoring sites) whereby Tao (2016) observed that the slope between 1,3-D use and concentration was 5 times greater in a dataset consisting only of inland locations as compared to a dataset containing only coastal locations. The large variation in coefficients from site-to-site indicates that the model described here fails to account for certain site-specific or region-specific characteristics that affect the use-concentration relationship. Such site-specific factors might include valley effects, differences in environmental conditions, long-range transport occurring over multiple days, chemical transformation and deposition, uncertainty in the spatial distribution of meteorological conditions, and errors resulting from incorrect or incomplete PUR data.

The failure to account for multi-day processes may partially explain the higher coefficients observed in the inland locations of Ripon and Shafter. Valley air basins (such as the Central Valley) experience less ventilation of the boundary layer relative to coastal areas, where land-sea pressure gradients drive coastal outflow of polluted air masses during evening hours. At least one case study has attempted to quantify the

effect of this coastal influence, finding that coastal effects played a large role in removal of pollutants in the boundary layer (Dacre et al. 2007). Long-term air quality monitoring throughout California's South Coast air basin has found similar spatial patterns in annual air pollutant concentrations, wherein annual concentrations for several pollutants steadily increase as one moves inland from the coastal region (Kim et al. 2000).

We used mean ER estimates to adjust use in accordance with application method, but there can be a substantial amount of variability around the mean ER for a given method. Sources of variation to ER include seasonal and regional differences in temperature and soil characteristics, as well as field-specific differences in tarp permeability due to weathering, tearing, stretching, or gluing of tarps. Therefore, the ER values applied here will over- or under-estimate emissions where the mean soil temperature is substantially different from HYDRUS assumptions, or where soil texture differs substantially from the mean soil physiochemical characteristics applied in HYDRUS.

Meteorological data in this study was obtained from the nearest available CIMIS sites since we thought they would adequately represent conditions at the sampling site locations. The methodology employed in this study is based on the premise that meteorological data at the CIMIS station is also representative of the conditions at the sampling site, as well as the conditions of all surrounding applications in the analysis (i.e. it assumes that all meteorological conditions are uniform within a 10 mi radius of the monitoring station). The validity of this assumption weakens with increasing distance from the CIMIS station, particularly in areas of complex terrain.

Spatial variables in this study of distance and direction between the sampling site location and a given application were only approximate. When an exact location of the sampling site was obtainable, the location of a given fumigant application was approximated using the centroid of the associated PLSS section reported in the PUR, rather than more precise field-level data. This approximation based on centroid may result in an error in the distance estimate of up to 1,100 m (~0.7 miles) and an error in the direction estimate that will increase the closer a fumigation is to the monitoring site. The error in the distance and direction estimates is likely minor for the majority of cases but may introduce a large amount of error for applications occurring within a relatively short distance of the sampling site location (i.e. 2-3 km) because the estimate of the GPF varies by several orders of magnitude over this range. Therefore, use of field-level

data could be one important method to reduce error, particularly for applications occurring near the monitoring site.

Lastly, errors or missing data fields in the PUR datasets will contribute additional error. The FFM code is an example of a field where missing values were common. Use of ER requires accurate and complete reporting of the FFM code for each pesticide application in order to correctly adjust the application amount. Where FFM code is missing in the data (mostly an issue for 2011-2012 data, and generally under 5% for 2013-2016 data), we substituted the most common method reported in a 10 mi radius of an AMN site. This was likely adequate at Shafter and Ripon sites due to the low diversity of application methods at these sites; however, these assumptions likely introduced at least a small amount of error at the Salinas site where methods vary more (Figure 59).

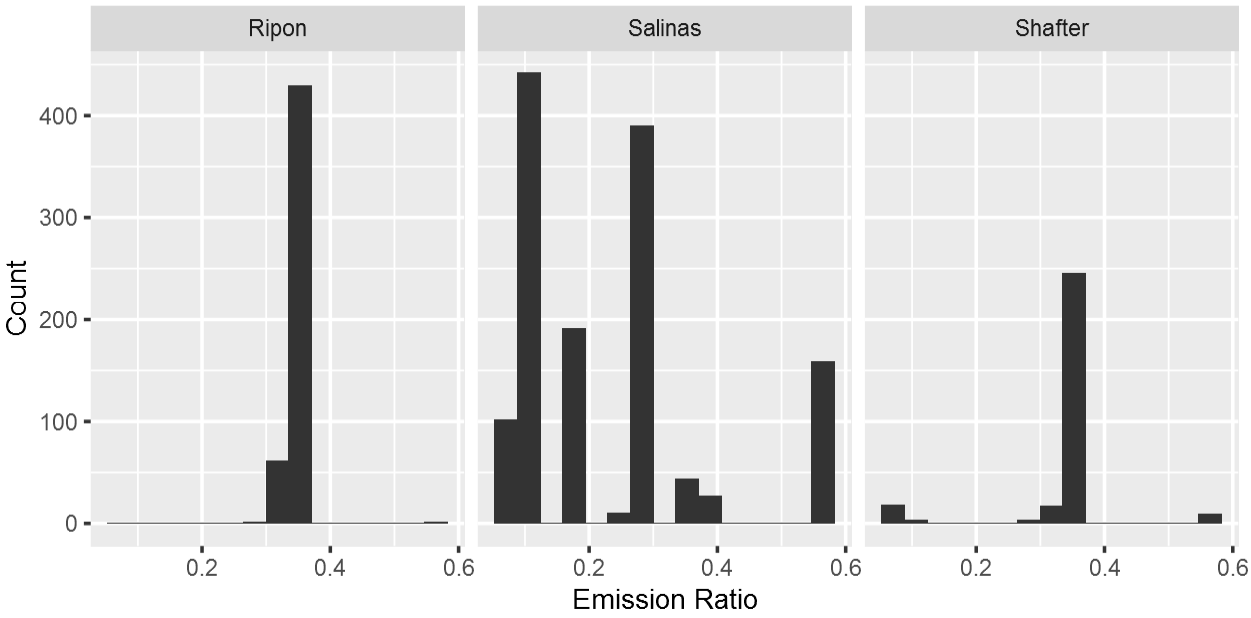


Figure 59. Distribution of emission ratios by site including all PUR records 2011-2016 falling within 10 miles of the site. The distributions reveal that method ERs for Shafter and Ripon locations are narrowly distributed; therefore, ER adjustment would not have a major effect. In contrast, method ERs around Salinas vary much more widely; as a result, ER adjustment has a major effect on the regression fit in this area.

In contrast to FFM code, the 'application date' field has effectively no missing data; however, anecdotal evidence suggests that this field is prone to errors. For example, multiple applications occurring over a time span of a week or more (termed 'rolling applications'), may be reported as all occurring on a single application date. Errors in this field are insidious because they are not easily identified and nearly impossible

to correct. The resulting errors in the date field can result in use of incorrect meteorological parameters and any deviation between the reported date and actual date of application will introduce error into the use-concentration relationship.

Model Applications and Future Work

Substantial site-to-site variation in regression slope coefficients, the requirement for detailed meteorological data, and the requirement for distance data limit the usefulness of this approach in predicting future air concentrations in a region based on use. Non-normal distribution of residuals also decreases the accuracy of confidence intervals, particularly when attempting to estimate values near the upper margins of the distribution (i.e. a 95^{th} percentile value of air concentration at a given total amount of seasonal use). With additional verification/validation against other 1,3-D monitoring datasets (such as those obtained in Brown (2016) or those air samples collected by the California Air Resources Board), it is possible the approach could be of some value in prioritizing future monitoring sites, particularly if generality of the approach can be established in certain regions (e.g. the Central Valley or in coastal areas). Once meteorological data, spatial data, and PUR data are obtained and properly formatted, the process is relatively simple to perform using a ready-built R script.

Section 8:

Analysis of Sampling Frequency

Introduction

The AMN is the first multi-year air monitoring project implemented by DPR. Due to the intensive nature of the sampling and to ensure that a "representative" weekly sample was collected at each of the three air sampling site locations, determining air sampling frequency at the start of the AMN was important since it directly affects the number of required air samples, personnel costs, and the number of communities that can be sampled. Before the AMN sampling began in 2011, monitoring data collected from a pilot project in Parlier was analyzed to evaluate: (1) whether different days of a week had the same probability to sample detectable concentrations, and (2) whether different locations of a community had a similar concentration distribution (Tao, 2009). The Parlier study collected 24-hr samples for three consecutive days a week at three sites from January 3 to December 26, 2006. The weekly starting day varied each week. The initial sampling frequency analysis determined that no significant differences existed in the sampling results of different days of a week and different locations of a community. Based on this analysis, it was determined that sampling once a week at one location in each of three communities was sufficient to provide a representative weekly air concentration for the AMN.

After collecting 6-years' worth of weekly air sampling data at the three sampling site locations, we wanted to revisit the sampling frequency questions with this larger data set. A data analysis on the sampling frequency is necessary to review the current sampling schedule, discover potential implementation issues, and provide recommendation for future monitoring activities. This analysis compares the sampling results between different days of a week for all the pesticides that had a certain amount of detections during 2011 – 2016. For some pesticides showing certain patterns, further analysis is performed to evaluate the possible cause and its impact on the AMN results.

Methodology

The monitoring results are usually composed of three types of concentration records: ND, trace, and numeric values. The concentrations that are not detected at a level above the MDL (the smallest amount of the chemical that can be identified in a sample with the employed method) are recorded as "ND". Adjusted concentrations for "ND" in this section use half of the MDL. "Trace" is a level between the MDL and the LOQ (the smallest amount of a chemical that can be measured); its adjusted value is the half between MDL and the LOQ. Percentages of non-detect (ND%) were calculated for all analytes (Table 50). Only chemicals (No.1-9 in Table 50) with ND% < 90% are selected for further analysis.

Table 50. Percentages of non-detects in samples of all monitored chemicals

No.	Chemical	Sample Size	Non-Detect Counts	Non-Detect %
1	Carbon Disulfide	921	544	59.1
2	Chlorothalonil	923	593	64.2
3	Chlorpyrifos	923	679	73.6
4	MITC	924	682	73.8
5	Chlorpyrifos OA	923	691	74.9
6	Chlorthal-dimethyl	923	727	78.8
7	1,3-Dichloropropene	921	746	81.0
8	Malathion OA	923	793	85.9
9	Methyl Bromide	921	800	86.9
10	Diuron	923	854	92.5
11	Trifluralin	923	862	93.4
12	DDVP	923	872	94.5
13	Malathion	923	882	95.6
14	Chloropicrin	924	887	96.0
15	Iprodione	923	889	96.3
16	Diazinon	923	890	96.4
17	Propargite	923	890	96.4
18	EPTC	923	893	96.7
19	Diazinon OA	923	894	96.9
20	Simazine	923	894	96.9
21	Oryzalin	923	909	98.5
22	Oxyfluorfen	923	911	98.7
23	Endosulfan	923	915	99.1
24	Permethrin	923	915	99.1
25	Bensulide	923	916	99.2
26	Metolachlor	923	918	99.5
27	Dimethoate OA	923	919	99.6
28	Methidathion	923	919	99.6
29	Norflurazon	923	919	99.6
30	Acephate	923	921	99.8
31	Dimethoate	923	922	99.9
32	Phosmet	923	922	99.9
33	Cypermethrin	923	923	100.0
34	DEF	923	923	100.0
35	Endosulfan Sulfate	923	923	100.0
36	Oxydemeton methyl	923	923	100.0
37	pp-Dicofol	923	923	100.0

For each selected pesticide, sample size, detection percentage (percentage of concentrations > MDL), and the 95th percentile concentration are summarized for each day of a week. Boxplots are also produced to show the concentration distribution. Because of the high portion of ND in the data, non-parametric statistical method (Kruskal-Wallis rank test) was conducted to compare days of a week. For chemicals showing significant difference, another non-parametric method the Mann-Whitney-Wilcoxon test (Wilcox test), is performed to examine which days have concentrations different than others. All the data analysis is conducted by R version 3.4.2.

Results

Comparison Between Days of a Week

Among the nine selected chemicals, chlorthal-dimethyl and malathion OA had only one quantifiable concentration; all the other measurements were trace or ND (Figure 60). Therefore, chlorthal-dimethyl and malathion OA were excluded from further comparison in this analysis. Table 51 shows that although the AMN planned sampling to occur on randomly selected days of the week (which would result in about the same number of samples collected on each day of the week), this did not occur. This analysis shows that the actual distribution of sampling days was skewed towards Mondays, Tuesdays, and Wednesdays. Some of the reasons for this skewed distribution include: site access restrictions (e.g., school closure on weekends or use of certain pesticides prohibited on certain days of the week) and budget constraints that limited the amount of overtime that DPR staff could accrue.

About 80% of the sampling started on Monday to Wednesday. There were 12.6% sampling starts on Thursday, 2% on Friday, 5% on Sunday, and < 1% on Saturday. Detection percentages and most of the 95th percentiles of concentrations on Monday to Thursday tend to be higher than those on other days (Table 51). All the days have close median concentrations (all below detection limits) and similar data distributions. The Krusaki-Wallis test calculates the rank of each data point and then compares average rank of different days of a week. The results show that samples collected on different days of a week are not significantly different for most of chemicals except for carbon disulfide and chlorothalonil, which have test p-value < 0.05 (Table 51). The pairwise comparison is conducted by Wilcox test for these two chemicals without assuming a distribution. For carbon disulfide, Tuesday and Wednesday presents higher concentrations than Thursday and Friday with $p < 0.05$ (Table 52). Concentrations monitored on Tuesday through Thursday were higher than on Sunday for chlorothalonil. However, because high amount of NDs causes a high amount of tie in ranking calculations, accuracy of p-values computed by this test is inadequate.

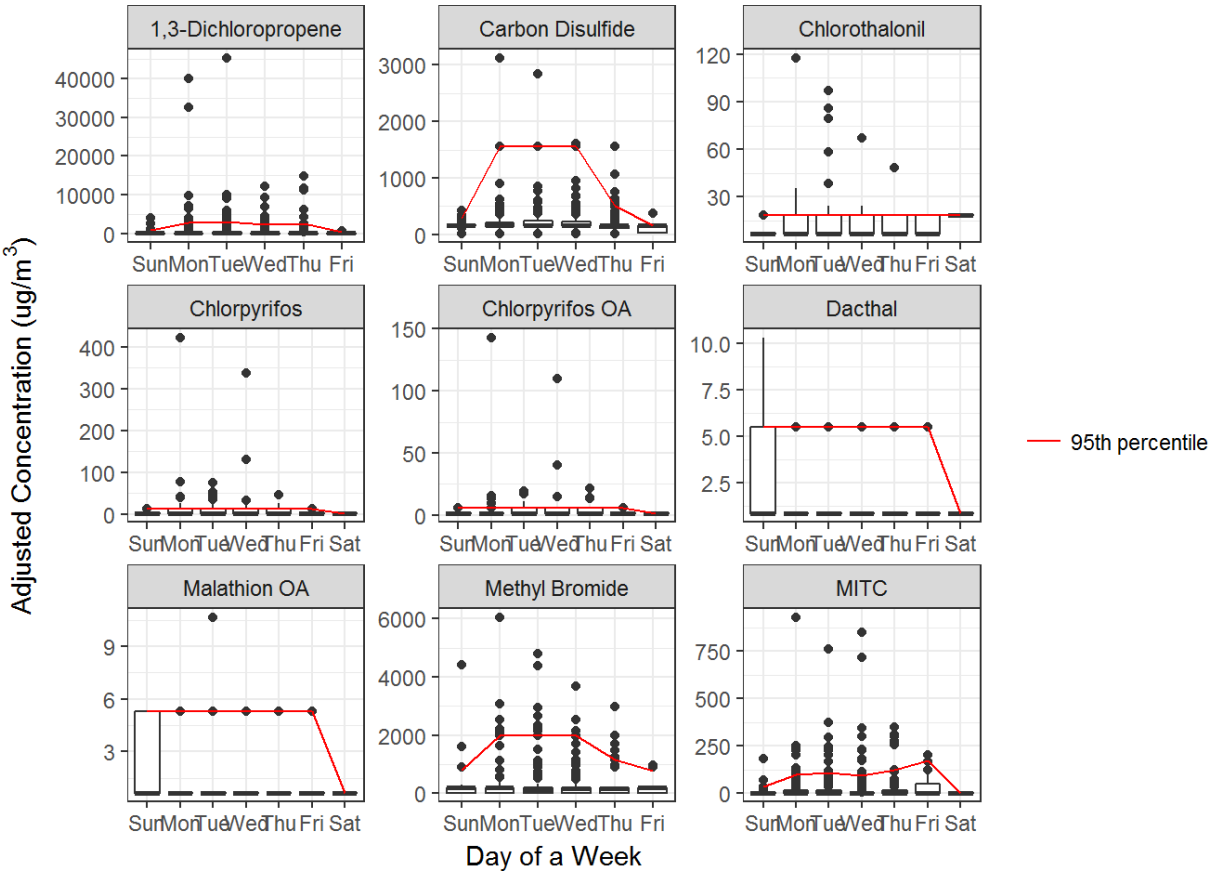


Figure 60. Boxplots for adjusted concentrations of nine selected chemicals on each days of a week.

Table 51. Summary of sampling results for seven selected chemicals

Chemical	Day	Sample Size	Sample Size%	ND%	Detect %	95th Percentile Adjusted	Krusaki-Wallis test p-value
1,3-Dichloropropene	Sun	44	4.8	90.9	9.1	971.9	0.48
	Mon	243	26.4	80.7	19.3	2952.1	
	Tue	239	26.0	78.2	21.8	2988.8	
	Wed	255	27.7	81.2	18.8	2270	
	Thu	116	12.6	81.9	18.1	2511.1	
	Fri	24	2.6	87.5	12.5	554.2	
Carbon Disulfide	Sun	44	4.8	63.6	36.4	290.1	0.00
	Mon	243	26.4	60.9	39.1	1555	
	Tue	239	26.0	54.4	45.6	1555	
	Wed	255	27.7	58	42	1555	
	Thu	116	12.6	61.2	38.8	503.5	
	Fri	24	2.6	79.2	20.8	163.6	
Chlorothalonil	Sun	46	5.0	87	13	18.4	0.00
	Mon	250	27.1	71.6	28.4	18.4	
	Tue	232	25.1	62.5	37.5	18.4	
	Wed	249	27.0	56.6	43.4	18.4	
	Thu	125	13.5	60.8	39.2	18.4	
	Fri	20	2.2	60	40	18.4	
	Sat	1	0.1	0	100	18.4	
Chlorpyrifos	Sun	46	5.0	91.3	8.7	14.1	0.11
	Mon	250	27.1	71.6	28.4	14.1	
	Tue	232	25.1	72.8	27.2	14.1	
	Wed	249	27.0	74.7	25.3	14.1	
	Thu	125	13.5	68.8	31.2	14.1	
	Fri	20	2.2	80	20	14.1	
	Sat	1	0.1	100	0	2.5	
Chlorpyrifos OA	Sun	46	5.0	91.3	8.7	6.1	0.10
	Mon	250	27.1	76.8	23.2	6.1	
	Tue	232	25.1	71.6	28.4	6.1	
	Wed	249	27.0	73.1	26.9	6.1	
	Thu	125	13.5	72.8	27.2	6.1	
	Fri	20	2.2	85	15	6.1	
	Sat	1	0.1	100	0	1.5	
Methyl Bromide	Sun	44	5.0	88.6	11.4	808.1	0.93
	Mon	243	27.1	86.8	13.2	1980	
	Tue	239	25.1	86.2	13.8	1980	
	Wed	255	27.0	87.5	12.5	1980	
	Thu	116	13.5	87.9	12.1	1165.4	
	Fri	24	2.2	79.2	20.8	786.4	
MITC	Sun	46	0.1	89.1	10.9	33.9	0.16
	Mon	251	5.0	71.7	28.3	98.6	
	Tue	235	27.1	71.5	28.5	110	
	Wed	246	25.1	76.8	23.2	93.6	
	Thu	126	27.0	70.6	29.4	121.5	
	Fri	19	13.5	73.7	26.3	172.7	
	Sat	1	2.2	100	0	2.8	

Table 52. Pairwise comparison between days of a week for adjusted concentrations of carbon disulfide and chlorothalonil

Carbon Disulfide							
Wilcox test p-value		Day of a week					
		Sun	Mon	Tue	Wed	Thu	Fri
Day of a week	Mon	1.00	-	-	-	-	
	Tue	0.71	0.96	-	-	-	
	Wed	0.71	0.96	1.00	-	-	
	Thu	1.00	0.38	0.02	0.02	-	
	Fri	0.65	0.17	0.03	0.03	0.94	
Chlorothalonil							
Wilcox test p-value		Day of a week					
		Sun	Mon	Tue	Wed	Thu	Fri
Day of a week	Mon	0.41	-	-	-	-	-
	Tue	0.02	0.48	-	-	-	-
	Wed	0.00	0.02	1.00	-	-	-
	Thu	0.02	0.60	1.00	1.00	-	-
	Fri	0.25	1.00	1.00	1.00	1.00	-
	Sat	0.32	1.00	1.00	1.00	1.00	1.00

Relationship of Detections and Sample Size

The comparison of different days of a week shows that Monday through Thursday tend to have higher percentages of detections and higher values of the 95th percentile concentration. Figure 61 provides two examples of pesticide use distribution in the three counties where the sampling sites were located; statistical analysis shows no significant pattern on different days of a week. Therefore, a larger sample size on Monday to Thursday was more likely to be the reason for a greater number of detections.

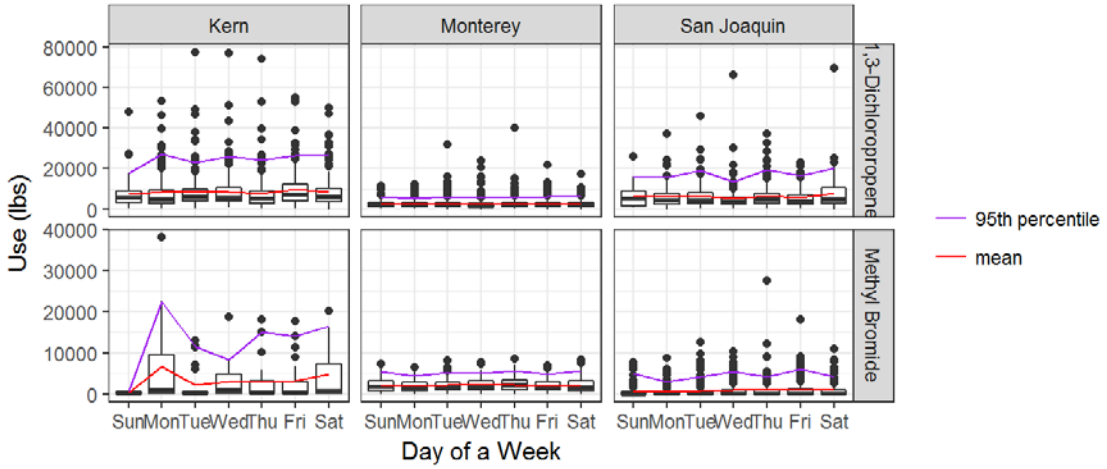


Figure 61. Examples of pesticide use (active ingredient use amount) distributions on seven days of a week in three counties where sampling sites were located during 2011 – 2016.

Because of the unbalanced (i.e., skewed towards start of week) sampling frequency, the monitoring data provided a chance to evaluate the relationship between air monitoring detections and sample size (i.e.,

number of samples collected on a particular day of the week) (Figure 62). Some pesticides showed significantly higher 95th percentile concentrations with higher sample size. The linear regression model is built to fit the detection percentages of a total of seven pesticides with their sample size and the result suggests that their relationship is statistically significant (p = 0.02). The slope is estimated as 0.038, which means that the detection percentage increases on average by 3.8 percentage points for every 100 additional samples. As a result, although larger sample size could result in more detections, the effect is relatively weak.

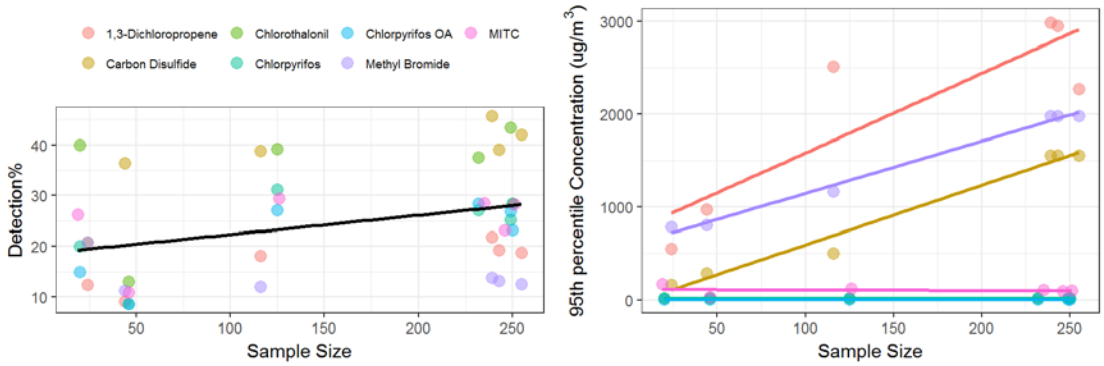


Figure 62. Relationship between detection percentages and the 95th percentile of concentrations with sample size.

Conclusion

Analysis of AMN data showed that the sampling frequency was not equally distributed among all seven days of the week during the 2011–2016 sampling period; more than 90% of the sampling started on Monday to Thursday. Given this information, DPR improved the AMN's random sampling schedule by ensuring that sampling start days include Fridays to Sundays more consistently.

Although the skewed sampling frequency limited our capability to analyze differences in sample results based on different days of the week. Using data for chlorothalonil and carbon disulfide, we were able to show a lack of significant difference between days of a week and measured concentrations. A linear regression model was used to establish that the percentage of quantifiable detections increases on average by 3.8 for every 100 additional collected samples. As a result, although larger sample size could result in more detections, the effect is relatively weak.

Section 9:

Analysis of Selected Non-Detected Pesticides

Introduction

Six pesticides monitored were never detected at concentrations above the MDL (i.e., at quantifiable concentrations) at any of three sampling sites: cypermethrin, DEF, dicofol, dimethoate, endosulfan sulfate and oxydemeton-methyl. In this section, we look further into these six pesticides, including the volatility, meteorological information, and pesticide use within a 5-mi radius of each sampling site location to explain why none of these pesticides were detected at any of the sampling sites during the 2011 - 2016 sampling period.

Volatility

Table 53 lists vapor pressures for these six pesticides. According to Hanson et al., (2016), these six pesticides ranked from moderate to low in terms of volatility. These are potentially classified as having no tendency or minimal tendency to turn into a vapor and get into air. Although chemical characteristics, weather conditions, and soil type and moisture level can affect a pesticide's volatility, the combination of these factors along with the application method greatly determine the portion and speed at which a pesticide transitions into the vapor phase.

Table 53. Vapor pressure and volatility of six pesticides not detected in sampling from 2011 - 2016.

Active ingredients	Vapor Pressure Pa @ 20 °C	Volatility*
Oxydemeton-methyl	3.80E-03	Moderate
Endosulfan sulfate	1.30E-03	Moderate
Dimethoate	1.12E-03	Moderate
DEF	2.30E-04	Moderate
Dicofol	5.30E-05	Low
Cypermethrin	2.30E-07	Low

* Hanson et al. (2016)

Pesticide Use

The PUR database was queried at spatial scale covering a radius of 5 miles surrounding each of the three sampling site locations. The PUR database provides location information in the form of PLSS 1 mi^2 sections. Sections use totals were included on the basis of any part of their 1 mi^2 area falling within the 5-mi radius from the sampling site location. No additional proportional adjustments in use and sections were performed on this data. Table 54 lists the total amount of each of these pesticides used within a 5-mile radius of a sampling site location during 2011-2016. Compared to other pesticides included in the AMN, these six pesticides had little to no reported use within a 5-mi radius of a sampling site. Dimethoate had the highest combined use of these six pesticides, with a total combined reported use of 9,509 lbs for the combined six year period. Oxydemeton-methyl and cypermethrin had the second and third highest agricultural use, respectively (Table 54). Endosulfan sulfate results from the breakdown product of endosulfan; therefore, detections of endosulfan sulfate depend on use of endosulfan.

We also looked into the general methods used to apply these pesticides as reported in the PUR database. Table 55 provides information about lbs applied by aerial and ground methods reported for these six pesticides at all three sampling sites.

Table 54. Total reported amount of AI used for six non-detected pesticides within 5-miles of the three sampling sites between 2011 and 2016.

Location	Active Ingredient Used (lb)					
	Cypermethrin	DEF	Dicofol	Dimethoate	Endosulfan	Oxydemeton-methyl
Salinas	2,522*	-	-	3,835*	-	8,446
Shafter	122	500	-	2,985	-	-
Ripon	382	-	-	2,689	1,014	-
Total	3,026	500	-	9,509	1,014	8,446

*Includes 34.1 and 6 pounds of cypermethrin and dimethoate, respectively, reported under the "Other" application method category.

Table 55. Total amount AI used by application method of six non-detected pesticides within 5 miles of the three sampling sites between 2011 and 2016.

Active Ingredients	Active Ingredient Used (lb)					
	Salinas		Shafter		Ripon	
	Aerial	Ground	Aerial	Ground	Aerial	Ground
Cypermethrin	817	1,671	110	12	23	359
DEF	-	-	89	411	-	-
Dicofol	-	-	-	-	-	-
Dimethoate	1,181	2,648	1,887	1,098	518	2,171
Endosulfan	-	-	-	-	-	1,014
Oxydemeton-methyl	2,133	6,313	-	-	-	-

Results by Community

Salinas

In Salinas, only cypermethrin, dimethoate and oxydemeton-methyl had any reported use within 5 miles of the monitoring station (Table 56). Figure 63 shows the total amount of cypermethrin, dimethoate and oxydemeton-methyl use within a 5-mi radius of the Salinas sampling site between February 1, 2011 and December 31, 2016. Figure 63 also includes a wind rose diagram of the region displaying the predominant wind direction and speed. Wind velocity data was obtained from CIMIS weather station located approximately 6 miles northwest of the Salinas sampling site. The wind rose figure indicates that the predominant wind direction in the area comes from northwest to southeast direction (Figure 63).

Of the three pesticides with any reported use within a 5-mi radius of the Salinas sampling site, only oxydemeton-methyl averaged over 1,000 lbs per year (1,408 lbs/yr). However, a declining trend is observed with oxydemeton-methyl use in the Salinas area as the use amount declined every year starting from 2011 to 2016 (Table 56).

Table 56. Total reported amount of AI used per year for six pesticides not detected within 5-miles of the Salinas sampling site between 2011 and 2016.

Active Ingredient	AI used (lb) per year in Salinas							
	2011	2012	2013	2014	2015	2016	Total	Yearly Average
Cypermethrin	442	335	339	437	423	546	2,522	428
DEF	-	-	-	-	-	-	-	-
Dicofol	-	-	-	-	-	-	-	-
Dimethoate	1,404	534	407	288	318	885	3,835	639
Endosulfan	-	-	-	-	-	-	-	-
Oxydemeton-methyl	3,793	2,475	971	815	355	37	8,446	1,408

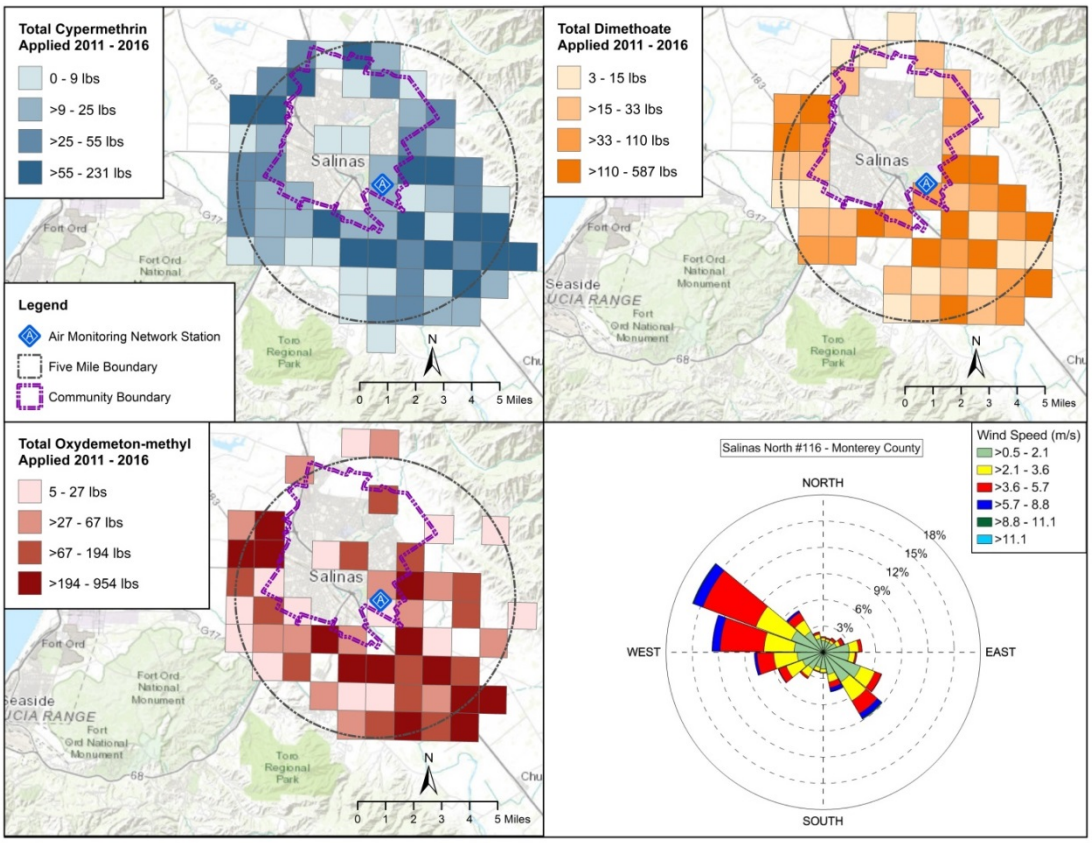


Figure 63. Reported 2011-2016 use of cypermethrin, dimethoate, and oxydemeton-methyl within 5 miles of the Salinas sampling site. Wind rose displaying the predominant wind direction of the Salinas area for the years 2011 – 2016 is also shown.

Table 57 shows the amount of AI applied via ground and air per year of the three pesticides with reported use near the Salinas sampling site. All three pesticides used in the Salinas area were predominately applied via ground applications. A majority of ground applications combined with the low to moderate volatilities (Table 53) may explain why there weren't any measured air concentrations for these pesticides at the Salinas sampling site.

Since there was no reported use of DEF, dicofol, and endosulfan within a 5-mi radius of the Salinas sampling site (Table 54), the lack of measureable air concentrations for these pesticides at this sampling site is expected.

Table 57. Reported annual use amount of AIs by application method for the six pesticides not detected within 5-miles of the Salinas sampling site between 2011 and 2016.

Active Ingredients	Active Ingredient Used (lb)											
	Aerial application						Ground application					
	2011	2012	2013	2014	2015	2016	2011	2012	2013	2014	2015	2016
Cypermethrin	128	150	120	122	161	135	315	184	217	313	259	384
DEF	-	-	-	-	-	-	-	-	-	-	-	-
Dicofol	-	-	-	-	-	-	-	-	-	-	-	-
Dimethoate	316	277	149	151	132	155	1088	257	258	136	187	723
Endosulfan	-	-	-	-	-	-	-	-	-	-	-	-
Oxydemeton-methyl	918	754	170	193	61	37	2875	1721	801	623	294	-

Shafter

In Shafter, only cypermethrin, DEF, and dimethoate had any reported use within 5 miles of the sampling site location (Table 58). Figure 64 shows total amount of AI use within a 5-mi radius of the Shafter sampling site between February 1, 2011 and December 31, 2016. Figure 64 also includes a wind rose that displays the distribution of hourly wind speed and wind direction for six years as obtained from Meadows Field Airport weather station located approximately 13 miles southeast of the Shafter sampling site. The wind direction in the area predominantly comes from northwest to southeast direction.

Of the three pesticides with reported use within 5-miles of the Shafter sampling site, only cypermethrin and dimethoate had any consistent reported use during all six years (Table 58). Table 59 shows that the majority of dimethoate (lbs) used was applied via aerial applications. Although, there were reported use of the three AIs within 5 miles of the Shafter sampling site, the low to moderate vapor pressures of these AIs (Table 53) may explain why there weren't any measured air concentrations for these pesticides at the Shafter sampling site from 2011-2016.

Table 59 shows there were no reported agricultural applications or use of dicofol, endosulfan, and oxydemeton-methyl within a 5-mi radius of the Shafter sampling site. The lack of reported use near the Shafter sampling site may explain the absence of any measurable air concentration of these AIs at this site during the period of 2011 to 2016.

Table 58. Total reported amount of AI used per year for six pesticides not detected within 5-miles of the Shafter sampling site between 2011 and 2016.

Active Ingredients	AI used (lb) per year in Shafter							
	2011	2012	2013	2014	2015	2016	Total	Yearly Average
Cypermethrin	26	17	29	7	26	17	122	20
DEF	456	29	-	-	7	8	500	83
Dicofol	-	-	-	-	-	-	-	-
Dimethoate	379	378	622	726	613	267	2,985	497
Endosulfan	-	-	-	-	-	-	-	-
Oxydemeton-methyl	-	-	-	-	-	-	-	-

Table 59. Reported annual use amount of AIs by application method for the six pesticides not detected within 5-miles of the Shafter sampling site between 2011 and 2016.

Active Ingredients	Active Ingredient Used (lb)											
	Aerial application						Ground application					
	2011	2012	2013	2014	2015	2016	2011	2012	2013	2014	2015	2016
Cypermethrin	24	10	26	7	26	17	2	7	3	-	-	-
DEF	73	16	-	-		-	383	13	-	-	7	8
Dicofol	-	-	-	-		-	-	-	-	-	-	-
Dimethoate	143	118	386	563	410	267	236	260	236	163	203	-
Endosulfan	-	-	-	-		-	-	-	-	-	-	-
Oxydemeton-methyl	-	-	-	-		-	-	-	-	-	-	-

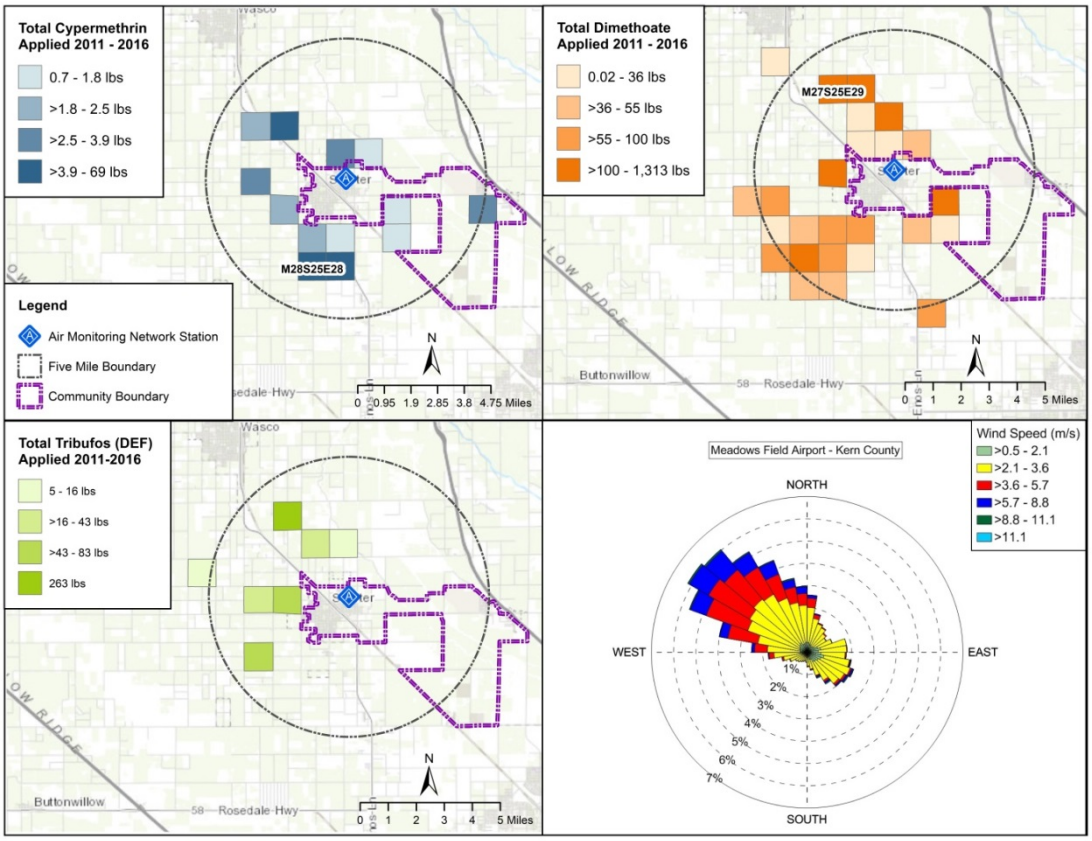


Figure 64. Reported 2011-2016 use of cypermethrin, dimethoate, and DEF within 5 miles of the Shafter sampling site. Wind rose displaying the predominant wind direction of the Shafter area for the years 2011 – 2016 is also shown.

Ripon

In Ripon, only cypermethrin, dimethoate, and endosulfan had any reported use within 5 miles of the sampling site location (Table 60 and Figure 65). Figure 65 also includes a wind rose that displays the distribution of hourly wind speed and wind direction for 2011-2016 as obtained from a nearby CIMIS weather station; the wind direction in the area is predominantly from northwest to southeast direction.

Of the three pesticides with any reported use within 5-miles of the Ripon AMN site, only dimethoate and cypermethrin had reported use for all six years (Table 60). No use of endosulfan was reported in 2016 within a 5-mi radius of the Ripon sampling site. Table 61 shows that the majority of applications for the three AIs used near the sampling site took place via ground application methods, which may explain why these pesticides were not detected at the Ripon sampling site. In addition, Figure 65 shows that most of

the dimethoate reported use occurred away from the predominant wind direction of the Ripon sampling site, which might further explain why dimethoate was not detected.

Table 61 shows there were no reported agricultural applications or use of DEF, dicofol, or oxydemeton-methyl within a 5-mi radius of the Ripon sampling site which would explain why these pesticides had no measurable air concentrations at this site during 2011-2016.

Table 60. Total reported amount of AI used per year for six pesticides not detected within 5-miles of the Ripon sampling site between 2011 and 2016.

Active Ingredients	AI used (lb) per year in Ripon							
	2011	2012	2013	2014	2015	2016	Total	Yearly Average
Cypermethrin	5	1	16	46	102	213	382	64
DEF	-	-	-	-		-	-	-
Dicofol	-	-	-	-		-	-	-
Dimethoate	416	307	368	530	611	458	2,689	448
Endosulfan	270	291	265	70	118	-	1,014	169
Oxydemeton-methyl	-	-	-	-		-	-	-

Table 61. Reported annual use amount of AIs by application method for the six pesticides not detected within 5-miles of the Ripon sampling site between 2011 and 2016.

Active Ingredients	Active Ingredient Used (lb)											
	Aerial application						Ground application					
	2011	2012	2013	2014	2015	2016	2011	2012	2013	2014	2015	2016
Cypermethrin	3	-	-	-	-	20	2	0	16	46	102	193
DEF	-	-	-	-		-	-	-	-	-	-	-
Dicofol	-	-	-	-		-	-	-	-	-	-	-
Dimethoate	146	80	6	80	49	157	270	227	362	450	562	300
Endosulfan	-	-	-	-		-	270	291	265	70	118	-
Oxydemeton-methyl	-	-	-	-		-	-	-	-	-		-

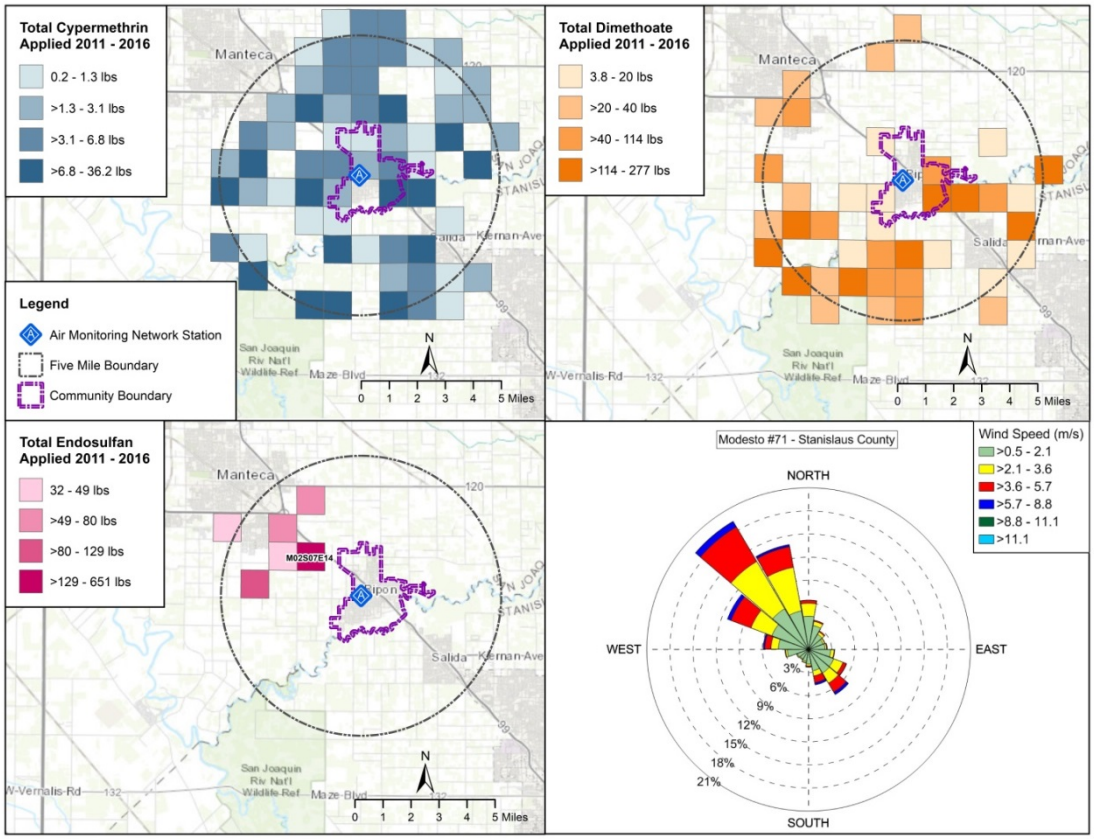


Figure 65. Reported 2011-2016 use of cypermethrin, dimethoate, and endosulfan within 5 miles of the Ripon sampling site. Wind rose displaying the predominant wind direction of the Ripon area for the years 2011 – 2016 is also shown.

Conclusions

In this section, we explored possible reasons why these six pesticides were not detected during 2011-2016 at any sampling site location. The pesticide use data indicate that with the exception of cypermethrin, dimethoate and oxydemeton-methyl, the other three pesticides (DEF, Dicofol, and endosulfan) had little to no reported use within a 5-mi radius of a sampling site location. Overall, oxydemeton-methyl use near the Salinas AMN site for 2011 - 2016 was the highest reported pesticide use (8,446 lbs) among these six pesticides at any location. The reported pesticide use for dimethoate and oxydemeton-methyl near the sampling sites were mostly applied via ground application methods, which have been shown to limit the pesticide that travels off-site during and immediately following applications compared to aerial application methods. Meteorological conditions (e.g., wind direction), volatility, application method, and use amount of the six pesticides during 2011-2016 were all potential factors that resulted in these six AIs having no quantifiable air concentrations at any of the sampling site locations in any year.

Section 10:

Assessment of Mitigation Effects Based on Time Series Analysis of Pesticide Air Concentrations

Introduction

Fumigant use can be affected by several factors, including market fluctuations, climate variations, improvement in agricultural technology, and shifts in agricultural practices. Given the available resources and data, it is impossible to clearly decipher all the factors responsible for driving the ambient air concentrations of the fumigants at the three sampling site locations. However, it is possible to broadly classify two main groups of factors driving a fumigant's air concentration: (1) factors that directly affect the use of the fumigant (e.g., market forces, regulatory actions, climatic conditions, etc.), and (2) factors that affect fumigant emissions into the air following an application (e.g., soil management practices and tarp type). The effects of the first group of factors can be quantified by referring to the amount of pesticide use as reported in the DPR's PUR database (DPR 2017a). Although some factors of the second group are also reported in the PUR, they are more qualitative in nature and therefore more difficult to account for. Previous results from the AMN have shown that three soil fumigants, MeBr, MITC, and 1,3-D, have had the greatest number of detections in air concentration compared with the other two fumigants, chloropicrin and carbon disulfide (King et al. 2017), Therefore, in this section, we review the quantifiable effects, if any, that statewide mitigations had on measured air concentrations of three soil fumigants, MeBr, MITC, and 1,3-D, near the AMN sampling locations of Ripon, Salinas, and Shafter.

Thus, to interpret and discuss changes in air concentrations as they relate to regulations and to mitigation actions, it is necessary to refer not only to trends in air concentrations, but also to examine the concomitant trends in pesticide use. In addition, factors that directly affect pesticide use will be referred to as "use-related factors" (UF). Use-related factors may include known regulations designed to decrease the allowed use of an AI per application or decrease its total use per year or unknown market forces that cause a positive or negative change in pesticide use overtime. Other factors that do not impart any change in pesticide use, but can still drive air concentrations by controlling emissions, are referred as "emission-related factors" (EF). Emission-related factors may include actions that increase fumigant emissions or regulations that

foster their reduction. In fact, the reduction of fumigant emissions can be achieved with application practices (e.g., the use of specific fumigant trapping tarps), or by enhancing soil/site conditions (e.g., irrigating the site to specific soil moisture levels or using agricultural practices that foster soil organic matter accumulation) (Ajwa et al. 2010). Additionally, throughout this section the term "mitigation" is used to refer to any regulatory action designed to reduce fumigant air concentrations.

The AMN data consists of temporal repeated measures of air concentrations for multiple pesticides collected in multiple locations (King et al. 2017). Traditional tests, such as the t-test, cannot be applied to address research inquiries about the effects of mitigations on a time series representing pesticide air concentrations, because the observations before and after any mitigation are not independent. Because of the need to account for temporal correlation and address site-specific research questions, the model development methods for time series analysis described by Wei (2006a) and those by Box and Tiao (1975) for intervention analysis were implemented when applicable using SAS PROC ARIMA[3] (SAS Institute 2014). The term "intervention" is used herein to refer exclusively to any abrupt change in a time series' mean, variance, or both that is also statistically significant based on the ARIMA models selected to interpret the time series. The timing of any interventions may or may not coincide with the timing of when any mitigation measures became effective. Thus, the main objectives of this work were to (1) investigate trends in air concentrations of MeBr, MITC, and 1,3-D, near the three AMN locations during 2011–2016; and (2) establish, based on time series analysis, any possible relationship between known mitigation measures and patterns in air concentrations.

Methodology

Mitigation Measures

Information on mitigation measures adopted through the years by the DPR and U.S. EPA was used for intervention analysis, considering that both UF and EF may drive abrupt changes in the considered time series. The specific timing of any mitigation measures may be known or unknown. In fact, although some measures had an effective date of implementation through specific new label requirements, e.g., the U.S. EPA-required phase 2 restrictions for soil fumigants starting on December 1, 2012, the use of old stock purchased prior to that date was still allowed following the old label. Mitigations comprised both federal and state regulations (Table 62). One set of mitigations common to all three fumigants used in California

[3] Several different names are used to describe this modeling approach, including "intervention", Box-Tiao modeling, and ARIMA models with input variables and regression with ARIMA errors.

was the December 2012 label revisions designed to add safety measures for agricultural workers and bystanders (Farnsworth 2012). For the purpose of this report, these 2012 mitigations can be classified as EF mitigations. In addition, some of the label changes, such as the adoption of tarps in exchange for "buffer-zone credits", were gradually implemented through time (Farnsworth 2013). Thus, the overall changes in the time series, as outlined in Table 62, are expected to be more the result of a combination of EF and UF measures occurring at different points in time, rather than due to a unique action at a specific point in time.

Table 62. Relevant federal and state regulations affecting fumigants in California (2011 – 2016).

Pesticide	Mitigation†	Dates	Use-related factor (UF) or Emission-related factor (EF)	Reference
MeBr	2012 USEPA-required phase 2 restrictions for all soil fumigants	December 1, 2012	EF	Farnsworth 2012
	Critical Use Exemption (CUE) and Quarantine and Pre-shipment Exemption (QPS)	Most exceptions ended in December 2016.	UF	USEPA 2015
MITC-generating compounds	2012 USEPA-required phase 2 restrictions for all soil fumigants	December 1, 2012	EF	Farnsworth 2012
		March 7, 2013	EF	Farnsworth 2012
	The 2015 DPR revised permit conditions for offsite movement	May 15, 2015	EF	Farnsworth 2015
1,3-D	2012 USEPA-required phase 2 restrictions for all soil fumigants	December 1, 2012	EF	Farnsworth (2012, 2013)
	2014 DPR township cap changes.	February 2014	UF	Verder-Carlos 2014

† "Mitigation" is any regulatory action designed to reduce pesticide air concentrations. Mitigations that directly affect pesticide use are classified as "use-related factors". Mitigations that reduce air concentrations patterns by controlling emissions are classified as "emission-related factors".

MeBr

In the United States, the U.S. EPA began to phase out the production and use of MeBr starting on January 1, 2005, through restrictions on its production and use under the Clean Air Act. At the same time, exemptions were allowed for critical use exemptions (CUE) and for quarantine and pre-shipment exemptions (QPS), because the complete elimination of MeBr would lead to significant market disruptions

in the absence of reliable alternatives. Certain MeBr field soil fumigations were also allowed beyond that date under the QPS exemption and were subject to an annual approval (Table 62). The U.S. EPA has subsequently published rules under the CUE for each of the control periods from 2006 to 2016 (U.S. EPA 2015).

While most exceptions ended in December 2016, certain critical uses are still allowed under the QPS exemption. Quarantine and pre-shipment uses include the use of MeBr as a pre-plant fumigant for California strawberry production (U.S. EPA 2015). Thus, based on mitigation measures implemented by the U.S. EPA (2015) and DPR (Zeiss 2017), an overall decrease of MeBr use during 2011–2016 and an abrupt reduction at the start of 2017 were expected. The 2005 phase out of MeBr was expected to also cause an increase in the use of other soil fumigants to compensate for the decline in the use of MeBr (Ajwa et al. 2010).

MITC-Generating Compounds

The main mitigation actions affecting MITC-generating compounds include the 2012 label restrictions for all soil fumigants required by U.S. EPA. The U.S. EPA required phase 2 restrictions for soil fumigants to be implemented in product labels released by registrants for sale on or after December 1, 2012 (Table 62). Greater details about California requirements are provided in the three letters by Farnsworth (2012, 2013, 2015). The March 2013 letter replaced the December 2012 version by revising recommended permit conditions regarding minimum buffer zones, isolation of application blocks, overlapping buffer zones, tarp perforation and removal, and combined work site plans and fumigation management plans. The 2013 letter was further amended by introducing additional restrictions and modifications specifically for MITC-generating compounds described in greater detail by Farnsworth (2015). These revised recommended permit conditions were designed specifically to mitigate hazards associated with offsite movement of metam sodium, metam potassium, and dazomet.

1,3-D

The use of 1,3-D had been capped at 90,250 lbs/year/township (“township cap”) under a program of restrictions developed after the pesticide was reintroduced to the California market in 1995. In 2001, DPR authorized use above the cap (not to exceed a total of 180,500 lbs) in five townships in recognition of specific circumstances facing a segment of the agricultural sector and based upon the fact that there had been not been any use in the state for the five year period between 1990 and 1995 (Verder-Carlos 2014). Starting in February 2014, DPR stopped approving requests for 1,3-D use above 90,250 lbs in townships

that have consistently exceeded that amount since 2002 and use over 180,500 lbs was prohibited in any township. Thus, until the end of 2016 the permitted use in certain townships could range 0-180,500 lbs/year, because the amount allowed depended on the amounts used in previous years. Since unused allocations could be carried over into the following years, California had essentially a two-tier cap system (Leahy 2014). Starting in January 2017, the use of 1,3-D has been limited to a single township use limit of 136,000 lbs/year that can no longer be exceeded in a township, and applications have been prohibited during December (Marciano 2017).

Air Concentration Data

Data used in this section consist of temporal repeated measures of air concentrations for the three fumigant pesticides, MeBr, MITC, and 1,3-D, collected on a weekly basis in the AMN locations of Ripon, Salinas, and Shafter during 2011–2016. 1,3-D observations collected in all three locations from June 2011 to July 2013 were not included in this analysis, because they consisted almost exclusively of NDs (percentage of NDs was always > 95 %).

Monthly and weekly averages were computed for all three AIs to assess whether the final results would differ if the same time analysis was conducted on the weekly or monthly air concentrations. Taking averages was necessary to carry out the time series analysis, whose assumptions include that of equally spaced measurements through time. Since there were no major differences in results between the two approaches, results are presented for MeBr and MITC on a monthly basis, and for 1,3-D on a weekly basis. The use of weekly rather than monthly 1,3-D data proved to be preferable for the convergence of the maximum likelihood (ML) estimation algorithm in SAS PROC ARIMA, given the relatively larger number of ND values in the 1,3-D dataset compared with the number of NDs in the data for the other AIs. In addition, this method produces ML parameter estimates. The ML function is maximized via nonlinear least squares using Marquardt's method. ML estimates are more time consuming to compute than the conditional least squares estimates; however, they may be preferable in some cases (SAS Institute 2014).

Pesticide Use

The PUR database was queried to calculate the mass of AIs (in lbs) applied within a certain area and interval of time, using the proportion use method outlined in Section 4. Thus, in this section the term "use" refers to the average mass of a specific AI (lbs) applied within a five-mile radius of the monitoring locations at the Ripon and Salinas locations, and 10-mile radius at the Shafter location. (During 2011–2016, the applications occurring within a five-mile radius of the Shafter monitoring station were negligible or zero.) Monthly averages were computed for MeBr and MITC-generating compounds, and the weekly observations for 1,3-D were considered as the corresponding weekly averages.

Statistical Analysis

Trend analysis

To investigate general trends in fumigant air concentrations and use, as well as dates corresponding to possible mitigation measures, trend analysis was performed in SAS PROC TIMESERIES (SAS Institute 2014). This procedure allows the seasonal decomposition of a time series to more clearly identify the underlying pattern while removing its irregular component. The additive decomposition model was used assuming that the data has the following form:

$$\text{Original series } (O_t) = \text{trend-cycle } (TC_t) + \text{seasonality } (S_t) + \text{error } (I_t)$$

The "trend-cycle-seasonal" component was obtained as

$$TCS_t = TC_t + S_t = O_t - I_t$$

The difference between the original series (O_t) and error component (I_t) was presented to more clearly visualize the underlying patterns in the data for both air concentration and use series. The identification of seasonal use patterns also helped the interpretation of the Box-Tiao modeling as described below, particularly when the variable "use" proved to be a useful predictor of air concentrations and was maintained in the selected ARIMA model.

ARIMA models

The SAS PROC ARIMA with input variables was applied to identify and select different autoregressive integrated moving average (ARIMA[*p, d, q*]) models. Briefly, Box-Tiao modeling consists of an iterative model building approach of successive identification of the model form, fitting, and diagnostics checking. The underlying question was whether or not there is any evidence for a significant change in the level of these highly variable time series.

The significance or non-significance of the autoregressive model parameters has important implications to assess the seasonality or cyclical pattern in air concentrations. For example, a model of monthly air concentrations, with only one significant intercept and one significant autoregressive parameter at lag 12 (p=[12]), indicates that air concentrations can be modelled solely based on an average value plus some fraction of its deviation from this average a year ago and plus a random error (SAS Institute 2014, p. 206).

After the general underlying ARIMA model was identified by analyzing portions of the series unaffected by any possible interventions, additional models were evaluated by including other meaningful covariates, i.e., input variables, as predictors of pesticide air concentration. This was necessary due to the cyclical nature of the temporal patterns in pesticide air concentrations and in use, changes in laboratory methods during 2011–2016, and possible effects of mitigation measures on the air concentration time series.

The first type of input variables included the corresponding time series of PUR use data as described above or a season variable. The term "season" refers instead to an *ad-hoc*-indicator variable that is equal to one for the months of peak air concentrations (e.g., winter months of November, December, January, and February), and zero during the remaining months.

The second type of input variables was the indicator variables for interventions. The dates corresponding to abrupt changes in the series mean and/or variance were identified through both trend analysis and/or visual inspection of the untransformed or log-transformed series. They were then evaluated as cutoff points to test whether or not the corresponding change in the series should be considered as an intervention. All considered interventions were tested as a "continuing intervention" by creating one or multiple input variables to be included as model input variables. Each variable had a value of 1 for observations collected after the date of an intervention, and of 0 for those collected prior the date of intervention. Abrupt changes may or may not coincide with the dates on which certain DPR mitigation measures went into effect, as in most cases the precise dates remained unknown. The stability of the

selected models with indicator variables for interventions was also evaluated by considering multiple dates that could potentially result in other statistically significant interventions.

If any of the first or second type of input variables were statistically significant at α = 0.05 or α = 0.1, then they were included in the final, selected model. In certain cases, maintaining a variable in the model—even if not significant at α = .05—would improve model fit based on the model selection criteria. The "best" model was selected based on satisfactory model assumptions and the Akaike's (AIC) and Schwarz Bayesian Information (SBC) model selection criteria. Based on this modeling approach, it was possible to draw specific conclusions only when certain conditions were met during the analysis, depending on the significance or non-significance of the model parameters.

Results

MeBr

For the **Ripon** dataset, a simple subset ARIMA model with input variables was used (Figure 66 and Table 63). It can be represented using the "backshift" operator, "B", as

$$y_t = \mu + I_1 x_{t1} + I_2 x_{t2} + I_3 x_{t3} + \frac{a_t}{(1-\phi_4 B^4 - \phi_8 B^8)} \quad \text{Eq. 1}$$

Where

x_{t1} = monthly average mass of applied MeBr

and

$$x_{t2} = \begin{cases} 0, & t \leq \text{October 2013} \\ 1, & t > \text{October 2013} \end{cases}$$

and

$$x_{t3} = \begin{cases} 0, & t \leq \text{October 2015} \\ 1, & t > \text{October 2015} \end{cases}$$

The variable y_t is the monthly average MeBr concentration measured at time t (log scale), and the ML-estimated parameters are μ= 5.43284, ϕ_4= -0.33673, ϕ_8= -0.51678, I_1= 0.0002390, I_2= -1.28055, and I_3 = -0.83898. The a_t term is the white noise. All parameters were significant at α=0.002. This model combines an autoregressive component with cycle of 4 and 8 months and an input variable component, i.e., interventions in October 2013 and October 2015. All model assumptions were satisfactory as indicated by the plots of the ACF, PACF, test of white noise, and the autocorrelation check of the residuals. The October 2013 intervention is an artifact because of a significant decline in the series mean due to a change in laboratory method. Both the MeBr air concentrations and use series had a similar pattern (Figure 67): major peaks occurred around the month of April followed by minor peaks in the remaining months.

For the **Salinas** dataset there was a significant annual cycle with significant autoregressive parameter to account for autocorrelation at lag 12, significant use parameter, and significant interventions for September 2013 and January 2015 (Figure 66 and Table 63):

$$y_t = \mu + I_1 x_{t1} + I_2 x_{t2} + I_3 x_{t3} + \frac{a_t}{(1-\phi_{12}B^{12})} \quad \text{Eq. 2}$$

Where

$x_{t1} =$ monthly average mass of applied MeBr

and

$$x_{t2} = \begin{cases} 0, & t \leq \text{September 2013} \\ 1, & t > \text{September 2013} \end{cases}$$

and

$$x_{t3} = \begin{cases} 0, & t \leq \text{January 2015} \\ 1, & t > \text{January 2015} \end{cases}$$

and y_t is the monthly average MeBr concentration measured at time t (log scale), and the ML-estimated parameters are μ= 5.36186, ϕ_{12} =, 0.32130, I_1= 0.00001977, I_2= --1.40743, I_3= -0.65157. The a_t term is the white noise. All parameters were significant at α=0.05. Similarly, to the previous case, MeBr air concentrations and use series had a similar pattern (Figure 66): major peaks occurred around the month of October followed by minor peaks in the remaining months.

For the **Shafter** dataset there were interventions for October 2013 and July 2015 (Figure 66 and Table 63):

$$y_t = \mu + I_1 x_{t1} + I_2 x_{t2} + I_3 x_{t3} + \frac{a_t}{(1-\phi B-\phi_3 B^3)} \quad \text{Eq. 3}$$

Where

$x_{t1} =$ monthly average mass of applied MeBr

The x_{t2} and x_{t3} variable were introduced to account for the change in the laboratory limit of detection and the intervention occurring in October 2013 and July 2015, respectively:

$$x_{t2} = \begin{cases} 0, & t \leq \text{October 2013} \\ 1, & t > \text{October 2013} \end{cases}$$

and

$$x_{t3} = \begin{cases} 0, & t \leq \text{July 2015} \\ 1, & t > \text{July 2015} \end{cases}$$

and y_t is the monthly average MeBr concentration measured at time t (log scale), and the ML-estimated parameters were μ= 5.31557, ϕ= 0.09544, ϕ_3= 0.14040, I_1= 0.00004084, I_2= -1.62804, and I_3= -0.51861.

The a_t term is the white noise. Most parameters were significant at α=.05. Even though the use parameter was not significant at α = 0.05 (p-value = 0.0529), its inclusion in the model would lead to the overall lowest AIC values; therefore, it was maintained in the final model. Similarly, the autoregressive model parameters were maintained in the model because they would provide more satisfactory model assumptions (Table 63).

Table 63. Comparison of model selection criteria for a limited set of models initially considered to identify the "best model" for MeBr air concentrations (log scale) during 2011–2016. The log transformation was sufficient to obtain a stationary series, and all considered models included the intercept term.

Location	Examined model[1]		Pr > ChiSq (Ljung-Box chi-square statistics)[2]	To Lag with overall lowest p-value	AIC[3]	SBC	Best Model
	Autoregressive component	Input variables					
Ripon	$(1-\phi_4 B^4-\phi_8 B^8)$	$I_1 x_{t1}(Use)+$ $I_2 x_{t2}\,(Oct2013)+I_3 x_{t3}(Oct2015)$	0.4324	12	166.5269	179.6649	X
	$(1-\phi_4 B^4-\phi_8 B^8)$	$I_1 x_{t1}(Oct2013)+I_2 x_{t2}\,(Oct2015)$	0.2932	12	179.0068	190.0303	
	$(1-\phi_4 B^4-\phi_8 B^8)$	$I_1 x_{t1}(Use)$	<.0001	48 and above	215.0837	223.8423	
	No	$I_1 x_{t1}(Use)$ $+I_2 x_{t2}\,(Oct2013)+I_3 x_{t3}(Oct2015)$	0.0501	12	182.8258	191.5845	
Salinas	$(1-\phi_{12} B^{12})$	$I_1 x_{t1}(Use)$ $+I_2 x_{t2}\,(Sep2013)+I_3 x_{t3}(Jan2015)$	0.7392	12	165.6482	176.5201	X
	No	$I_1 x_{t1}(Use)$ $+I_2 x_{t2}\,(Sep2013)+I_3 x_{t3}(Jan2015)$	0.1605	12	170.5401	179.2376	
	No	$I_1 x_{t1}\,(Sep2013)+I_2 x_{t2}(Jan2015)$	0.0002	36	200.898	207.5565	
	$(1-\phi_{12} B^{12})$	$I_1 x_{t1}(Use)$	<.0001	6 and above	202.7097	209.2329	
Shafter	$(1-\phi B-\phi_3 B^3)$	$I_1 x_{t1}(Use)$ $+I_2 x_{t2}\,(Oct2013)++I_2 x_{t2}\,(Jul2015)$	0.3821	6	124.7059	137.934	X
	No	$I_1 x_{t1}(Use)$ $+I_2 x_{t2}\,(Oct2013)++I_2 x_{t2}\,(Jul2015)$	0.3865	6	122.4182	131.2369	
	No	$I_2 x_{t2}\,(Oct2013)++I_2 x_{t2}\,(Jul2015)$	0.4425	6	123.1184	129.7325	
	$(1-\phi_3 B^3)$	$I_1 x_{t1}(Use)$ $+I_2 x_{t2}\,(Oct2013)++I_2 x_{t2}\,(Jul2015)$	0.3687	6	123.3313	134.3548	

[1] MeBr air concentration were log transformed to conduct the analysis on a stationary time series, and then back transformed for the presentation of final results.
[2] Test for the hypothesis that the model residuals are white noise. A p-value < 0.005 indicates significant autocorrelation, thereby rejecting the null hypothesis of a white noise.
[3] The "best" model was selected based on both satisfactory model assumptions and the Akaike's (AIC) and Schwarz Bayesian Information (SBC) model selection criteria. In presence of satisfactory model assumptions, the overall lowest values indicate "best" model fit.

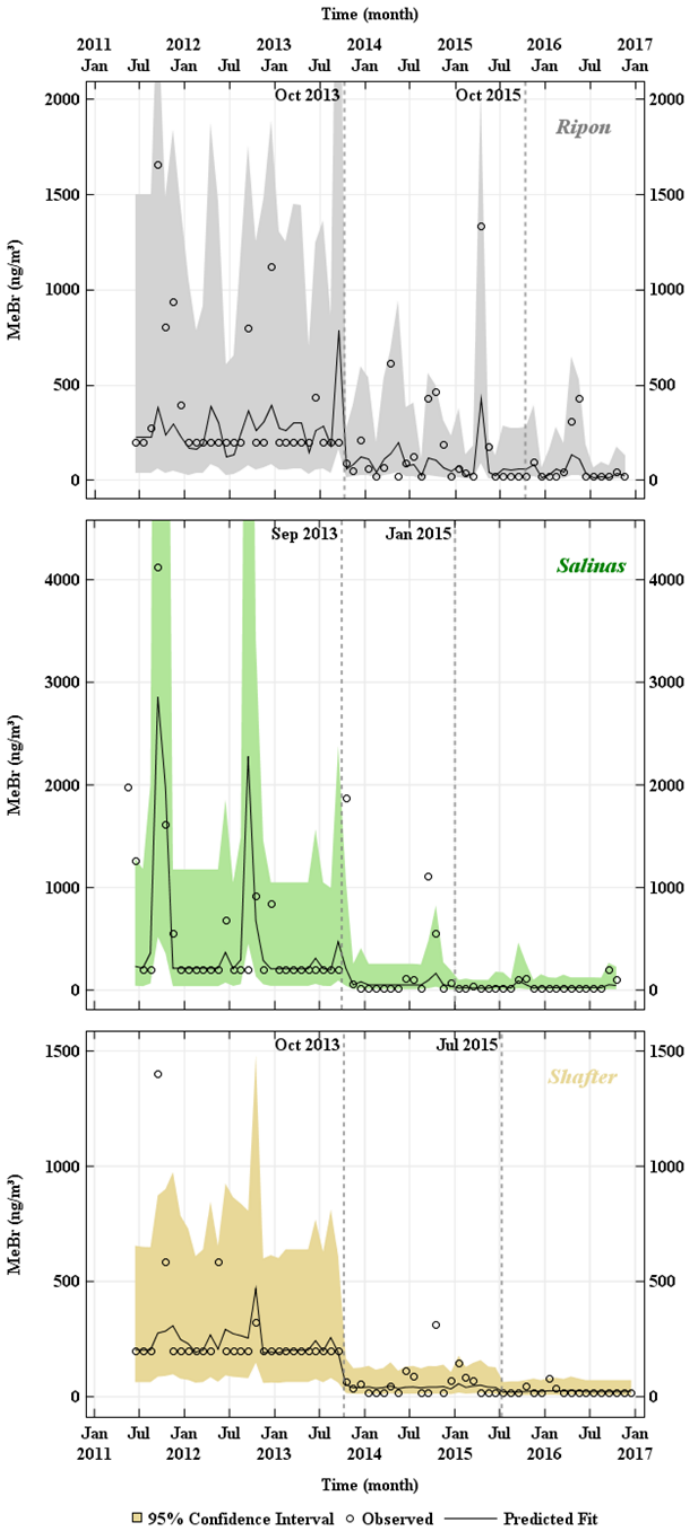


Figure 66. Methyl bromide monthly air concentrations: Plots of the observed and predicted and corresponding 95 % confidence interval (shaded area) for the fitted ARIMA models with input variables by location (2011–2016). Vertical dashed lines indicate significant and abrupt changes in the series.

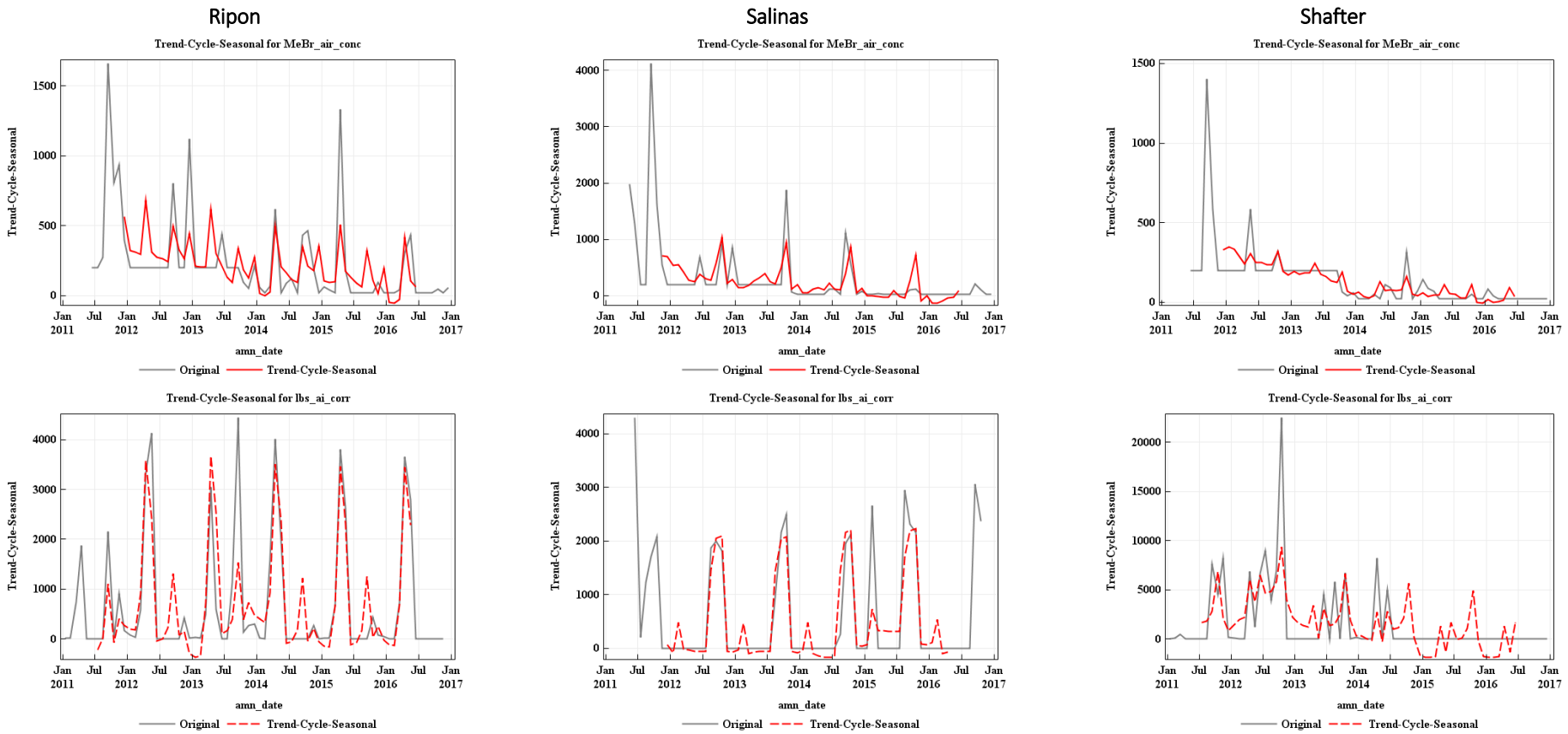


Figure 67. Trend-cycle-seasonal component (TCS) for methyl bromide air concentrations (µg/m^3, solid lines) and corresponding use (lbs, dashed lines) by location. The TCS component is to show the underlying series pattern while removing its "irregular" or error component (based on the additive decomposition performed in SAS PROC TIME SERIES).

MITC

As in the previous case, the underlying model for the three locations was a simple subset ARIMA model, to account for the seasonality (i.e., annual periodicity of the series) in air concentrations showing a general and significant 12-month pattern (Figures 68 and 69). The ARIMA analysis confirmed the results of an overall general decline of the MITC air concentration series during 2011–2016, as indicated by the significance of some of the intervention parameters of the models with the overall lowest AIC and SBC model selection criteria (Table 64), and as described in greater details below.

The "best" model for the Ripon dataset was

$$y_t = \mu + I_1 x_{t1} + I_2 x_{t2} + I_3 x_{t3} + \frac{a_t}{(1-\phi_3 B^3 - \phi_4 B^4 - \phi_5 B^5 - \phi_{12} B^{12} - \phi_{13} B^{13})} \quad \text{Eq. 4}$$

Where

$x_{t1} =$ monthly average mass of applied MITC-generating products

and

$$x_{t2} = \begin{cases} 0, & t \leq \text{June 2012} \\ 1, & t > \text{June 2012} \end{cases}$$

and

$$x_{t3} = \begin{cases} 0, & t \leq \text{January 2016} \\ 1, & t > \text{January 2016} \end{cases}$$

and y_t is the monthly average MITC concentration measured at time t (log scale), and the parameters estimated through the maximum likelihood (ML) method are μ= 2.07611, ϕ_3= 0.12487, ϕ_4= -0.29433, ϕ_5= -0.22274, ϕ_{12}= 0.20262, ϕ_{13}= 0.30363, and I_1= 0.0053153, I_2= -0.40832, and I_3= -0.49572. The a_t term is the random disturbance term or white noise. The parameters ϕ_3, ϕ_5, ϕ_{12}, I_1 (use), and the intervention I_2 were not statistically significant at α = 0.05, but were maintained because this model had the overall lowest AIC and SBC criteria (Table 64). The significance of the intervention parameter I_3 underscores that there was a significant and gradual decline starting in August 2015.

The best model for the Salinas dataset was:

$$y_t = \mu + I_1 x_{t1} + I_2 x_{t2} + \frac{a_t}{(1-\phi_{11} B^{11} - \phi_{12} B^{12})} \quad \text{Eq. 5}$$

Where

$x_{t1} =$ monthly average mass of applied MITC-generating products

and

$$x_{t2} = \begin{cases} 0, & t \leq \text{July 2015} \\ 1, & t > \text{July 2015} \end{cases}$$

and y_t is the monthly average MITC concentration measured at time t (log scale), and the ML-estimated parameters are μ= 1.52603, ϕ_{11}= 0.29862, ϕ_{12}= 0.37231, and I_1= 0.00004618, and I_2= -0.42797. All parameters with the exception of the I_1 (use) parameter were significant at α = 0.05. As in the previous case this model was the one with lowest AIC and SBC parameters, thereby the parameter use was maintained in the model. The a_t term is the random disturbance term or white noise. Similar to the previous case, the significance of the intervention parameter I_2 underscores that there was a significant and gradual decline starting in July 2015.

The best model for the **Shafter** location presented below consisted again in a subset model with a statistically significant use term:

$$y_t = \mu + I_1 x_{t1} + \frac{a_t}{(1-\phi_1 B-\phi_{11} B^{11}-\phi_{12} B^{12}\phi_{13} B^{13})} \quad \text{Eq. 6}$$

and

$$x_{t1} = \text{monthly average mass of applied MITC-generating products}$$

Where y_t is the monthly average MITC concentration measured at time t (log scale), and the ML-estimated parameters are μ= 2.66458, ϕ_1= 0.25192, ϕ_{11}= 0.23249, ϕ_{12}= 0.19967, ϕ_{13}= 0.26708, and I_1= 6.67905E-6. The a_t term is the white noise. The only parameter not significant at α = 0.05 was ϕ_{12} but was maintained in the model based on the AIC and SBC criteria. The significance of the use parameter underscores that patterns in MITC air concentration directly depend on use, contrary to the previous two situations.

Table 64. Comparison of model selection criteria for a limited set of models initially considered to identify the "best model" for methyl isothiocyanate (MITC) air concentrations (log scale) during 2011–2016. The log transformation was sufficient to obtain a stationary series, and all considered models included the intercept term.

Location	Examined model[1]		Pr > ChiSq (Ljung-Box chi-square statistics)[2]	To Lag with overall lowest p-value	AIC[3]	SBC	Best Model
	Autoregressive component	Input variables					
Ripon	$(1-\phi_4B^4-\phi_5B^5-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jun2012)+I_3x_{t3}(Jan2016)$	0.0644	6	203.9074	224.2715	X
	$(1-\phi_3B^3-\phi_4B^4-\phi_5B^5-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jun2012)+I_3x_{t3}(Aug2015)$	0.0367	6	203.9803	224.3444	
	$(1-\phi_4B^4-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jun2012)+I_3x_{t3}(Aug2015)$	0.0146	2	206.597	224.6985	
	$(1-\phi_4B^4-\phi_5B^5-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jun2012)$	0.0348	6	206.4658	224.5672	
Salinas	$(1-\phi_{11}B^{11}-\phi_{12}B^{12})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jul2015)$	0.0961	24	145.1177	156.2152	X
	$(1-\phi_{11}B^{11}-\phi_{12}B^{12})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jul2012)+I_3x_{t3}(Jul2015)$	0.1211	24	145.4982	158.8152	
	$(1-\phi B-\phi_{11}B^{11}-\phi_{12}B^{12})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jul2012)+I_3x_{t3}(Jul2015)$	0.0946	6	146.1217	161.6583	
	$(1-\phi B-\phi_2B^2-\phi_{11}B^{11}-\phi_{12}B^{12})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jul2012)+I_3x_{t3}(Jul2015)$	0.0653	6	147.28	165.0361	
Shafter	$(1-\phi B-\phi_{11}B^{11}-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)$	0.0653	6	193.3323	206.9084	X
	$(1-\phi B-\phi_{11}B^{11}-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jul2012)+I_3x_{t3}(Jul2015))$	0.0789	6	196.9672	215.0687	
	$(1-\phi_{11}B^{11}-\phi_{12}B^{12}-\phi_{13}B^{13})$	$I_1x_{t1}(Use)+I_2x_{t2}(Jul2012)+I_3x_{t3}(Jul2015))$	0.6222	4	200.8954	216.7341	
	$(1-\phi_{11}B^{11}-\phi_{12}B^{12}-\phi_{13}B^{13})$	No	0.0402	6	201.241	210.2917	

[1] MITC air concentration were log transformed to conduct the analysis on a stationary time series, and then back transformed for the presentation of final results.

[2] Test for the hypothesis that the model residuals are white noise. A p-value < 0.005 indicates significant autocorrelation, thereby rejecting the null hypothesis of a white noise.

[3] The "best" model was selected based on both satisfactory model assumptions and the Akaike's (AIC) and Schwarz Bayesian Information (SBC) model selection criteria. In presence of satisfactory model assumptions, the overall lowest values indicate "best" model fit.

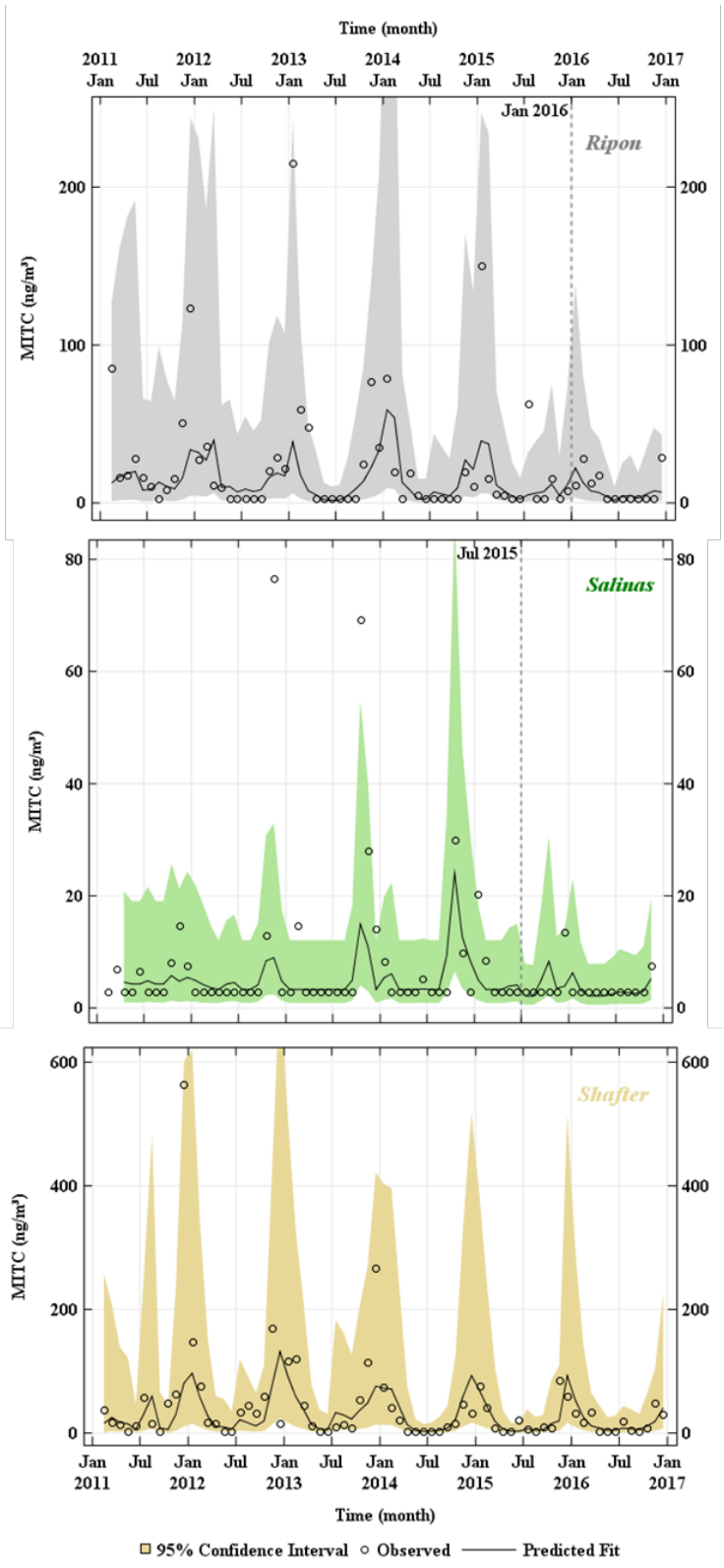


Figure 68. Methyl isothiocyanate (MITC) air concentrations (monthly average). Plots of the observed and predicted and corresponding 95 % confidence interval (shaded area) for the fitted ARIMA models with input variables by location (2011–2016). Vertical dashed lines indicate significant and abrupt changes in the series.

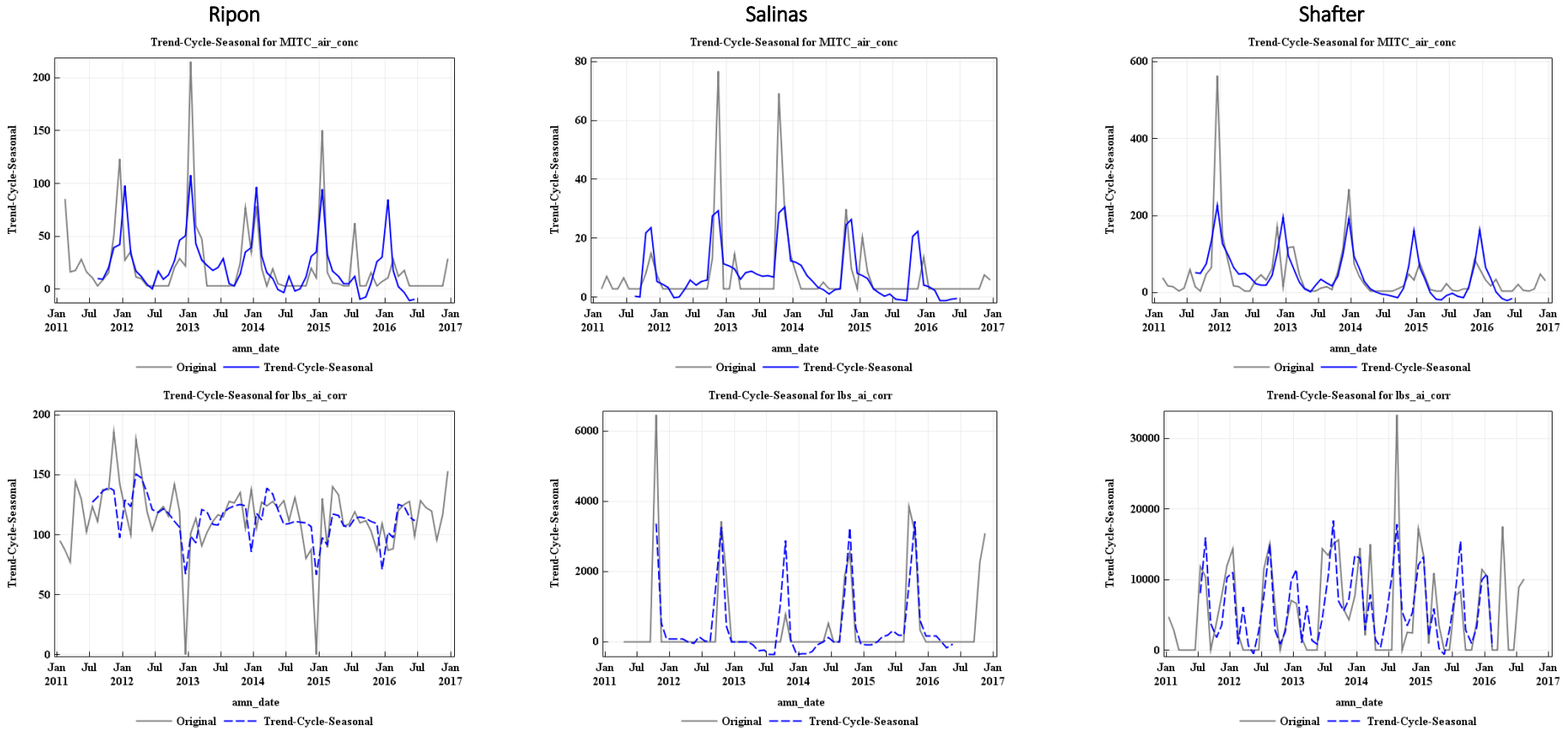


Figure 69. Trend-cycle-seasonal component (TCS) for MITC air concentrations (µg/m^3, solid lines) and corresponding use (lb, dashed lines) by location. The TCS component is to show the underlying series pattern while removing its "irregular" or error component (based on the additive decomposition performed in SAS PROC TIME SERIES).

1,3-D

For the Ripon dataset, the selected best model was a subset ARIMA model with significant autoregressive component to account for seasonality, and input variables to account for abrupt variations in the series (Table 65 and Figure 70). In fact, there was a significant drop in the series occurring on October 16, 2013, corresponding to a change in the MDL, and on February 1, 2014, corresponding to a rapid drop in the series following a high peak (Figure 71). The following model was found to be the "best" model for this sampling location:

$$y_t = I_1 x_{t1} + I_2 x_{t2} + I_3 x_{t3} + \frac{a_t}{(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4-\phi_{50} B^{48})} \quad \text{Eq. 7}$$

Where

$x_{t1} =$ weekly average mass of applied 1,3-D

and

$$x_{t2} = \begin{cases} 0, & t \leq \text{October, 2013} \\ 1, & t > \text{October,2013} \end{cases}$$

and

$$x_{t3} = \begin{cases} 0, & t \leq \text{Feb 2014} \\ 1, & t > \text{Feb 2014} \end{cases}$$

and y_t is the weekly 1,3-D concentration measured at time t, and the autoregressive parameters are ϕ_1= 0.27696, ϕ_2= 0.17689, and ϕ_4 = -0.25783, and ϕ_{48} = 0.33477; and the input parameters are I_1 = 0.07751, I_2 = 2593.6, and I_3 = -2458.9. The a_t term is the random disturbance term or white noise. All model parameters were significant at α = 0.05.

For the Salinas dataset, the best model (Table 65) included autoregressive parameters to account for the seasonality and indicator variables to account for observed significant changes in measured air concentrations occurring in September 2013 and November 2013.

$$y_t = \mu + I_1 x_{t1} + I_2 x_{t2} + I_3 x_{t3} + \frac{(1-\theta_1)}{(1-\phi_1 B-\phi_2 B^2-\phi_{49} B^{49}-\phi_{50} B^{50}-\phi_{52} B^{52})(1-\phi_{50} B^{50}-\phi_{52} B^{52})} a_t \quad \text{Eq. 8}$$

Where

$x_{t3} =$ weekly average mass of applied 1,3-D

and

$$x_{t1} = \begin{cases} 0, & t \leq \text{September 2013} \\ 1, & t > \text{September 2013} \end{cases}$$

and

$$x_{t2} = \begin{cases} 0, & t \leq \text{November 2013} \\ 1, & t > \text{November 2013} \end{cases}$$

and y_t is the 1,3-D concentration measured at time t, and the ML-estimated parameters are reported in Appendix C. The a_t term is the random disturbance term or white noise. All parameters except ϕ_1, ϕ_{49}, and I_1 were significant at α = 0.001.

For the **Shafter** dataset, there was a seasonality component, i.e., seasonal patterns had a one- and three-month frequency and the following indicator variables were significant and included in the selected model:

$$y_t = I_1 x_{t1} + \frac{a_t}{(1-\phi_1 B-\phi_4 B^4)} a_t \qquad \text{Eq. 9}$$

Where the x_{t1}variable was introduced to account for seasonality and is equal to 1 for observations collected in September, October, or November and to 0 for all remaining months. The yt is the 1,3-D concentration measured at time t, and the ML-estimated parameters are ϕ1= 0.21851, ϕ4= 0.18638, and I1= 3692.8. The a_t term is the random disturbance term or white noise. All parameters were significant at α = 0.05 (Appendix C).

Table 65. Comparison of model selection criteria for the final candidate models considered to identify the "best model" for 1,3-dichloropropene air concentrations from July 2013 to December 2016.

Location	Examined model components[1]			Pr > ChiSq (Ljung-Box chi-square statistics)[2]	To Lag with overall lowest p-value	AIC[3]	SBC	Best model
	Autoregressive component	Moving average component	Input variables					
Ripon[4]	$(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4-\phi_{48} B^{48})$	No	$I_1 x_{t1}(Use)+I_2 x_{t2}(Oct2013)+I_3 x_{t3_t}(Feb2014)$	0.2371	6	2983.297	3005.53	X
	$(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4-\phi_{48} B^{48}-\phi_{49} B^{49})$	No	$I_1 x_{t1}(Use)+I_2 x_{t2}(Oct2013)+I_3 x_{t3}(Feb2014)$	0.2932	12	2984.024	3009.433	
	$(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4-\phi_{48} B^{48}-\phi_{49} B^{49})$	No	$I_1 x_{t1}(Use)+I_2 x_{t2}(Oct2013)$	0.0199	6	3001.29	3023.523	
	$(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4-\phi_{48} B^{48})$	No[5]	$I_1 x_{t1}(Season)+I_2 x_{t2}(Oct2013)+I_3 x_{t3}(Feb2013)$	0.0501	12	3044.975	3067.326	
Salinas	$(1-\phi_1 B-\phi_2 B^2-\phi_{49} B^{49}-\phi_{50} B^{50}-\phi_{52} B^{52})\cdot(1-\phi_{50} B^{50}-\phi_{52} B^{52})$	$(1-\theta_1 B^1)$	$I_1 x_{t1}(Use)+I_2 x_{t2}(Sep2013)+I_3 x_{t3}(Nov2013)$	0.1181	12	2581.841	2619.818	X
	$(1-\phi_1 B-\phi_2 B^2-\phi_{49} B^{49}-\phi_{50} B^{50}-\phi_{52} B^{52})\cdot(1-\phi_{50} B^{50}-\phi_{52} B^{52})$	No	$I_1 x_{t1}(Use)+I_2 x_{t2}(Sep2013)+I_3 x_{t3}(Nov2013))+I_4 x_{t4}(Jul2014)$	0.0043	12	2604.074	2638.886	
	$(1-\phi_1 B-\phi_2 B^2-\phi_{49} B^{49}-\phi_{50} B^{50}-\phi_{52} B^{52})\cdot(1-\phi_{50} B^{50}-\phi_{52} B^{52})$	$(1-\theta_1 B^1)$	$I_1 x_{t1}(Season)+I_2 x_{t2}(Sep2013)+I_3 x_{t3}(Nov2013)$	0.0946	12	2644.47	2682.785	
	$(1-\phi_1 B-\phi_2 B^2-\phi_{49} B^{49}-\phi_{50} B^{50}-\phi_{52} B^{52})\cdot(1-\phi_{50} B^{50}-\phi_{52} B^{52})$	$(1-\theta_1 B^1)$	$I_1 x_{t1}(Season)+I_2 x_{t2}(Sep2013)+I_3 x_{t3}(Nov2013+I_4 x_{t4}(Jul2014)$	0.0889	12	2645.743	2687.252	
Shafter	$(1-\phi_1 B-\phi_4 B^4)$	No[4]	$I_1 x_{t1}(Season)$	0.5995	6	3570.679	3580.258	X
	$(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4)$	No	$I_1 x_{t1}(Season)$	0.4320	6	3572.666	3585.438	
	$(1-\phi_1 B-\phi_2 B^2-\phi_4 B^4)$	$(1-\theta_1 B^1)$	$I_1 x_{t1}(Season)$	0.6222	6	3573.621	3589.586	
	$(1-\phi_1 B-\phi_2 B^2-\phi_3 B^3-\phi_4 B^4)$	No	$I_1 x_{t1}(Season)$	0.2703	6	3574.607	3590.572	

[1] MeBr air concentration were log transformed to conduct the analysis on a stationary time series, and then back transformed for the presentation of final results.

[2] Test for the hypothesis that the model residuals are white noise. A p-value < 0.005 indicates significant autocorrelation, thereby rejecting the null hypothesis of a white noise.

[3] The "best" model was selected based on both satisfactory model assumptions and the Akaike's (AIC) and Schwarz Bayesian Information (SBC) model selection criteria. In presence of satisfactory model assumptions, the overall lowest values indicate "best" model fit.

[4] Season" is the indicator variable equal to 0 for observations prior to and equal to 1 for the others.

[5] The models fitted to the Ripon datasets did not include an intercept parameter.

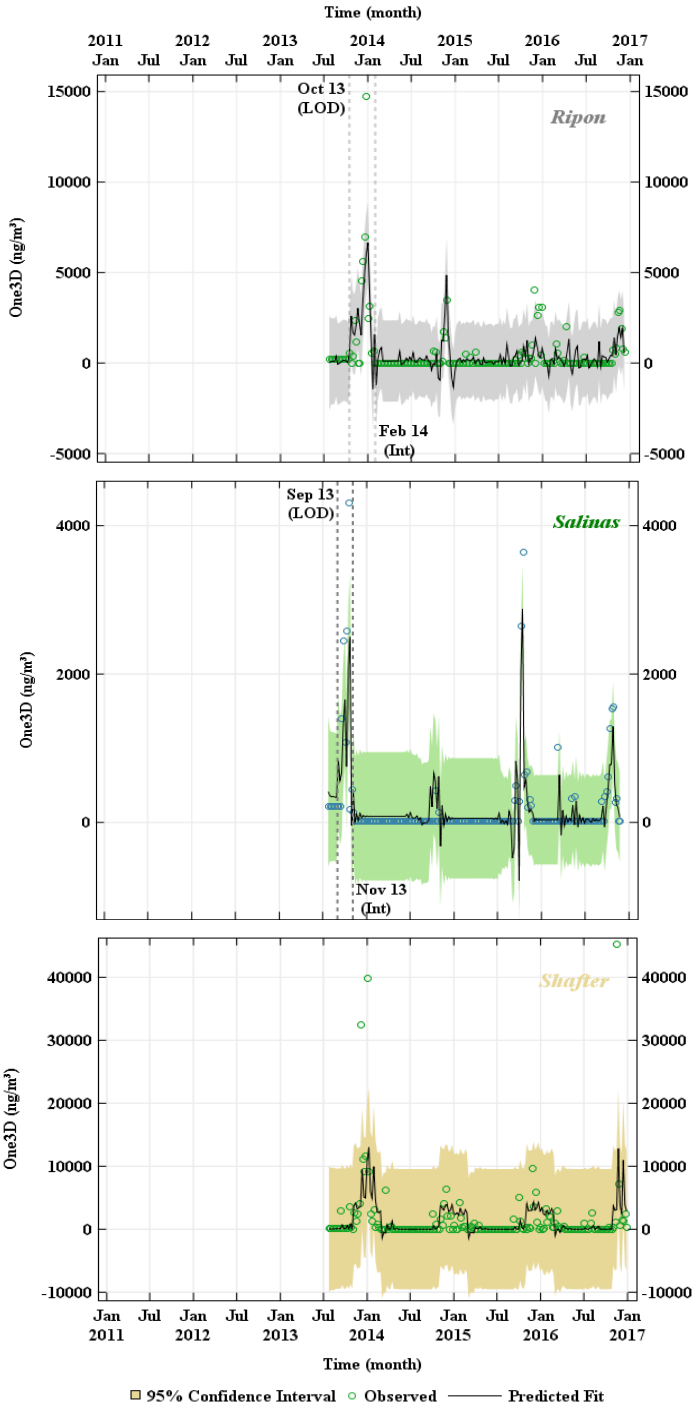


Figure 70. 1,3-dichloropropene weekly air concentrations: Plots of the observed and predicted and corresponding 95 % confidence interval (shaded area) for the fitted ARIMA models with input variables by location (2013–2016). Vertical dashed lines indicate an intervention.

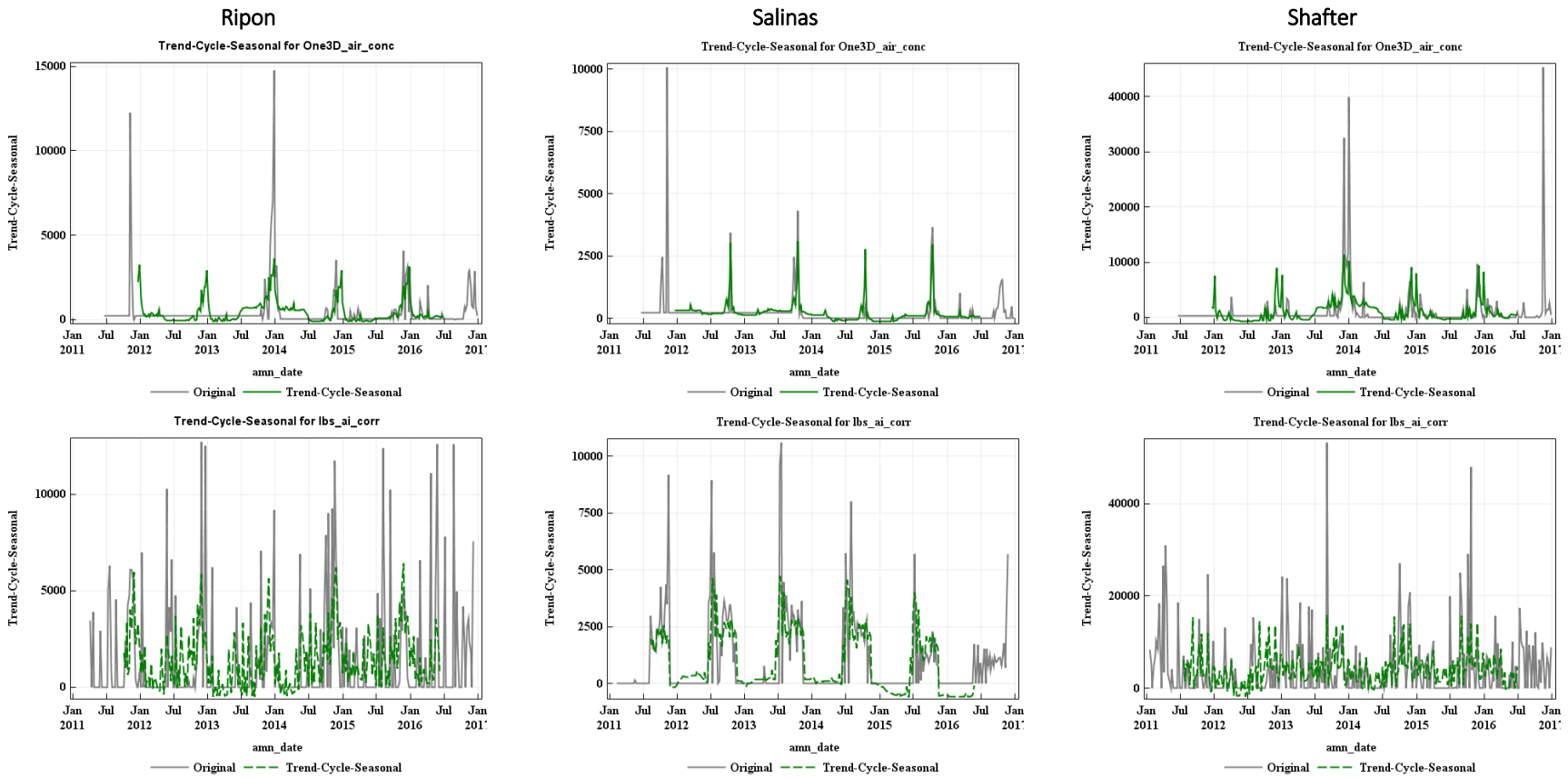


Figure 71. Trend-cycle-seasonal component (TCS) for 1,3-dichloropropene (1,3-D) air concentrations (µg/m3, solid lines) and corresponding use (lb, dashed lines) by location. The TCS component is to show the underlying series pattern while removing its "irregular" or error component (based on the additive decomposition performed in SAS PROC TIME SERIES).

Discussion and Conclusions

Overall, the significance of the use parameter and of the autoregressive parameters for all three fumigants in most locations indicates that detections are related to use in a clear cyclical pattern. The MeBr air concentrations showed a significant decreasing pattern and interventions occurring at the end of 2015 in all three locations. Overall results support evidence that the MeBr interventions were related to both the U.S. EPA UF mitigations and the 2015 DPR EF mitigation. In general, there was a small but significant decrease in MITC concentrations in 2015 for Ripon and Salinas, indicating that both the U.S. EPA and DPR EF restrictions had a greater influence compared with UF mitigations. Contrary to the other two fumigants, the overall trend of the 1,3-D series remained somewhat constant.

MeBr

A cyclical pattern of reported use of either four or eight months was present in the time series for Ripon. The significance of the use indicator variable underscores that there was a significant correlation between the use series and corresponding air concentration series. When (1) any UF mitigation was implemented through regulatory action, i.e., in this case the UF mitigation measures introduced to gradually phase out MeBr; (2) the use parameter was statistically significant; and (3) both air concentrations and use were decreasing overtime, then that specific UF mitigation can be considered effective in reducing air concentrations through reduction of pesticide use. IN other words, the validity of all conditions 1–3 is necessary to be able to conclude that UF mitigations were effective. For the Ripon air concentration time series, conditions 1–3 were all met, thus, it can be concluded that U.S. EPA UF mitigations were effective. At the same time, the significant and abrupt decline occurring in October 2015 indicates that also EF mitigations adopted by DPR in 2015 may have played a role in the gradual reduction in MeBr air concentrations. It is impossible to draw comparisons between observations before and after September 2013 or October 2013 due to differences in laboratory procedures leading to the adoption of two different MDLs.

More general conclusions can be drawn for the Salinas dataset, because, contrary to the previous case, use remained somewhat constant during 2011–2016, while the MeBr air concentrations declined overtime. Such combination of patterns and the significance of the use parameter indicate that EF UF mitigations were likely responsible for such decline in air concentrations.

For the Shafter dataset there was a significant decline after the October 2013 intervention due to a change in the laboratory method: such decline is purely an artifact. Instead, the July 2015 intervention supports the hypothesis of an overall gradual decline in MeBr air concentrations.

MITC

In all three locations, the significance of the autoregressive component of the model indicates significant cyclical patterns, that is, the MITC air concentration series has a seasonal component which repeated annually during the 2011-2016 years. The significance of the intervention parameters corresponding to August 2015 in Ripon and July 2015 in Salinas combined with the non-significance of the use parameter indicate that such interventions likely depended only on EF mitigations. This conclusion is supported also by the nature and timing of the EF mitigations implemented as USEPA-required phase 2 restrictions for all soil fumigants, and of those by DPR in 2015, i.e., the 2015 DPR revised permit conditions for offsite movement. The selected model for the Shafter site shows that the MITC air concentration did not significantly decrease as for the previous two locations.

1,3-D

At all three sampling sites, the significance of the "seasonality" variables, either as autoregressive or indicator parameters in the selected models, indicates that there is a significant annual pattern in the series, with detections occurring during the "winter" months and non-detections during the remaining of the year.

The significant and abrupt declines occurring in February 2014 and November 2013 in Ripon and Salinas, respectively, are the result of an abrupt change following a peak of high use. Contrary to the other two fumigants, the overall trend of the series remain is somewhat constant in the remaining years likely due an increasing demand in the use of soil fumigants to compensate for the decline in MeBr.

We were unable to determine any significant correlation between the 1,3-D use series and corresponding air concentration series with the available data and model used. This is likely due an increase in 2011–2016 demand in its use to compensate for the decline in MeBr use.

Although multiple mitigation measures adopted by DPR or U.S. EPA were used in this intervention analysis, assessing the specific implementation timing of the mitigation measures was almost impossible to determine due to implementation time lags and other factors that make it difficult to incorporate in the

statistical models used for this analysis. Therefore, the intervention analysis was based on a combination of multiple measures occurring at different points in time, rather than due to a unique action at a specific point in time. Overall some significant relationships were established between air concentrations and mitigation measures at some sampling sites and for some fumigants. However, caution should be taken when attempting to expand on these results in a mechanistic way, because additional unknown covariates may also be responsible for driving fumigant air concentrations. However, this empirical approach does provide DPR with another tool to investigate the possible effects of mitigation measures on air concentrations.

References

Ajwa, H., W.J. Ntow, R. Qin, and S. Gao. 2010. "Chapter 9 - Properties of Soil Fumigants and Their Fate in the Environment A2 - Krieger, Robert." In Hayes' Handbook of Pesticide Toxicology (Third Edition), edited by, 315-330. New York: Academic Press. doi: https://doi.org/10.1016/B978-0-12-374367-1.00009-4.

Box, G., Tiao, G. 1975. Intervention Analysis with Applications to Economic and Environmental Problems. Journal of the American Statistical Association. 70 (349): 70-79. doi: 10.1080/01621459.1975.10480264.

Brown, C. 2016. Study #309: Monitoring of 1,3-D in Merced and Fresno Counties. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study309_1,3d_merced_and_fresno.pdf

Brown, C. and Spurlock, F. 2018. Variability in Simulated Volatilization From Approved Label Application Methods for the Fumigant 1,3-Dichloropropene. In Preparation. Department of Pesticide Regulation. Sacramento, CA.

CDFA, 1999. Determination of Chloropicrin Desorbed from XAD-4 Resin Tubes. California Department of Food and Agriculture. Sacramento, CA. http://www.cdpr.ca.gov/docs/specproj/lompoc/99append/append_m.pdf

CDFA, 2004. Determination of MITC in air by GC/NPD or GC/TSD. California Department of Food and Agriculture. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/bio_282.pdf

CDFA, 2008. Determination of Selected Pesticides Collected on XAD-4 Resin by High Performance Liquid Chromatography Ion Trap Mass Spectrometry and Gas Chromatography Mass Spectrometry. California Department of Food and Agriculture. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/imeth_309.pdf

Collett, R.S. & Oduyemi, K. 1997. Air quality modelling: a technical review of mathematical approaches. Meteorological Applications, 4, 235-246. https://rmets.onlinelibrary.wiley.com/doi/pdf/10.1017/S1350482797000455

Craig, K. 2017. Advanced Processing of Pesticide Use Reports for Data Analysis Conducted by Environmental Monitoring Branch's Air Program. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/pur_memorandum_final.pdf

Dacre, H., Gray, S., & Belcher, S. 2007. A Case Study of Boundary Layer Ventilation by Convection and Coastal Processes. Journal of Geophysical Research, 112, D17106. DOI: 10.1029/2006JD007984.

DPR, 1996. Risk Characterization Document: Dichlorvos (DDV). Department of Pesticide Regulation. Sacramento, CA. https://www.cdpr.ca.gov/docs/risk/rcd/ddvp.pdf

DPR, 2000. Overview of Pesticide Use Reporting. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/pur/purovrvw/ovr52000.pdf

DPR. 2002. Evaluation of Methyl Isothiocyanate as a Toxic Air Contaminant. Dpeartment of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/mitc/augfinl02/augparta.pdf

DPR, 2015. 1,3-Dichloropropene Risk Characterization Document – Inhalation Exposure to Workers, Occupational and Residential Bystanders and The General Public. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/risk/rcd/dichloro_123115.pdf

DPR, 2017a. Pesticide Use Reporting. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/pressrls/dprguide/chapter9.pdf

DPR, 2017b. Field Fumigation Method Codes Allowed, by Geographic Area. Department of Pesticide Regulation, Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/method_table_simple.pdf

DPR, 2018. Cancer Potency Estimate for Chlorothalonil. Memorandum to Pam Wofford, April 3, 2018.

Farnsworth, G. 2012. Soil Fumigant Label Changes - Phase 2. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/county/cacltrs/penfltrs/penf2012/2012016.htm

Farnsworth, G. 2013. Letter to County Agricultural Commissioners. Subject: Soil Fumigant Phase 2 Label Implementation - Enforcement Status, and Revisions to Restricted Materials and Permitting Compendium Volume 3 (Amended March 2013). Department of Pesticide Regulation. Sacramento, California.http://www.cdpr.ca.gov/docs/county/cacltrs/penfltrs/penf2012/2012021.htm

Farnsworth, G. 2015. Letter to County Agricultural Commissioners. Subject: Updates to Compendium Volume 3, Restricted Materials and Permitting: Recommended Permit Conditions for Mitc-Producing Metam Sodium, Metam Potassium, and Dazomet. Department of Pesticide Regulation. Sacramento, California.http://www.cdpr.ca.gov/docs/county/cacltrs/penfltrs/penf2015/2015008.htm

Green, A., Singhal, R., Venkateswar, R. 1980. Analytic Extensions of the Gaussian Plume Model. Journal of the Air Pollution Control Association, 30(7), 773-776.

Hanson, B., Bond, C., Buhl, K. 2016. Pesticide Vapor Pressure Fact Sheet. National Pesticide Information Center, Oregon State University Extension Services. http://npic.orst.edu/factsheets/vaporpressure.html

Kim, B., Teffera, S., Zeldin, M. 2000. Characterization of PM_{25} and PM_{10} in the South Coast Air Basins of Southern California: Part 1-Spatial Variations. Journal of the Air & Waste Management Association, 50:12, 2034-2044. DOI: 10.1080/10473289.2000.10464242.

King, K., Vidrio, E., Wofford, P., Segawa, R. 2017. Air Monitoring Network Results for 2016: Volume 6. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/airinit/amn_2016_report.pdf

Leahy, B. 2014. Suspension of Exceptions to Township Limitations on Use of 1, 3-Dichloropropene (1,3-D). Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/methbrom/telone/susp_of_excptn_telone.pdf

Luo, Y. 2017. Meteorological Data Processing for ISCST3 and AERMOD. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/metproc_final.pdf

Marciano, D. 2017. Update to Volume 3, Restricted Materials and Permitting, Pesticide Use Enforcement Program Standards Compendium, 1,3-D Recommended Permit Conditions. Sacramento, California: Department of Pesticide Regulation. http://www.cdpr.ca.gov/docs/county/cacltrs/penfltrs/penf2017/2017001.htm

Neal, R., Segawa, R., Wofford, P. 2010. Pesticide Air Monitoring Network Monitoring Plan. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/airinit/air_network_plan_final.pdf

Rubin, 2016. 1,3-Dichloropropene: Revision of Human Equivalent Concentrations, Margins of Exposure, Air Unit Risk, and Cancer Risk Values for Occupational Seasonal, Annual, and Lifetime Exposure Scenarios. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/risk/rcd/13-d_correction_of_occupational_hecs_etc.pdf

SAS Institute. 2014. SAS/ETS® 13.2 User's Guide. SAS Institute Inc., Cary, NC.

Tao, J. 2009. Analysis of Sampling Intensity for Proposed Air Monitoring Network Based on Pesticide Monitoring Data From Parlier, California. Memorandum to Pam Wofford, November 9, 2009. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2176_wofford.pdf

Tao, J. 2016. Analysis of Agricultural Use and Average Concentrations of 1,3-Dichloropropene in Nine Communities of California in 2006-2015, and Calculation of a Use Limit (Township Cap). Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/whs/pdf/1_3_d_data_analysis.pdf

Tuli, A., Vidrio, E., Wofford, P., Segawa, R. 2017. Air Monitoring Network Results for 2015: Volume 5. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/airinit/amn_2015_report_final.pdf

US EPA. 2000. Meteorological Monitoring Guidance for Regulatory Modeling Applications. EPA-454/R-99-005. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. https://www3.epa.gov/scram001/guidance/met/mmgrma.pdf

US EPA. 2015. Protection of Stratospheric Ozone: The 2016 Critical Use Exemption from the Phaseout of Methyl Bromide. Washington, DC: Title 40 Code of Federal Regulations, Part 82. 2015. https://www.federalregister.gov/documents/2015/10/15/2015-26301/protection-of-stratospheric-ozone-the-2016-critical-use-exemption-from-the-phaseout-of-methyl

US EPA. 2016. Guidance on the Use of the Linked AGDISP-Gaussian Extension Models for Estimating Far Field Drift of Pesticides in FIFRA Ecological Risk Assessments. https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-use-linked-agdisp-gaussian-extension-models

Verder-Carlos, M. 2014. Recommendation on Township Cap Exception Requests for for 1,3-Dichloropropene. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/methbrom/telone/rec_on_twnshp_telone.pdf

Vidrio, E. 2012. 1,3-Dichloropropene Risk Characterization Document – Environmental Fate. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/13-d.pdf

Vidrio, E., Wofford, P., Segawa, R., Schreider, J. 2013. Air Monitoring Network Results for 2011: Volume 1. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/airinit/amn_vol1_final.pdf

Wei, W. 2006a. Time Series Analysis: Univariate and Multivariate Methods, Second Edition. New York, NY, United States: Addison-Wesley Publishing Company.

Wei, W. 2006b. Intervention Analysis and Outlier Detection. In Time Series Analysis: Univariate and Multivariate Methods, edited by, 212-236. Addison-Wesley Publishing Company.

Yamartino, R. J. 1977. A New Method for Computing Pollutant Concentrations in the Presence of Limited Vertical Mixing. Journal of the Air Pollution Control Association, 27(5), 467-468.

Zeiss, M. 2017. Mitigation of Methyl Bromide Field Soil Fumigations. Department of Pesticide Regulation. Sacramento, CA.

Glossary

Acute exposure: Short-term exposure. Acute exposure can be defined as the toxicity manifested within a relatively short time interval. Acute exposure can be as short as a few minutes or as long as a few days but is generally not longer than one day. In animal toxicity studies, exposure is usually for 24 hours or less.

Analyte: The individual pesticide active ingredient or breakdown product that is subject to analysis.

ARB: California Air Resources Board, part of California Environmental Protection Agency.

ARIMA: Autoregressive integrated moving average. A model of a time series based on auto-regressive (p) parameters, differencing (d) of the series (integrated) and moving average (q) parameters.

CalEPA: California Environmental Protection Agency. The Department of Pesticide Regulation is one of six boards, departments, and offices within CalEPA.

Chronic exposure: Long-term exposure. Chronic exposure is generally for a significant portion of an animal or human lifetime. Exposure may be through repeated single doses or may be continuous.

CIMIS: California Irrigation Management Information System. A network of automated weather stations managed by the California Department of Water Resources.

Co-located sampler: A second sampler located within 1 meter of the primary sampler.

Concentration: The amount of a chemical (by weight) in a given volume of air. Concentrations in air can be expressed in units of volume or weight. In this report, pesticide concentrations are expressed as nanograms per cubic meter (ng/m^3).

Detected: Pertains to a chemical that is found in a sample above the method detection limit (see MDL).

Detection limit: see MDL (method detection limit) and LOQ (limit of quantitation)

DPR: California Department of Pesticide Regulation, part of CalEPA

Duplicate sample: Same as a primary sample, but it is obtained from a co-located sampler as a replicate.

ER: Emission Ratio. A ratio between the cumulative flux of a fumigant (i.e., the total amount of fumigant emitted to the atmosphere) over a certain time period following completion of a fumigant application, and the total amount of fumigant initially applied. ER varies by application method, fumigant compound, and environmental conditions across a range of 0 to 1, where a smaller value indicates proportionally less fumigant emitted.

Exposure: Contact with a chemical. Common routes of exposure are dermal (skin), oral (by mouth) and inhalation (breathing).

Field spiked sample: A sample with a known amount of chemical spiked onto the sample media, which is placed next to a primary sample that undergoes the same air flow and run time conditions. The field-spiked sample, when compared to the primary sample, provides some information about any change in the ability to recover the analyte during air sampling.

FFM code: Field Fumigation Method code. A four-digit number used in reporting of fumigant applications to the Pesticide Use Report (see PUR) database. A FFM code describes a specific set of application practices (e.g., tarped application on a bedded field) approved for use by DPR.

FQPA: U.S. Food Quality Protection Act

Goodness-of-fit measures: A general term used to describe any number of methods used to assess the ability of a function (e.g., a line or curve) to match a set of observations (i.e., data points). The coefficient of determination (R^2) is a goodness-of-fit measure commonly applied in linear regression and has a value between 0 and 1, where a value of 1 indicates a function that completely describes a set of observations.

GPF: Gaussian Plume Function. An equation used to describe the dispersion (i.e., the 'spreading out') of an airborne pollutant downwind of a continuous point source (e.g., a smokestack) in three dimensions (e.g., distance downwind, vertical distance from the plume centerline, and horizontal distance from the plume centerline) under a given set of meteorological and environmental conditions.

Health screening level: The calculated air concentration based on a chemical's toxicity that is used to evaluate the possible health effects of exposure to the chemical. Screening levels can be useful in the process of evaluating the air monitoring results although they are not regulatory standards. A measured air concentration that is below the screening level for a given pesticide generally would not undergo further evaluation, unless additional data presents the necessity to do so. A measured concentration that is above the screening level would not necessarily indicate a health concern but would indicate the need for a further and more refined evaluation. Different screening levels are determined for different exposure periods, i.e., acute, subchronic, and chronic. DPR develops a health screening level when a regulatory target has not been established. Also see definition of regulatory target.

Heteroscedasticity: In regression analysis, a term used to describe error in the estimation of a dependent variable that consistently increases or decreases across the range of an independent variable. Heteroscedasticity creates problems in accurately describing the amount of uncertainty associated with the estimate of a dependent variable.

HI: Hazard index. The HI is the sum of all hazard quotients (HQs). It is used to estimate the potential health risk for non-cancer effects from exposure to several chemicals for a given time period (acute, subchronic, or chronic). That is,

$$HI = HQ1 + HQ2 + HQ3 + \ldots$$

HQ: Hazard quotient. The HQ is the ratio of an exposure level for a chemical (measured air concentration of a pesticide) to a reference concentration for the chemical (screening level or regulatory target for that pesticide) over the same time period. An HQ less than 1 is generally considered to be health protective.

Independence: Absence of any systematic pattern in the observations or measurements taken through time or space (i.e., they are distributed at random).

Intervention analysis: A statistical technique to evaluate the effect of external events (e.g., regulations directed at reducing pesticide use)—called "interventions"—on a time series. The timing of interventions may be known or unknown. In the latter case, intervention analysis will involve the analysis of outliers.

LOQ: Limit of quantitation. The LOQ is the smallest amount of the chemical that can be reliably measured. Samples with concentrations above the MDL but below the LOQ can be identified as containing a trace amount but the concentration cannot be measured reliably. When calculating average concentrations or other statistics, DPR assumes that samples with a trace concentration have a concentration at the midpoint between the MDL and the LOQ. As with the MDL, the LOQ is a characteristic of both the method and the chemical. Different methods can have different LOQs for the same chemical. The same method can have different LOQs for different chemicals.

Matrix: The substance in the sampling tubes, such as XAD resin or charcoal, that traps and removes organic compounds from the atmosphere during sampling

MDL: Method detection limit. The MDL is the smallest amount of the chemical that can be identified (although not necessarily quantified) in a sample with the method employed. If nothing is detected, the sample may contain none of the chemical or may have a concentration less than the MDL. In either instance, the sample is designated as

containing no detectable amount. When calculating average concentrations or other statistics, DPR makes a conservative assumption that a sample with no detectable amount has a concentration of one-half the MDL. The MDL is a characteristic of both the method and the chemical. That is, different methods can have different MDLs for the same chemical. Similarly, one method can have different MDLs for different chemicals. (See also LOQ, limit of quantitation)

MLD: Monitoring and Laboratory Division. The MLD is the monitoring and laboratory division of the California Air Resources Board.

Monitored chemical: Refers to a chemical that was sampled for in air and analyzed to determine its possible concentration. Air sampling apparatus can consist of pumps and sampling tubes or vacuum canisters. Pumps draw air over sampling tubes containing absorptive media which trap chemicals from the air. The media is then chemically analyzed in the laboratory to determine if the monitored chemical was in the air. Vacuum canisters are air-tight metal containers which utilize a starting vacuum to draw air inside during the monitoring period. The air in the canisters is then subjected to chemical analysis in the laboratory to determine if the monitored chemical was in the collected air. In this study, air sampling periods were 24 hours long.

ND: None detected. This is the concentration below the method detection limit (MDL).

OA: Oxygen analog. This is the breakdown product from certain organophosphate pesticides. An Oxygen analog is usually more toxic than its parent compound.

OEHHA: California Office of Environmental Health Hazard Assessment, part of CalEPA.

PLSS: Public Lands Survey System. A method of subdividing and describing land in the United States (U.S.) regulated by the U.S. Department of the Interior's Bureau of Land Management. PLSS components include description of state, meridian, township, range, and section which together describe a unique, discrete, typically rectangular area measuring approximately 1 mi^2. Pesticide use data in the Pesticide Use Report is reported on the basis of PLSS location.

Primary sample: Sample collected in the field to measure pesticide air concentrations.

PUR: Pesticide use report. All agricultural pesticide use in California is required to be reported to the County Agricultural Commissioners. DPR collects these pesticide use reports; it evaluates and annually publishes the data.

QAS: Quality Assurance Section of ARB.

QC: Quality control

RCD: Risk characterization document. DPR's human health risk assessment for a pesticide is presented in the RCD. The RCD explains the results of the risk assessment and assembles, critiques, and interprets all pertinent scientific data on a chemical's toxicology and exposure.

RED: Reregistration eligibility document. As part of its reregistration process, U.S. Environmental Protection Agency (U.S. EPA) reevaluates and relicenses existing pesticides originally registered prior to current scientific and regulatory standards. U.S. EPA's human health risk assessment for a pesticide is presented as part of its RED.

Regulatory target: Regulatory targets are concentrations that DPR's legal requirements are designed to stay below. DPR puts measures in place based on the regulatory target to limit exposures so that adverse effects can be avoided. Exceeding a regulatory target does not necessarily mean an adverse health effect occurs, but it does indicate that the restrictions on the pesticide use may need to be modified. DPR normally establishes a regulatory target after completing a comprehensive risk assessment of a chemical's toxicity and potential exposures. DPR determines a regulatory target based on the risk assessment, as well as risk assessments from other agencies, pesticide use patterns, potential effects on use of alternative pesticides, and other factors. A regulatory target is based on a more

comprehensive evaluation than a health screening level. Therefore, a regulatory target supersedes a health screening level (i.e., a specific pesticide at a specific exposure duration will have either a regulatory target or a health screening level, but not both).

Risk: Risk is the probability that a toxic effect (adverse health effect) will result from a given exposure to a chemical. It is a function of both the inherent toxicity of the chemical as well as the exposure to the chemical.

Sample cross-correlation function in SAS PROC ARIMA: Represents the correlation between two time series (e.g., pesticide use and pesticide air concentrations), at different lags. Investigating the cross-correlation between two time series can identify one series as a useful predictor of the other. If there is a significant correlation between these series, the cross-correlation functions will indicate at which lag or lags the correlation is the greatest.

Screening level: see Health screening level

Simple linear regression: A statistical method by which a linear relationship between two variables is established by minimizing residuals (i.e., the vertical distance between data points and a fitted linear function) and subsequently allowing estimation of an unknown variable from a known variable (e.g., estimation of air concentrations from pesticide use data). Various goodness-of-fit measures are used as a method of evaluating how well the resulting function matches the data points.

SOP: Standard operating procedure. A document that describes the materials and methods used for various monitoring tasks.

Sorbent cartridge: A Teflon® cartridge filled with a measured amount of trapping media and then sealed. The tube is attached to an air pump and ambient air is drawn through the trapping media in the tube.

Stationary time series: A time series with constant mean and variance.

Subchronic exposure: A medium time interval of exposure to a chemical. Subchronic exposure is longer than acute exposure, but shorter than chronic exposure. Subchronic exposure may be through repeated single doses or may be continuous.

Trace: see LOQ (limit of quantitation)

Trend analysis: Analysis of time series data based on smoothing of the data in order to separate the underlying pattern in the data series from randomness. The underlying pattern can then be split into sub-components to identify the main factors affecting the original series.

Trip blank sample: A clean sample cartridge capped and stored on dry ice with the rest of the samples collected from the monitoring site. Its purpose is to determine if handling conditions in the field, sample transporting, or storage procedures may have contaminated the samples.

U.S. EPA: U.S. Environmental Protection Agency

VOC: Volatile organic compound

White noise: A stationary time series (with mean usually equal to zero) without any significant autocorrelation.