MATERIALS AND METHODS

Air Sampling Equipment and Methods
There were a total of four methods used for the collection of air samples as part of the AMN. Each of these methods required specific equipment as described below.

Multi-Pesticide Residue Sampling

Original AMN Equipment:
For all samples taken in Shafter during the months of January through March: 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-h period. The cartridge was connected to the pump using a combination of threaded ABS plastic fittings, nitrile o-rings, and approximately 8 feet of Tygon® 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 finish of the sampling period.

New Equipment:
For samples collected at Shafter starting in April, as well as all other samples collected as part of the AMN: as part of sample collection, ambient air was drawn through the XAD-4 media using channel 1 of a custom-built 3-channel pesticide sampling version of a Speciation Air Sampling System (SASS) manufactured by Met One Instruments, hereafter referred to as Met One® pesticide sampler. Channel 1 provided a sustained flow of 15.0 L/min ± 5%. The average of flow measurements collected at 5-minute intervals was used to directly calculate the volume sampled which was reported by the instrument. This allowed for more certainty than that of the previous method of calculation which used the mean from only two data points (measurements at the start and finish of sample collection). The Met One® pesticide sampler includes a solar shield of a sufficient size to shield the multi-pesticide cartridges from direct sunlight exposure during the sampling period.

Volatile Organic Compounds

Original AMN Equipment:
For all samples taken in Shafter during the months of January through March: as part of sample collection, ambient air was drawn into a 6-L SilcoCan canister (cat. # 24142) 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-h sampling period. The air sampling inlet of the flow controller was placed at a sampling height of 3-10 meters, depending on the sampling site location, with a sufficient amount of 1/16” internal diameter PTFE (Teflon®) tubing to reach the canister. Bios Defender 530® or DC-Lite® flow meters were used to check the flow rate at the start and finish of the sampling period.
New Equipment:
For Samples collected at Shafter starting in April, as well as all other samples collected as part of the AMN: as part of sample collection, ambient air was drawn through 1/16” internal diameter PTFE (Teflon®) tubing into a Xontec model 901 ambient air sampler into a 6-L SilcoCan canister. The flow rate using this method was 7.5 mL/min (± 10%) and was sustained for a 24-h period. The sampler itself included an automatically initiated 60-second purge period to clear the sampling lines immediately prior to sample collection.

MITC

Original AMN Equipment:
For all samples taken in Shafter during the months of January through March: as part of sample collection, Anasorb sorbent sample tubes containing activated charcoal as the sampling media (cat. # 226-16-02) were used for the collection of 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-h 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 finish of the sampling period.

New Equipment:
For samples collected in Shafter starting in April, as well as all other samples collected as part of the AMN: as part of sample collection, ambient air was drawn through the SKC® Anasorb® CSC sorbent sample tubes containing activated coconut charcoal media using channel 2 of the Met One pesticide sampler. Channel 2 provided a sustained flow of 1.5 L/min ± 5%. The average of flow measurements collected at 5-minute intervals was used to directly calculate the volume sampled which was reported by the sampler. This allowed for more certainty than that of the previous method of calculation, which used the mean from only two data points (measurements at the start and end of sample collection). The glass sorption tubes containing the sampling media and any collected analyte were shielded from sunlight by the sampler’s radiation shield.

Chloropicrin

Original AMN Equipment:
For all samples taken in Shafter during the months of January through March: as part of sample collection, SKC® XAD-4 sorbent sample tubes (cat. # 226-175) were used for the collection of 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-h 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 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 finish of the sampling period.
**New Equipment:**
For all samples collected in Shafter starting in April, as well as all other samples collected as part of the AMN: as part of sample collection, ambient air was drawn through the SKC® XAD-4 sorbent sample tubes using channel 3 of the Met One pesticide sampler. Channel 3 provided a sustained flow of 50 mL/min ± 5%. The average of flow measurements collected at 5-minute intervals was used to directly calculate the volume sampled which was reported by the machine. This allowed for more certainty than from the previous method of calculation which used the mean from only two data points (measurements at the start and finish of sample collection). The glass sorption tubes containing the sampling media and any collected analyte were shielded from sunlight by the sampler’s radiation shield.

**Field Sampling Procedure**
One 24-h sample was collected each week at each of the eight sites, once they were active. The starting day varied each week with the actual dates being randomly selected as much as possible. Actual sampling start times were left to the discretion of the field sampling personnel.

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 sample tubes, cartridges, and canister tags prior to sampling.

Each of the four sample types detailed above were set up and started as closely as possible to the same time, except for the occasional make-up sample needed to replace an invalid 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 (i.e., 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 (± 5% for the new equipment, ± 10% for the old equipment) that sampling equipment was recalibrated to within an acceptable tolerance. As the air sampling commenced 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.

**Quality Control Methods**
In addition to the primary samples, DPR collected quality control (QC) samples including trip blanks, field spikes, and co-located duplicate samples at a rate of 10% of primary samples. The QC results section located at the end of this report summarizes the results of these QC procedures.

A trip blank sample provides information on possible contamination of field collected samples. For the manufactured pre-packed XAD-4 and charcoal sample tubes, trip blank sample 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 were collected from the monitoring station in Watsonville (designated DPR’s QC sampling site) at least once every month of sampling. Trip blank samples containing detectable amounts of any of the pesticides 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 like 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 changes 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 at various concentrations. For chloropicrin- and MITC-spiked samples, concentrations varied every month. VOC canister spike samples were scheduled for collection once per month at the monitoring station in Watsonville.

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 are then established at the mean percent recovery ± 3 SDs. Spike samples outside the control limits established for each pesticide do 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 root issue. Depending on the results of this assessment, changes to field and laboratory procedures may be necessary.

Additionally, to look for sample analyte breakthrough in the sampling media, a method trapping efficiency was conducted for AMN sample collection media with the exception of air canisters (DPR, 1995). 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.

The site at Watsonville was designated as DPR’s QC site for the DPR-operated portion of the AMN. A second set of sampling equipment dedicated to the collection of QC samples was installed at this location.
Appendix K: Health Evaluation and Calculations

Calculation of Subchronic Rolling Averages

13-week Rolling Averages
In 2016, DPR eliminated the practice of using a 4-week rolling average concentration to represent a subchronic time period for 1,3-Dichloropropene (1,3-D) and chloropicrin for comparisons to subchronic screening levels and regulatory targets. This determination was based on an evaluation conducted by DPR’s Human Health Assessment Branch that looked at seasonal reference concentrations for these two chemicals. Greater details are provided elsewhere (DPR, 2016b)

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 high potential for 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, damage to the nervous system, cancer, and birth defects. Vidrio et al. (2013a) summarizes the potential health effects of each pesticide. 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) developed health screening levels or regulatory targets to place the results in a health-based context.

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. (2013a) summarizes more information on DPR-determined screening levels including information on deriving screening levels for each pesticide.

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 formal risk assessment of a chemical’s toxicity and potential exposures. DPR management determines a regulatory target using its 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 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, MeBr, MITC, and 1,3-D) have regulatory targets for one or more exposure periods.
Cumulative Exposures

Cumulative exposure and risk were estimated using a hazard quotient and hazard index approach for pesticides that have a common mode of action (such as 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 hours, 4 weeks, 1 year) with the screening level derived for a similar exposure (i.e., acute, subchronic, chronic). The ratio of measured air concentration of a pesticide to a reference concentration or screening level for that pesticide is called the hazard quotient (HQ). In this case,

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

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

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

An 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 only considering the pesticides individually.