Appendix I: Laboratory Analysis

Pesticides Monitored

As part of the Air Monitoring Network (AMN), DPR monitors for 31 pesticides and 5 breakdown products. Chemicals included in the AMN were selected based primarily on potential health risk (Vidrio et al., 2013a). A total of four analytical methods were used to analyze the collected air samples as part of the AMN:

1. Multi-pesticide residue analysis
2. Volatile organic compounds (VOC) analysis
3. MITC analysis
4. Chloropicrin analysis

Multi-Pesticide Residue Analysis

Prior to sampling, personnel from the California Department of Food and Agriculture Center for Analytical Chemistry laboratory (CDFA CAC laboratory) washed, rinsed, and packed 30 mL of XAD-4 sorbent material into a custom-built Teflon® cartridge to be used for the collection of 32 analytes via multi-pesticide residue analysis.

Multi-pesticide residue analysis using XAD-4 resin was performed by laboratory staff using gas chromatography – mass spectrometry (GC-MS) and liquid chromatography – mass spectrometry (LC-MS) methods as described elsewhere (CDFA, 2018a). 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 multi-pesticide residue analysis with XAD-4 resin.

Chemical	Chemical Class	Pesticide Group
Acephate	Organophosphate	Insecticide
Bensulide	Organophosphate	Herbicide
Chlorothalonil	Chloronitrile	Fungicide
Chlorpyrifos	Organophosphate	Insecticide
Chlorpyrifos Oxygen Analog	Organophosphate	Degradate
Chlorthal-dimethyl (DCPA, Dacthal)	Phthalate	Herbicide
Cypermethrin	Pyrethroid	Insecticide
DDVP	Organophosphate	Insecticide
DEF (SSS-tributyl phosphorotrithioate)	Organophosphate	Defoliant
Diazinon	Organophosphate	Insecticide
Diazinon Oxygen Analog	Organophosphate	Degradate
Dicofol	Organochlorine	Insecticide
Dimethoate	Organophosphate	Insecticide
Dimethoate Oxygen Analog	Organophosphate	Degradate
Diuron	Urea	Herbicide
Endosulfan	Organochlorine	Insecticide
Endosulfan Sulfate	Organochlorine	Degradate

EPTC	Carbamate	Herbicide
Iprodione	Dicarboximide	Fungicide
Malathion	Organophosphate	Insecticide
Malathion Oxygen Analog	Organophosphate	Degradate
Methidathion	Organophosphate	Insecticide
Metolachlor	Chloracetanilide	Herbicide
Norflurazon	Pyridazinone	Herbicide
Oryzalin	Dinitroaniline	Herbicide
Oxydemeton-methyl	Organophosphate	Insecticide
Oxyfluorfen	Diphenyl ether	Herbicide
Permethrin	Pyrethroid	Insecticide
Phosmet	Organophosphate	Insecticide
Propargite	Organosulfite	Insecticide
Simazine	Triazine	Herbicide
Trifluralin	Dinitroaniline	Herbicide

Volatile Organic Compound Analysis

Collected air canisters were analyzed for the presence of two analytes (Table 2) using a volatile organic compound (VOC) GC-MS method similar to the United States Environmental Protection Agency's (US EPA) Method TO-15. The standard operating procedure for this analysis is described in detail elsewhere (CDFA, 2010). Analysis of 1,3-D, includes results for both *cis*- and *trans*- isomers, which are then consolidated and reported as a total 1,3-D concentration for use in this report.

Table 2. Target analytes in volatile organic compound analysis.

Pesticide	Pesticide Group	Chemical Class
1,3-dichloropropene	Fumigant	Halogenated organic
Methyl bromide	Fumigant	Halogenated organic

MITC

Samples collected on Anasorb coconut charcoal sorbent tubes were analyzed by CDFA CAC laboratory for the presence of MITC by GC-MS as described by CDFA (2018b). MITC extraction from the sorbent medium involves using carbon disulfide in ethyl acetate. The proportion of carbon disulfide used was recently increased to 1.0% (CDFA, 2018b). This is followed by analysis using a gas chromatography-nitrogen phosphorous detector (GC-NPD) (Table 3).

Chloropicrin

Samples collected on XAD-4 sorbent tubes were analyzed by CDFA CAC laboratory for the presence 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 GC equipped with an ECD (Table 3).

Table 3. Target analytes in individual analyte residue analysis.

Pesticide	Pesticide Group	Chemical Class
MITC	Fumigant	-
Chloropicrin	Fumigant	Halogenated organic

Laboratory Methods

Method Calibration

The laboratory established method 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 conducting a regression analysis of standard concentrations measured by 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 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. Tables 4 and 5 list all the quantitation and detection limits for AMN analytes.

Table 4. Quantitation and detection limits for Air Monitoring Network samples collected on sorbent media analyzed by the CDFA CAC laboratory.

Chemical	MDL (ppb)	LOQ (ppb)	MDL (ng/m^3)	LOQ (ng/m^3)
Acephate	0.000087	0.0012	0.65	9.3
Bensulide	0.000054	0.00057	0.88	9.3
Chloropicrin	0.033	0.10	222	694
Chlorothalonil	0.000081	0.0021	0.88	23.1
Chlorpyrifos	0.000061	0.0016	0.88	23.1
Chlorpyrifos OA	0.000058	0.00068	0.79	9.3
Cypermethrin	0.00014	0.0014	2.31	23.1
Chlorthal-dimethyl	0.000065	0.00068	0.88	9.3
DDVP	0.000082	0.0026	0.74	23.1
DEF	0.000022	0.00072	0.28	9.3
Diazinon	0.000030	0.00075	0.37	9.3
Diazinon OA	0.000031	0.00079	0.37	9.3

Dimethoate	0.000079	0.00099	0.74	9.3
Dimethoate OA	0.000069	0.0011	0.6	9.3
Diuron	0.000039	0.00098	0.37	9.3
Endosulfan	0.00011	0.0014	1.76	23.1
Endosulfan Sulfate	0.000051	0.0013	0.88	23.1
EPTC	0.00019	0.0030	1.44	23.1
Iprodione	0.000076	0.0017	1.02	23.1
Malathion	0.000096	0.00069	1.3	9.3
Malathion OA	0.000029	0.00072	0.37	9.3
Methidathion	0.000071	0.00075	0.88	9.3
Metolachlor	0.000091	0.00080	1.06	9.3
MITC	0.0019	0.0077	5.44	23.1
Norflurazon	0.000044	0.00069	0.6	9.3
Oryzalin	0.00012	0.0016	1.67	23.1
Oxydemeton methyl	0.00014	0.00089	1.44	9.3
Oxyfluorfen	0.000088	0.0016	1.3	23.1
Permethrin	0.00010	0.0014	1.62	23.1
Phosmet	0.00029	0.00072	3.7	9.3
pp-Dicofol	0.00030	0.0015	4.49	23.1
Propargite	0.000071	0.0016	1.02	23.1
Simazine	0.000039	0.0011	0.32	9.3
Trifluralin	0.000085	0.0017	1.16	23.1

Table 5. Method detection limits for Air Monitoring Network volatile organic compound (VOC) samples, by laboratory.

Chemical	MDL (CARB-OLS) (ppb)	MDL (CARB-OLS) (ng/m^3)	MDL (CDFA CAC) (ppb)	MDL (CDFA CAC) (ng/m^3)
1,3-dichloropropene	0.1	454	0.01	45.4
Methyl bromide	0.1	396	0.01	39.6

Air Concentration Calculations

For the sorbent tube and cartridge samples, air concentrations are 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:

$$\frac{Sample\ results\ (ug) x\ 1000\ L/m^3}{Flow\ rate\ \left(\frac{L}{\min}\right) x\ run\ time\ (\min)} \text{ x } 1000\ ng/\mu g = ng/m^3$$

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

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

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 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)).

Data Validation/Quality Assurance

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 standard deviation were determined based on these 25 data points. The control limits were established as the mean percent recovery ± 3 SDs. In addition, 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 CAC laboratory or the California Air Resources Board – Organic Laboratory Section (CARB-OLS) 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 1 to 20 actual samples and 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.

Quality Control Results

Laboratory matrix spikes and matrix blanks were included with every set of samples extracted and analyzed at the CDFA CAC 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 media packed in the sorption tubes or cartridges. The blank matrix materials were not fortified, but were extracted and analyzed along with the matrix spikes and field samples. Table 6 lists the average for the QC samples that were extracted and analyzed with the air samples for the entire monitoring period. Average laboratory matrix spike recoveries ranged from 81% to 99% for all chemicals analyzed.

Field blanks, blind field spikes, and duplicate samples are part of DPR's field and laboratory QC program. The field spikes were fortified by a CDFA chemist not associated with the analysis. The field spikes were given to DPR staff, relabeled, and then intermingled and delivered with field samples to the laboratory for analysis. Table 6 lists the average percent recovery results which ranged from 72% to 138%.

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

The trip blanks were blank matrix samples that were transported to and from the field locations, but were not placed on air pumps. These samples were a control to check for contamination during transportation. All field blanks resulted in non-detections. These results are shown in Table 6.

Table 7 summarizes the results of duplicate samples. A duplicate sample is a sample that is collocated with another sample in the field. These samples serve to evaluate the overall precision in sample measurement and analysis. Consistent with previous reports, there were a large number of non-detection pairs among co-located samples. For sample pairs in which both samples produced a quantifiable detection these concentrations were compared to find the relative difference, expressed as a percentage. This was possible for a total of eight sample pairs, and range from 3% to 16%.

Table 6. Average results for quality control/quality assurance samples from the 2018 AMN.

Chemical	Lab spikes (% recovery)	Field spikes (% recovery)	Lab blanks (ng/m^3)	Field blanks (ng/m^3)
1,3-dichloropropene	99%	94%	ND	None Taken
Acephate	91%	87%	ND	ND
Bensulide	84%	91%	ND	ND
Chloropicrin	94%	99%	ND	ND
Chlorothalonil	94%	73%	ND	ND
Chlorpyrifos	95%	77%	ND	ND
Chlorpyrifos OA	88%	None Taken	ND	ND
Chlorthal-dimethyl	91%	107%	ND	ND
Cypermethrin	95%	76%	ND	ND
DDVP	91%	98%	ND	ND
DEF	81%	75%	ND	ND
Diazinon	88%	92%	ND	ND
Diazinon OA	94%	98%	ND	ND
Dimethoate	94%	84%	ND	ND
Dimethoate OA	94%	95%	ND	ND
Diuron	92%	108%	ND	ND
Endosulfan	94%	87%	ND	ND
Endosulfan Sulfate	96%	80%	ND	ND
EPTC	88%	83%	ND	ND
Iprodione	97%	91%	ND	ND
Malathion	97%	72%	ND	ND
Malathion OA	91%	138%	ND	ND
Methidathion	89%	97%	ND	ND
Methyl bromide	99%	94%	ND	None Taken
Metolachlor	87%	92%	ND	ND
MITC	88%	78%	ND	ND
Norflurazon	94%	94%	ND	ND
Oryzalin	91%	None Taken	ND	ND
Oxydemeton methyl	93%	123%	ND	ND

Oxyfluorfen	99%	None Taken	ND	ND
Permethrin	95%	93%	ND	ND
Phosmet	86%	None Taken	ND	ND
pp-Dicofol	98%	100%	ND	ND
Propargite	97%	103%	ND	ND
Simazine	94%	92%	ND	ND
Trifluralin	96%	97%	ND	ND

Table 7. Results for duplicate (collocated) sample pairs in 2018.

Primary/duplicate paired results category	Chloropicrin	MITC	Multi-residue	VOC
ND †/ND	11	3	336	28
Trace ‡/Trace	1	3	12	N/A
ND/Trace	0	0	2	N/A
ND/ > LOQ	0	0	0	0
Trace/ > LOQ	0	0	1	N/A
> LOQ/ > LOQ	0	5	1	2
Relative Difference *	N/A	3%	16%	12%

† ND = Not Detected.
‡ Trace = Pesticide detection confirmed, but less than the quantitation limit.
* For pairs with both concentrations >LOQ.

Lost and Invalid Samples

As previously stated on page 8 of the report, four samples were lost or invalidated during the year of sampling. Table 8 lists the location, date, and type of samples.

Table 8. Lost or invalid samples in 2018.

Location	Date	Type
Ohlone	6/12/2018	VOC
Chualar	8/14/2018	VOC
Santa Maria	9/5/2018	Multi-pesticide Residue
Lindsay	11/25/2018	VOC