TOXIC AIR CONTAMINANT PROGRAM MONITORING RESULTS FOR METHYL BROMIDE AND 1,3-DICHLOROPROPENE 2011-2018

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INTRODUCTION

In September 2010, as part of the California Department of Pesticide Regulation's (DPR) Toxic Air Contaminant (TAC) Program, DPR submitted a request to the California Air Resources Board (ARB) for monitoring to be conducted pursuant to Food and Agricultural Code section 14022(c) for methyl bromide (MeBr) and 1,3-dichloropropene (1,3-D) pesticides in Oxnard[1], Santa Maria, and Watsonville. As of 2018, the only monitoring location remaining in the TAC program was Oxnard as the sampling sites in Santa Maria and Watsonville were transitioned into DPR's Air Monitoring Network (AMN) in 2017. Monitoring at the Oxnard monitoring location began in October 2011 and remained in operation as a TAC site until August 14, 2018 when it was also transitioned into DPR's AMN, which monitors for a greater number of pesticides and pesticide breakdown products than those included in the TAC monitoring.

This report includes results for 1,3-D and MeBr monitoring from Oxnard for the 2010-2018 calendar years.

MATERIALS AND METHODS

Air Sampling Equipment

Air samples were collected using a Tisch Environmental® 3–Channel Canister Sampler (TE-323). The sampler was automated to collect a 24-h air sample into a SilcoCan® 6-liter (6-L) canister (Restek cat. # 24142) pre-evacuated to a pressure of -30"Hg. Air sample collection occurred once per week. Sample collection would automatically commence at 00:00 (midnight) and would automatically be terminated at 23:59 of the sampling day. Bios Defender 530® or DC-Lite® flow meters were used to check the flow rate at the start of the sampling period.

A total of 450 valid air canister samples from October 10, 2010 to August 14, 2018 were collected for Oxnard. Canister air samples were analyzed for 1,3-D and MeBr. Canister samples were transported by vehicle to the ARB Organics Laboratory Section (OLS) laboratory in Sacramento for analysis.

Analytical Methods

Air canisters were analyzed for MeBr and 1,3-D using the method described in ARB (2000). This gas chromatographic method utilizes an automated sample concentrator, capillary gas chromatography, and ion trap mass spectrometry. ARB's OLS laboratory reports measured air concentrations in relation to an established analytical reporting limit (RL), which is the lowest concentration of a pesticide (analyte) that a chemical method can reliably detect. The laboratory determined the RL for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. Table 1 lists the analytical limits for each analyte.

[1] Sampling site was moved from Camarillo to Oxnard on October 24, 2011.

Table 1. Analytical limits for each analyte.

Pesticide	Reporting Limit (RL)
1,3-D	0.10 ppb
MeBr	0.03 ppb

Health Evaluation Methods

No state or federal agency has established regulatory human health standards for pesticides in ambient air (some agencies have developed occupational standards, or site-specific standards). Therefore, DPR, in consultation with the California Office of Environmental Health Hazard Assessment and others established health screening levels or regulatory targets to place the results in a health-based context.

These 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 that is below the screening level for a given pesticide would generally not be considered to represent a significant health concern and would not generally undergo further evaluation. A measured concentration that is above the screening level would not necessarily indicate a significant health concern but would indicate the need for a further and more refined evaluation. Health screening levels vary by pesticide and exposure period. For example, the screening level for a 24-h exposure is different than the screening level for a 1-year exposure.

DPR normally establishes a regulatory target after completing a comprehensive risk assessment of a chemical's toxicity and potential exposures. DPR management determines a regulatory target based on its risk assessment, as well as risk assessments from other agencies, pesticide use patterns, potential effects on use of alternative pesticides, and other factors. Regulatory targets 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. Regulatory targets vary by pesticide and exposure period. For example, the regulatory target for a 24-h exposure is different than the regulatory target for a 1-year exposure. Table 2 lists the monitoring period, screening level, regulatory target and potential health effects for 1,3-D, while Table 3 presents these values for MeBr.

Table 2. Screening levels and regulatory targets for 1,3-dichloropropene.

Monitoring period	Screening level (ppb)	Regulatory target (ppb)	Potential health effect
1 day	110	-	Body weight change
90 days	3	-	Tissue damage in nose and lung
1 year	2	-	Tissue damage in nose and lung
Lifetime (70-yr avg)	-	0.56	Cancer

Table 3. Screening levels and regulatory targets for methyl bromide.

Monitoring period	Screening level (ppb)	Regulatory target (ppb)	Potential health effect

1 day	-	210	Brain/nerve damage
4 weeks	-	5	Brain/nerve damage
1 year	1	-	Nose tissue damage

RESULTS

Counts and comparison of detections

A total of 450 valid air canister samples were collected from Oxnard during the 2011-2018 calendar years. Each air canister sample was then analyzed for MeBr and 1,3-D. A total of 900 analyses were performed for Oxnard during the 2011-2018 calendar years. Of the 900 analyses, 786 (87%) contained no detectable amount, while 114 (13%) contained concentrations above the RL. Detections of 1,3-D have hovered around roughly 10% of the total possible detections. Detections of MeBr have dropped to zero in 2017 and 2018. These results are detailed in Table 4 for 1,3-D, and in Table 5 for MeBr.

Table 4. Number and percentage of positive samples for 1,3-dichloropropene by year.

Year	Number of collected samples	Total number of detections	Percent of possible detections
2011	15	0	0%
2012	71	7	9.9%
2013	70	11	15.7%
2014	69	4	5.8%
2015	62	4	6.5%
2016	59	4	6.8%
2017	56	5	8.9%
2018	48	3	6.3%
Total	450	38	8.4%

Table 5. Number and percentage of positive samples for methyl bromide by year.

Year	Number of collected samples	Total number of detections	Percent of possible detections
2011	15	6	40.0%
2012	71	19	26.8%
2013	70	10	14.3%
2014	69	20	29.0%
2015	62	13	21.0%
2016	59	8	13.6%
2017	56	0	0%
2018	48	0	0%
Total	450	76	16.9%

Acute Concentrations

The acute concentrations for 1,3-D and MeBr did not exceed their respective screening level or regulatory target in 2018 or in any previous year of TAC monitoring at Oxnard. The highest observed 24-

hour concentration for 1,3-D was 8.7 ppb and occurred 2015, while a MeBr concentration of 8.7 ppb was the maximum observed 24-hour concentration for that chemical and was observed in 2014. These values are detailed by year for 1,3-D in Table 6 and MeBr in Table 7.

Table 6. Highest 24-h air concentrations, acute screening level, and percent of acute screening level for 1,3-dichloropropene by year.

Year	Highest 24-hr Concentration (ppb)	Screening Level (ppb)	Percent of Screening Level
2011	ND	110	-
2012	6.4	110	5.8%
2013	3.0	110	2.7%
2014	2.2	110	2.0%
2015	8.7	110	7.9%
2016	2.9	110	2.6%
2017	1.2	110	1.1%
2018	0.4	110	0.3%
2011-2018	8.7	110	7.9%

Table 7. Highest 24-h air concentrations, acute regulatory target, and percent of acute regulatory target for methyl bromide by year.

Year	Highest 24-hr Concentration (ppb)	Regulatory Target (ppb)	Percent of Regulatory Target
2011	0.5	210	0.2%
2012	3.4	210	1.6%
2013	0.2	210	0.1%
2014	8.7	210	4.1%
2015	0.5	210	0.2%
2016	0.6	210	0.3%
2017	ND*	210	-
2018	ND	210	-
2011-2018	8.7	210	4.1%

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

Subchronic Concentrations

Table 8 shows the highest 90-day rolling average concentrations for 1,3-D at Oxnard by year while Table 9 shows the highest 28-day rolling average concentration for MeBr observed at Oxnard by year. The rolling average concentrations are calculated using a value of one-half of the MDL for all non-detections falling within the given time interval. The highest 90-day rolling average 1,3-D concentration (0.7 ppb) was observed in 2015. No 90-day rolling average concentration exceeded the subchronic screening level for that chemical. The highest 28-day rolling average concentration of MeBr (2.0 ppb) was observed in 2014. No subchronic concentration of MeBr was found to exceed its subchronic regulatory target. Due the longer interval used in averaging the subchronic concentration of 1,3-D versus that of MeBr, and the start date of sampling in Oxnard falling in late October, a subchronic concentration cannot be calculated for the 2011 calendar year for 1,3-D. Figure 1 presents the 24-h and 90-day rolling average concentrations of 1,3-D for 2011-2018 at Oxnard, while Figure 2 presents 2011-2018 time series of both 24-h and 28-day MeBr concentrations.

Table 8. Highest 90-day rolling average air concentrations, subchronic screening level, and percent of subchronic screening level for 1,3-dichloropropene by year.

Year	Highest rolling 90-day average concentration (ppb)	Subchronic screening level (ppb)	Percent of subchronic screening level
2012	0.62	3.0	20.5%
2013	0.54	3.0	17.9%
2014	0.19	3.0	6.3%
2015	0.71	3.0	23.7%
2016	0.27	3.0	8.9%
2017	0.18	3.0	6.0%
2018	0.07	3.0	2.4%
2012-2018	0.71	3.0	23.7%

Table 9. Highest 28-day rolling average air concentrations, subchronic regulatory target, and percent of subchronic regulatory target for methyl bromide by year.

Year	Highest rolling 28-day average concentration (ppb)	Subchronic regulatory target (ppb)	Percent of subchronic regulatory target
2011	0.15	3	5.0%
2012	0.90	3	30.0%
2013	0.05	3	1.7%
2014	1.97	3	65.7%
2015	0.27	3	9.0%
2016	0.18	3	6.0%
2017	ND	3	-
2018	ND	3	-
2011-2018	1.97	3	65.7%

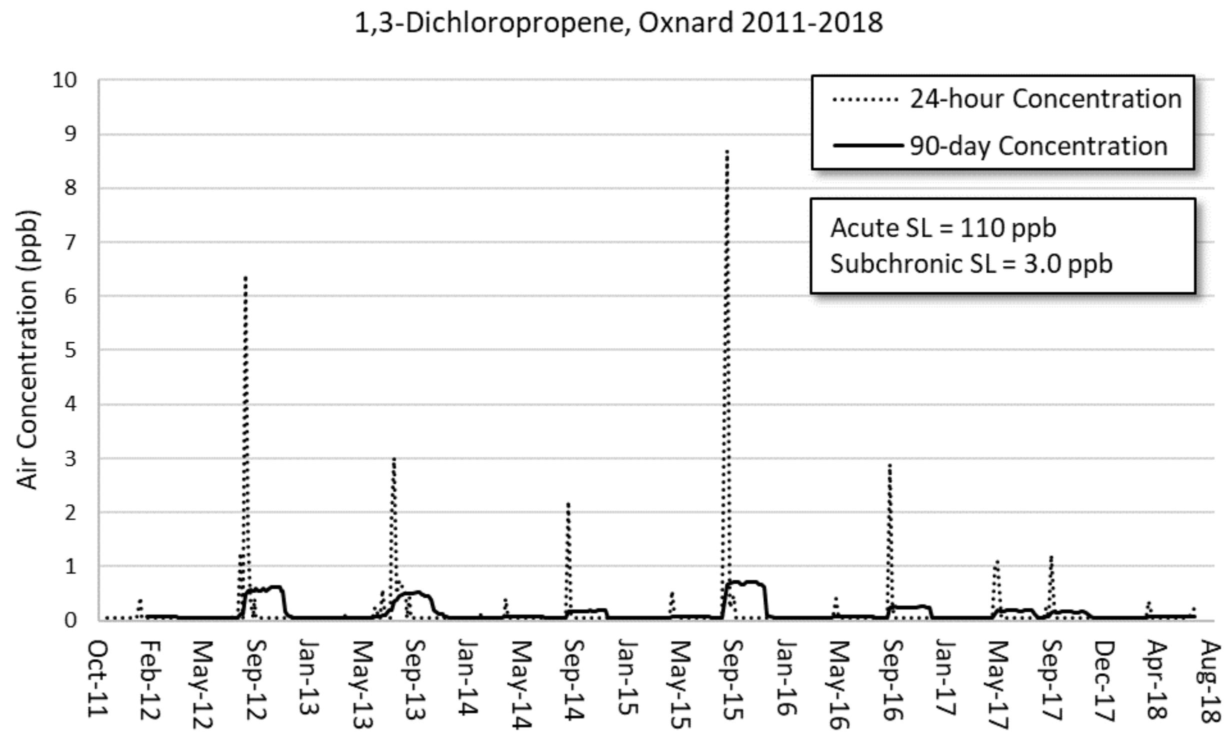

Figure 1. 24-hour and 90-day rolling average concentrations of 1,3-dichloropropene in Oxnard, 2011-2018.

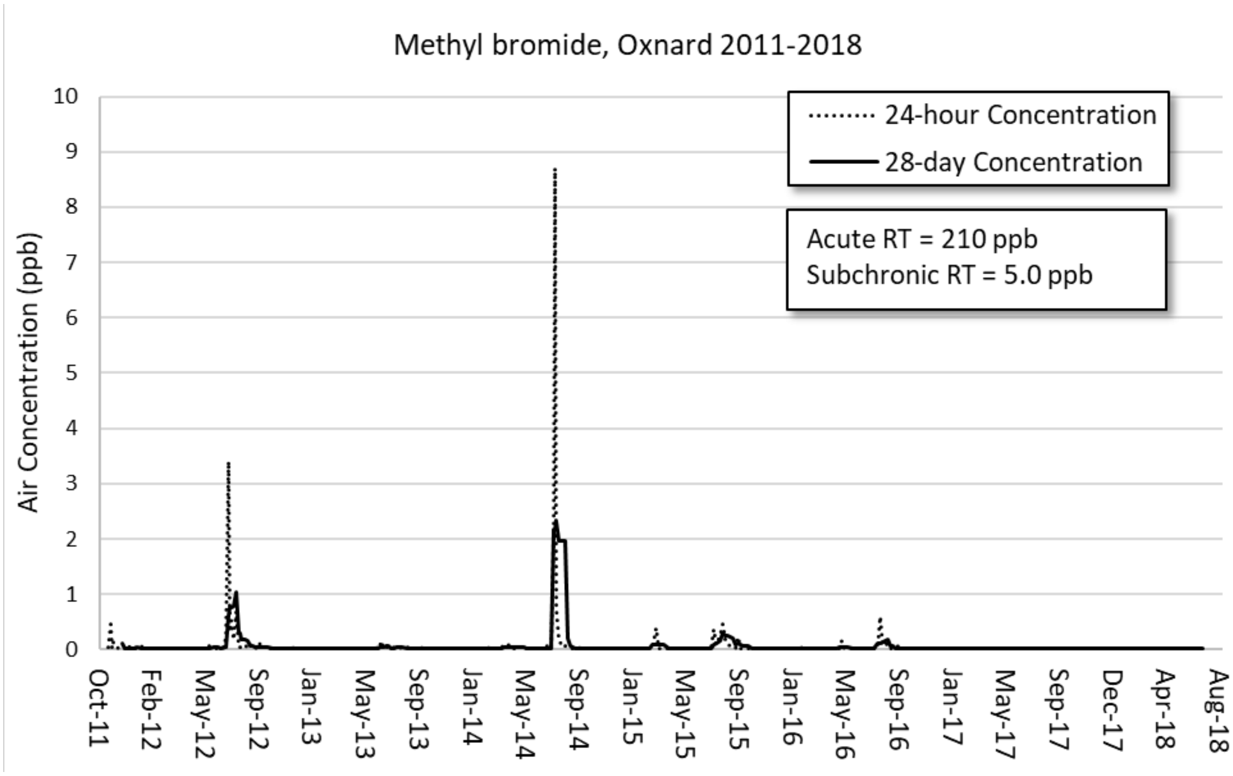

Figure 2. 24-hour and 28-day rolling average concentrations of methyl bromide in Oxnard 2011-2018.

Chronic Concentrations

The annual average concentrations for 1,3-D are detailed by year in Table 10, while Table 11 presents this data for methyl bromide. The years 2011 and 2018 are not included in this section since monitoring at this site did not include a full 12 months. The year showing the highest concentration of 1,3-dichloropropene was 2015, while the year with the highest concentration of methyl bromide was 2014.

Table 10. Annual average air concentrations, chronic screening level, and percent of chronic screening level for 1,3-dichloropropene by year.

Year	1-year average concentration (ppb)	Screening Level (ppb)	Percent of Screening Level
2011	--	2.0	--
2012	0.19	2.0	9.6%
2013	0.17	2.0	8.4%
2014	0.09	2.0	4.4%
2015	0.21	2.0	10.4%
2016	0.11	2.0	5.5%
2017	0.11	2.0	5.5%
2018	--	2.0	--
2012-2017	0.15	2.0	7.5%

Table 11. Annual average air concentrations, chronic screening level, and percent of chronic screening level for methyl bromide by year.

Year	1-year average concentration (ppb)	Screening Level (ppb)	Percent of Screening Level
2011	--	1.0	--
2012	0.10	1.0	9.8%
2013	0.02	1.0	2.1%
2014	0.19	1.0	19.4%
2015	0.05	1.0	4.9%
2016	0.03	1.0	3.4%
2017	ND	1.0	--
2018	ND	1.0	--
2012-2017	0.08	1.0	8.0%

Cancer Risk Estimates

1,3-D is classified as a human carcinogen by both the United States Environmental Protection Agency and Proposition 65. Cancer risk is typically expressed as the estimated probability of developing cancer over a 70-year lifetime (e.g., 1 in 100,000 or 1 in 1,000,000, also expressed as 1×10^{-5} or 1×10^{-6}, respectively).

DPR set a regulatory cancer risk goal for 1,3-D of 1 in 100,000 (1×10^{-5}) in the 2016 Risk Management Directive (DPR 2016). Cancer risk can be estimated using air monitoring results and evaluated against the cancer risk goal using the following equation:

$$\text{Cancer Risk} = CPF_H * LAC * nBR$$

Where:

Risk = probability of an additional case of cancer over a 70-year period.

CPF_H = estimated cancer potency factor in humans $(mg/kg/day)^{-1}$.

LAC = mean lifetime (70-year) air concentration (mg m^{-3}).

nBR = normalized breathing rate of a human adult (m^3 kg^{-1} day^{-1}).

The DPR-estimated value of CPF_H based on a portal-of-entry effect, is 0.014 $(mg/kg/day)^{-1}$ (DPR 2015).

DPR assumes nBR to be 0.28 m^3 kg^{-1} day^{-1} (DPR 2015). For this study and based on the available monitoring data, LAC is taken as the mean annual concentration of total 1,3-D at a monitoring location for all available years, with non-detection samples assigned a value of one-half of the RL. Alternatively, the cancer risk can be expressed relative to DPR's regulatory target of 0.56 ppb (CPF_H * nBR, and converting units). Table 12 shows the estimated cancer risk from 1,3-D exposures for Oxnard based on 2011-2018 monitoring data.

Table 12. 1,3-dichloropropene cancer risk estimate comparisons for Oxnard 2011-2018.

2011-2018 Average Concentration (TWA) (ppb) *	Lifetime (70-year) Regulatory Target (ppb)	Average Cancer Risk Estimate
0.19	0.56	2.5×10^{-6}

* This value is a time-weighted average (TWA), rather than the mean concentration used to calculate the annual averages in the previous section of this report.

Quality Control Samples

Quality control samples collected in the field included both collocated ("field duplicate") samples and field spike samples. Percent recoveries for field spikes of the *cis*- isomer of 1,3-D ranged from 95.1% to 111.9%, while percent recoveries of the *trans*- isomer of 1,3-D ranged from 96.6% to 116.8%. The percent recovery for field spikes of MeBr ranged from 91.7% to 107.4%. The results for all of these field spikes is presented in Table 13.

Table 13. Percent recoveries for field spike QC samples.

Sample Start Date	*cis*-1,3-D (% recovery)	*trans*-1,3-D (% recovery)	MeBr (% recovery)
1/20/18	No Matching Primary Sample	No Matching Primary Sample	No Matching Primary Sample
2/19/18	100.2%	105.4%	91.7%
3/21/18	95.1%	100.0%	92.0%
4/20/18	96.6%	96.6%	98.3%
5/20/18	111.9%	116.8%	103.7%
6/19/18	108.8%	114.7%	105.0%
7/19/18	106.2%	112.6%	107.4%

Collocated samples collected at Oxnard in 2018 resulted in paired non-detections which allow for a qualitative confirmation of results obtained from primary samples, but do not allow for any quantitative comparison. One collocated sample produced a quantifiable detection which was within 8.3% of the primary sample for *cis*-1,3-D, and within 15.4% of the primary sample for *trans*-1,3-D. MeBr was not detected in any primary or collocated samples during TAC operation in Oxnard in 2018. The results of the collocated samples are detailed in Table 14.

Table 14. Comparison of results of primary samples to collocated QC samples.

Sample Start Date	Primary Result (*cis*-1,3-D) (ppb)	QC Result (*cis*-1,3-D) (ppb)	Primary Result (*trans*-1,3-D) (ppb)	QC Result (*trans*-1,3-D) (ppb)	Primary Result (MeBr) (ppb)	QC Result (MeBr) (ppb)
2/6/18	ND	ND	ND	ND	ND	ND
2/13/18	ND	ND	ND	ND	ND	ND
3/3/18	ND	ND	ND	ND	ND	ND
4/8/18	0.23	0.25	0.12	0.14	ND	ND
5/8/18	ND	ND	ND	ND	ND	ND
6/7/18	ND	ND	ND	ND	ND	ND
7/7/18	ND	ND	ND	ND	ND	ND

Invalid Samples

Of the 50 air canister samples collected at Oxnard during 2018, two primary samples were invalid. Invalidated samples are due to one of the following reasons: an ending pressure outside the accepted criteria; power failure during sample extraction; sampler malfunction; or sample leakage during transit. The invalid air samples were not replaced. Both invalid samples in 2018 were due to arrival at the laboratory at zero pressure.

DISCUSSION

No detected concentrations exceeded their respective screening levels or regulatory targets for the duration of TAC monitoring at Oxnard. This is consistent across acute (24-h), subchronic (28- or 90-day), and chronic exposure timeframes. In general the observed concentrations of 1,3-D have been decreasing over the years covered by TAC monitoring. MeBr has not been detected at Oxnard following the discontinuation of most uses of MeBr on December 31, 2016.

REFERENCES

CARB (2000). Standard Operating Procedure for the Determination of Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry. California Air Resources Board. Northern Laboratory Branch. Monitoring and Laboratory Division. Available at: https://www.arb.ca.gov/aaqm/sop/mld058.pdf