Pesticide Drift Monitoring in Minnesota 2012-2014

Technical Report

PAN

PESTICIDE ACTION NETWORK • NORTH AMERICA

Pesticide Action Network North America
March 2021

Pesticide Action Network North America (PAN) works to replace hazardous pesticide use with ecologically sound and socially just alternatives. For over 30 years, our international network of over 600 citizens groups in more than 90 countries has created a global pesticide reform movement with regional coordinating centers in Africa, Asia, Europe, Latin America and North America. PAN North America links the collective strengths and expertise of groups in Canada, Mexico and the U.S. with their counterparts in other countries to further sustainable agriculture, environmental protection, workers' rights, improved food security, and guaranteed human rights for all.

PAN also maintains the world's most comprehensive set of databases on pesticides available on the web. For information on pesticide toxicity, registration status, poisoning symptoms and many other factors, see www.pesticideinfo.org. For information about pesticide residues on food, see www.whatsonmyfood.org.

Support for air monitoring in Minnesota was generously provided by the Ceres Foundation and others.

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List of Abbreviations

DPR Department of Pesticide Regulation, California
EC European Commission
EPA Environmental Protection Agency
EU European Union
HHRA Human Health Risk Assessment
MIC Methyl Isocyanate
MITC Methyl Isothiocyanate
MOE Margin of Exposure
MRL Maximum Residue Level
NOAEL No Observable Adverse Effect Level
NOEL No Observable Effect Level
PAN Pesticide Action Network
REL Reference Exposure Level
US United States
USDA United States Department of Agriculture

Executive Summary

Pesticide Action Network (PAN) conducts air monitoring with community partners at sites where agricultural pesticides are used in order to monitor for pesticide drift.

This report is on air monitoring done with PAN's community air monitoring tool, the Drift Catcher, in Minnesota from 2012-2015 at four sites. All of the sites were located by residences, with three sites monitored near a single metam sodium application and the fourth site monitoring a chlorpyrifos application. The results indicate that community members at these sites were likely exposed to pesticide drift from metam sodium or chlorpyrifos applications, at concentrations exceeding levels of concern for certain health screening levels. Because there is no legal standard for concentrations of pesticide in the air, and thus screening levels are the primary agency-derived standard for indicating potential effects on human health.

A 2013 monitoring site in Melrose was located 25 feet away from an alfalfa field where chlorpyrifos was applied. Five of the six samples taken were positive for chlorpyrifos. The levels of chlorpyrifos found at Melrose result in risk estimates exceeding levels of concern for residential bystander children (1 to <2 years old) and adults, according to the U.S. EPA's 2016 revised human health risk assessment. A family, including a woman and her one-year old child, lived in a house at the Melrose site during the time of the application.

Two other sites were monitored in October 2015, near a field where metam sodium was applied. Metam sodium is used in fall for pre-plant fumigation of potato fields before spring planting. The residue of concern for metam sodium is the breakdown product methyl isothiocyanate (MITC), which is formed when the fumigant pesticide metam sodium is hydrolyzed in moist soil. At one site (Sazama/Enslin), samples were taken at a residence within approximately 500 and 732 feet of the fumigated field. All five samples taken at the Sazama/Enslin were positive for MITC. The other site, Perham, was approximately 1.25 miles away from the nearest known potato field application of metam sodium. Two of the eight samples analyzed from the Perham site were positive for MITC, suggesting the possibility that MITC may have drifted for over a mile.

For four out of five days of sampling at Sazama/Enslin, the levels of MITC at the sampling sites exceeded chronic and subchronic screening levels (at which the potential for health effects could be expected over a longer period of time (see discussion) as determined by California Department of Pesticide Regulation (DPR), as well as one day where the DPR's 24-hour acute exposure screening level was exceeded, indicating that exposure at these levels are potentially of concern to residents living near sites where metam sodium is used. The DPR screening levels were used for analysis since the Minnesota state agencies do not have comparable information on pesticide concentrations in the air.

Introduction

In this report, we document the results of air monitoring work at a site at Melrose, in central Minnesota, where the insecticide chlorpyrifos was detected, and two sites in northern Minnesota where methyl isothiocyanate (MITC) was detected. PAN conducts air monitoring for pesticides with community partners, usually at residences in close proximity to sites where agricultural pesticides are used. Air monitoring results from several other monitoring projects with negative data are reported in Appendix 4.

Chlorpyrifos

Chlorpyrifos is the most widely used insecticide in Minnesota, with over a million pounds used in 2017.[1] One of the top crops where chlorpyrifos is used in Minnesota is soybeans, with 484,000 pounds used on soybeans in 2018.[2] The organophosphate insecticide chlorpyrifos is known to have neurotoxic effects. A 2016 revised human health risk assessment (HHRA) by U.S. EPA found unacceptable risks for dietary chlorpyrifos exposure of children and pregnant women, based on epidemiological data from a cohort study conducted at the Columbia University Center for Children's Environmental Health.[3] Based on the revised HHRA, EPA scientists recommended a ban on agricultural uses of chlorpyrifos, which was

[1] http://www.startribune.com/court-epa-violated-law-on-harmful-pesticide-orders-ban/490477821/

[2] USDA Quickstats. https://www.nass.usda.gov/Surveys/Guide_to_NASS_Surveys/Chemical_Use/

[3] U.S. EPA. "Chlorpyrifos: Revised Human Health Risk Assessment for Registration Review." Washington, D.C., September 21, 2020.

subsequently denied by then EPA Administrator Scott Pruitt.[4] A third revised HHRA of chlorpyrifos was published in September 2020, with changes such as reduction of adjustment factors that were recommended in the 2016 HHRA.[5] This report uses the information from the 2016 HHRA, which used a more sensitive endpoint than the 2020 revision.

Metam sodium and methyl isothiocyanate

Minnesota is one of the top eight potato producing states in the U.S.[6] USDA data from 2019 reported 44,000 harvested acres of fall potatoes with a value of $185,812,000 in Minnesota.[7] Potatoes are primarily grown in northern Minnesota and the fumigant pesticide metam sodium is applied via several methods, primarily to manage nematodes, late blight, and *Verticillium dahliae*.[8] Chemigation, soil injection (shanked-in), sprinkler, flood and furrow, and drip irrigation (with tarp and watering-in variations) can all be used in pre-plant applications of metam sodium. These typically take place in the late fall, prior to the ground freezing for the winter.[8] In Minnesota, fumigation of fields to be planted with potatoes takes place before the ground freezes, generally in October. Metam sodium or metam potassium are used for fumigating potato fields and both active ingredients convert to MITC in the soil.

The U.S. Department of Agriculture (USDA) collects statistics on pesticide use on major crops in each state. In Minnesota, 2016 USDA data indicated that metam sodium is used for fall potatoes. The amount used is not reported publicly however, in order to avoid disclosing use data for individual operations.[9] USDA data from 2019 reported 46,000 acres of potatoes planted in Minnesota.[7] The application rate for metam sodium on potatoes varies, with one study reporting a rate of 663 liters per hectare within a 0.7 hectare test plot (the total applied active ingredient was 226 kilograms).[10]

MITC is very irritating to the ocular and respiratory tissues. A 1991 railway accident and spill of metam sodium into the Sacramento River in California provided real world information on effects experienced by residents near the spill.[11]

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[4] Environmental Protection Agency. "Chlorpyrifos; Order Denying PANNA and NRDC's Petition to Revoke Tolerances. EPA-HQ-OPP-2007-1005; FRL-9960-77," April 5, 2017.

[5] U.S. EPA. "Chlorpyrifos: Third Revised Human Health Risk Assessment for Registration Review." Washington, D.C., November 3, 2016.

[6] https://www.nass.usda.gov/Quick_Stats/Ag_Overview/stateOverview.php?state=MINNESOTA

[7] USDA National Agricultural Statistics Service, Minnesota Field Office. Available at https://www.nass.usda.gov/Statistics_by_State/Minnesota/index.php. Accessed June 15, 2020.

[8] Professor Carl Rosen, University of Minnesota. Personal communication, September 9, 2015.

[9] USDA QuickStats. Available at https://quickstats.nass.usda.gov/. Accessed June 15, 2020.

[10] Littke, Matt H, et al. "Comparison of Field Methyl Isothiocyanate Flux Following Pacific Northwest Surface-Applied and Ground-Incorporated Fumigation Practices: Comparison of Field Methyl Isothiocyanate Flux Following Different Fumigation Practices." *Pest Management Science* 69, no. 5 (May 2013): 620–26. https://doi.org/10.1002/ps.3414.

[11] Cone JE, Wugofski L, Balmes JR, et al. Persistent Respiratory Health Effects After a Metam Sodium Pesticide Spill. *Chest*. 1994;106(2):500-508. doi:10.1378/chest.106.2.500

Sampling site descriptions and other information

Melrose
Air monitoring at the Melrose site was conducted in 2013. The Melrose site consisted of a residence on a 1.7-acre lot with cornfields to the north and southwest, wooded pasture and a road directly west of the lot, and an alfalfa field (approximately 38 acres) to the east. The cornfields adjacent to the Melrose site were sprayed with unknown substances close to the time that air monitoring was done. The field owner gave notice to the residents regarding the alfalfa field application as a courtesy, due to a previous 2012 chlorpyrifos poisoning incident at that residence.

In 2012, a chlorpyrifos application at the same site, also to alfalfa, drifted into the home through an air conditioner unit in the window, severely poisoning a female resident who at the time was indoors, and resulting in a near-cardiac arrest. [12] Samples taken from the clothing she was wearing at the time and wipes of surfaces in the room indicated chlorpyrifos exposure, especially on her clothing. The resident's child was in the next room but did not display any symptoms at the time of the drift incident. The 2013 chlorpyrifos application to the alfalfa field was done on the morning of July 2nd, and air sampling was initiated the day before, on July 1, 2013.

Perham
The Perham monitoring, conducted in October 2015, was at a residence about one mile away from a corn field that was sprayed with an unknown pesticide. The potato field to be fumigated was about 1.25 miles away from the residence, and was fumigated on October 16th. The Enslin and Sazama monitoring was done for a field fumigated on the same date, but it is highly likely that these were different fields given the distance between the sites.

The Perham site was drifted on by other agricultural chemicals at least three times in subsequent years, in 2011, 2017 and again in 2018, with the Minnesota Department of Agriculture confirming the 2011 drift incident with analysis of vegetation at the site, finding difenoconazole and mandipropamid; while the 2017 drift incident with analysis of plant samples that found the fungicides chlorothalonil and cyazofamid.[13]

Enslin and Sazama
These sites were located by the same field, but at two residences located at adjacent sides of the fumigated potato field. Enslin was 732 feet north and Sazama was 500 feet southwest of the nearest field-edge of the same potato field,

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[12] "Environmentalists sue EPA for reversing Obama-era move to ban pesticide." *The Guardian*, April 5, 2017. Accessed December 18, 2018 at https://www.theguardian.com/environment/2017/apr/05/environmentalists-sue-epa-pesticide-chlorpyrifos

[13] Community partner, personal communication (May 12, 2018) and shared copy of results from Minnesota Department of Agriculture Laboratory Analysis Report, (December 29, 2017).

respectively. A trailer court buffered by trees on its western side was located to the east of the fumigated field. Sazama was located between a residence and outbuildings located on the west side of the field. The application of metam sodium (VAPAM HL, Amvac) was done via chemigation on October 16, 2015 at 12 PM, and monitoring at Enslin/ Sazama took place from October 17 to October 21. According to a posted sign (Fig. 1a), field entry was restricted until October 18th.

Methods

The Drift Catcher™ air monitoring device was designed by PAN, based on the design of air sampling equipment used by the California Air Resources Board. This design has been evaluated by a Scientific Advisory Committee comprised of scientists from the California Department of Pesticide Regulation, the California Air Resources Board, US EPA Region 9, the U.S. Geological Survey, and the California Department of Health Services.

The Drift Catcher consists of a vacuum pump (McMaster-Carr No. 41675K41) connected with 3/8" Teflon tubing and compression fittings (Swagelok Northern California) to a manifold equipped with two Cajon-type, vacuum-tight Teflon fittings (International Polymer Solutions, Irvine, CA) as tube holders (Figure 2). Flow controller valves for each sample allowed for adjustment of airflow to each tube independently.

Based on photographs taken by community partners who were conducting the air monitoring, the application near Enslin/Sazama appeared to be a chemigation using a center-pivot spray rig (Fig. 1b).

Figure 1. Photographs from Sazama/Enslin Sampling Site.

(a) Sign posted at fumigated field.

(b) Center-pivot irrigation rig used for this application. Photographs courtesy of community partners.

Sample Collection

Samples were collected by drawing air through airtubes using a vacuum pump, at a rate of approximately 2 L/min. For MITC sampling, sample tubes were obtained from SKC Inc. (#226-09, coconut shell charcoal Anasorb CSC, 8 x 110 mm, 400/200 mg in front/rear beds, respectively), and were generally changed every 12 hours, at approximately 7 AM and 7 PM. This sampling method was based on that used by the California Air Resources Board (ARB) in its monitoring of MITC. The ARB employed the same sample tubes, utilized the same or similar flow rates (2.5 L/min), and collected each sample over a similar duration (12–24 hrs).[14]

For chlorpyrifos sampling, XAD-2 sample tubes from SKC Inc. (#226-30-05) were used. The ARB has monitored for chlopyrifos field applications using XAD-2 airtubes using a similar flow rate (3 L/min) and collected samples over a similar duration (approximately 24 hours for post-application samples).[15]

Pre-labeled sample tubes were attached to the manifold, which stood about 1.5 meters in height. Flow rates were measured with a 0.4–5 L capacity rotameter (SKC Inc., Cat. #320-4A5). The initial flow rate through each of the tubes was set to two liters per minute. The flow rate was set at the beginning of the sampling run and then measured at the end to check for any changes. If the difference between the start and stop flow rates was less than 25%, these two values were averaged together to calculate an average flow rate for the sampling period. If the ending flow rate differed by more than 25% from the starting flow rate, then the greater flow rate was used (e.g., the flow rate set when starting the sample), providing a conservative, or minimum value, estimate of the final pesticide concentration.

Sample tubes were covered with mylar light shields during the sampling period to prevent photolytically catalyzed degradation of the sample. Sample identification, start and stop times, and flow rates were recorded on a Sample Log Sheet (see Appendix 4). In addition, wind speed and direction, as well as temperature, weather conditions and any additional observations were noted at the beginning and end of each sampling period. At the end of each sampling period, labeled tubes were capped and placed in a zip-lock plastic bag with the completed log sheet.

Within 10 minutes of removal from the sampling manifold, samples were placed into either a -20°C freezer or into a cooler at 0°C for transfer to freezer storage. After storage, samples were shipped from the field to PAN at -10 to 0°C by overnight express mail for analysis. At PAN, data from sample log sheets were entered into a sample log notebook and the samples were stored in a -20°C freezer for 13 days or

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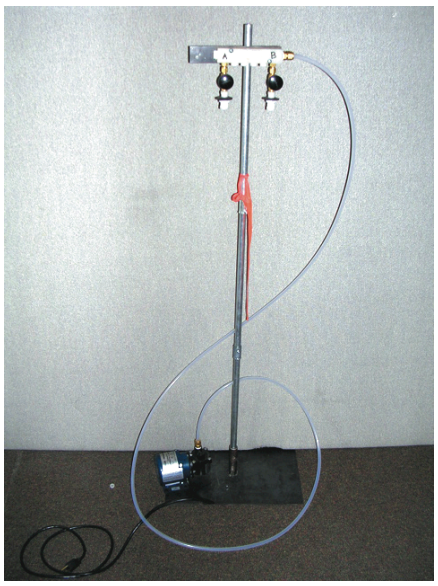
[14] California Air Resources Board. "Protocol for Air Monitoring Around a Drip Irrigation Application of Metam Sodium During Spring 2002." California Environmenta Protection Agency, April 23, 2002.

[15] California Environmental Protection Agency Air Resources Board. "Pesticide Application Site Monitoring for Chlorpyrifos and Chlorpyrifos-Oxon in Imperial County in October 2014." Sacramento, CA, November 21, 2016.

less, prior to being shipped by overnight express mail to a commercial laboratory (Environmental Micro Analysis Laboratories, Inc., Woodland, California) for analysis. A chain of custody form accompanied one of the two batches of samples during handling and transport. At the laboratory, samples were stored in a -20°C freezer prior to analyses, which were done within one month of receipt at the laboratory. Prior sample storage stability assessments have indicated that MITC is stable on charcoal for a period of about 2-3 months at -20°C.[16, ,17, 18] Chlorpyrifos is stable on XAD-2 resin in a freezer for at least 28 days.[15]

(a) 

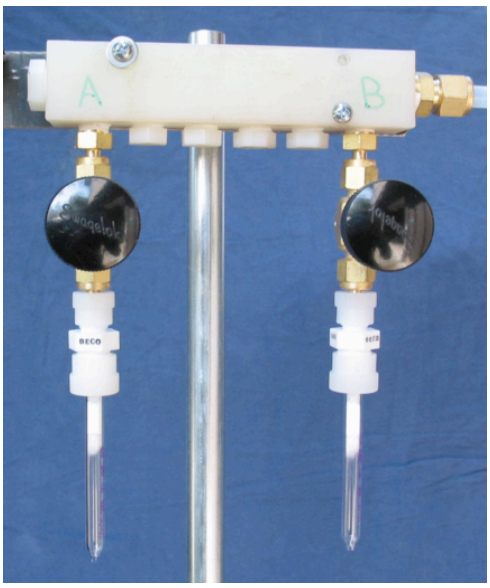
(b) 

Figure 2. (a) The Drift Catcher™ air monitoring device. (b) Close-up of manifold with flow control valves and sample tubes attached. The design is based on sampling equipment used by the California Air Resources Board. This design has been evaluated by a Scientific Advisory Committee comprised of scientists from the California Department of Pesticide Regulation, the California Air Resources Board, U.S. EPA Region 9, the US Geological Survey, and the California Department of Health Services.

Sample Analysis and Quality Assurance

Samples were analyzed by EMA Laboratory using EMA's CDFA multiresidue screen (including organophosphorous, organonitrogen, carbamate, and organochlorine

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16 Woodrow, James E., James N. Seiber, James S. LeNoir, and Robert I. Krieger. "Determination of Methyl Isothiocyanate in Air Downwind of Fields Treated with Metam-Sodium by Subsurface Drip Irrigation." *Journal of Agricultural and Food Chemistry* 56, no. 16 (August 2008): 7373–78. https://doi.org/10.1021/jf801145v.

17 California Air Resources Board. Final Report for the 2001 Ambient Air Monitoring for Chloropicrin and Metam Sodium Breakdown Products in Monterey and Santa Cruz Counties, California Air Resources Board, P-01-004, December 23, 2003. http://www.cdpr.ca.gov/docs/emon/pubs/tac/tacpdfs/chlor_metsod04.pdf.

18 California Air Resources Board. Final Report for the 2001 Ambient Air Monitoring for Chloropicrin and Metam Sodium Breakdown Products in Kern County, California Air Resources Board, P-01-004, November 13, 2003. http://www.cdpr.ca.gov/docs/emon/pubs/tac/tacpdfs/chlormitc03.pdf.

screens) for the Melrose, MN samples and a specific screen for metam sodium (MITC) for the Enslin/Sazama samples.[19]

Additional samples and the trip blank from the Melrose air monitoring were sent to another analytical laboratory, Analytical Pesticide Technology (APT) Laboratories (Reading, Pennsylvania) for confirmation of the positive chlorpyrifos results about a month later, with APT's results reported back within about 6 weeks of receiving the samples.

Samples from Melrose, MN
The reporting limit for chlorpyrifos from EMA Laboratory ranged from 0.02 to 0.05 μg, the latter value corresponds to an air concentration of 17 ng/m^3 for a 24 h sample assuming a flow rate of 2 L/min. The Melrose samples were taken in July 2013 but were not received at the PAN office until December 7, 2013. Samples were sent to EMA labs on December 10, 2013 and results were received about one week later.

Duplicate samples from Melrose, along with the trip blank, were sent to APT on January 9, 2014, with analyses done within two weeks of receipt. The duplicates were sent for confirmation of the positive chlorpyrifos results and to test the trip blank negative control. The APT duplicate samples were positive for chlorpyrifos and the trip blank result was nondetectable (<0.010 μg) (Table 2b). The APT results were used in order to confirm chlorpyrifos detections, and were not averaged with the EMA analyses due to the delay of about two months between receiving results from the different analytical laboratories.

Samples from Sazama/Enslin
The laboratory reporting limit for MITC was 0.50 μg/tube, which corresponds to an air concentration of 174 ng/m^3 for a 24 h sample assuming a flow rate of 2 L/min. The samples taken at Perham and Sazama-Enslin were analyzed for MITC only by EMA Laboratories. Sixteen samples were tested, with a subset of six samples tested for "breakthrough" to the rear resin bed of the airtube, in order to evaluate whether there had been breakthrough to the rear bed. Front and rear beds of the sample tubes were analyzed separately. None of the six samples had breakthrough to the rear bed and due to budget limitations at the time, no further testing of the rear beds was conducted in the remaining samples.

Samples from Frazee, MN
The reporting limit for chlorothalonil was 0.03 μg/tube, which corresponds to an air concentration of 10 ng/m^3 for a 24 h sample assuming a flow rate of 2 L/min. These samples are reported in Appendix 4.

Negative controls

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[19] Environmental Micro Analysis website, "Testing," accessed March 5, 2019. www.emalab.com/Testing.html

In addition to the field samples, one trip blank sample taken at each of the three sampling sites discussed in this report was sent to the lab for analysis. Trip blanks are a negative control; please see Appendix 5 (Quality Assurance – Quality Control) for a more detailed explanation of the trip blank. The laboratory was not informed regarding which samples were field samples and which were blanks. For the Sazama/Enslin air sampling, the trip blank was taken several days after the time of sampling (Table 3). Five samples from the Sazama/Enslin sampling run came back nondetectable, as did the two trip blanks and some of the back resin beds, indicating that the sample media were likely not contaminated prior to use.

Positive controls
Laboratory spikes were sent to both analytical labs for chlorpyrifos only in October 2014. No MITC laboratory spikes were created for analysis due to difficulty in obtaining an analytical standard of metam sodium.

The labs were not informed of which samples were laboratory spikes. Percent recovery for chlorpyrifos laboratory spikes are shown below. An analytical standard (100 ng/ml) was obtained for chlorpyrifos (Sigma-Aldrich, 31553-2ML) and applied to the front resin bed of XAD-2 airtubes. Laboratory spikes were prepared 1-2 days prior to shipping and were then immediately capped and stored at -20°C prior to shipping to the analytical laboratory.

Table 1. Percent Recovery for Chlorpyrifos Laboratory Spikes

Sample name	Analytical lab	Chlorpyrifos applied (µg/tube)	Amount detected (µg/tube)	Percent recovery
Candy-A	EMA	0.35	0.36	103
Candy-B	EMA	0.20	0.23	115
Pick-A	APT	0.35	0.0552	6.3
Pick-B	APT	0.20	ND <0.014	≤15*

*This estimated percent recovery was calculated assuming a detection of 13 µg, below the nondetection limit.

Weather Monitoring

Driftcatching participants took data on the log sheet (see Appendix 6) for wind speed and temperature.

Results

All of the trip blanks (negative controls) that were analyzed were nondetectable, as expected. See Appendix 4 for a summary of negative data as well as two samples found positive for chlorothalonil reported in Results, but not included in the Discussion section. These samples were part of a week-long sample run that yielded

two samples positive for chlorothalonil. Previous air sampling work at the same site in Minnesota had yielded many air samples positive for chlorothalonil.[20]

Melrose, MN

At the Melrose site, five of six samples taken had detectable levels of chlorpyrifos (Table 2). The risk estimates based on EPA's 2016 human health risk assessment for the data from the Melrose site exceeded EPA's levels of concern for volatilization risk exposures for residential adult bystanders (which includes the sensitive population of women of childbearing age) and for young children (1-2 years old, see Tables 4 and 5 in Appendix 3b, and Figure 3) due to the neurotoxicity of chlorpyrifos.[3]

[20] Tupper K, Kegley S, Jacobs N, et al. *Pesticide Drift Monitoring in Minnesota, June 13, 2006- August 13, 2009.* Pesticide Action Network North America; 2012.

Table 2a. Chlorpyrifos Air Monitoring Results

Sample Name	Start Date	Start Time	Stop Date	Stop Time	Total Time (min)	Total Sample Volume (m^3)	Chlorpyrifos Concentration ($\mu g/m^3$)	Notes[a, b]
Stalk-B	7/1/13	10:10 PM	7/2/13	8:46 PM	1,356	2.71	1.03	MV
Spring-B	7/2/13	8:46 PM	7/3/13	9:00 AM	734	1.38	None detected[b]	
Fall-A	7/2/13	10:18 AM	-	-	0	0	None detected[a,b]	Trip
Dew-B	7/3/13	9:20 AM	7/3/13	10:00 AM	760	1.60	0.690	
Bulb-A	7/3/13	10:05 PM	7/4/13	10:00 AM	715	1.43	0.180[a]	
Petal-A	7/4/13	10:04 AM	7/5/13	9:55 AM	1,431	2.86	0.160 [a]	
Drop-B	7/5/13	10:00 AM	7/6/13	10:06 AM	1,446	2.86	0.800	

[a] Sent to analytical lab about 4 weeks after preliminary samples were sent out.
[b] D = duplicate was analyzed, both were nondetectable at 0.01-0.05 µg; MV = minimum value (see "Methods: Sample Collection" in text).

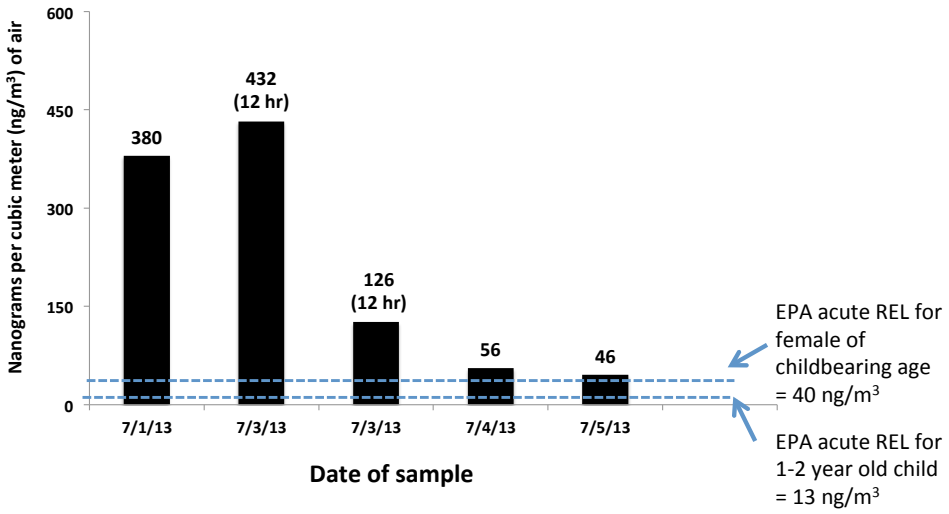
Table 2b. Chlorpyrifos Results from APT Laboratories

Sample Name	Start Date	Start Time	Stop Date	Stop Time	Total Time (min)	Total Sample Volume (m^3)	Chlorpyrifos Concentration ($\mu g/m^3$)	Notes[a, b]
Stalk-A	7/1/13	10:10 PM	7/2/13	8:46 PM	1,356	2.71	0.201	MV
Fall-B	7/2/13	10:18 AM	-	-	0	0	None detected	Trip[a]
Dew-A	7/3/13	9:20 AM	7/3/13	10:00 AM	760	1.60	0.011	
Bulb-B	7/3/13	10:05 PM	7/4/13	10:00 AM	715	1.43	0.085	
Petal-B	7/4/13	10:04 AM	7/5/13	9:55 AM	1,431	2.86	0.028	
Drop-A	7/5/13	10:00 AM	7/6/13	10:06 AM	1,446	2.86	0.017	

[a] D = duplicate was analyzed, both were nondetectable at 0.01-0.05 µg; MV = minimum value (see "Methods: Sample Collection" in text).

Figure 3. Chlorpyrifos concentration in the air, Melrose MN

Monitoring was conducted from 7/1 to 7/5/13. Samples were taken for 12 or 24 hours as indicated. The numbers at the top of each column indicate the concentration of chlorpyrifos in the air at the time of sampling. Reference exposure levels (REL) for chlorpyrifos from EPA's 2016 human health risk assessment are indicated at right.



Enslin/Sazama and Perham, MN

Five samples were collected at the Enslin/Sazama site, with all samples having detectable levels of MITC (Table 3).

The results indicate that for four out of five days of sampling at Sazama/Enslin, the levels of MITC on single days at the sampling sites exceeded chronic and subchronic screening levels as determined by California's Department of Pesticide Regulation, although these screening levels are taken over longer periods of time than the sampling conducted at these sites (see Discussion). These samples were taken adjacent to the same field fumigated with metam sodium, with one sample taken at Enslin (the other side of the field) on the second day of sampling for 24 hours. On one day, the level of MITC in the air exceeded California's acute 24-hour exposure screening level (66,000 ng/m^3). The time-weighted average for samples collected at the Sazama site during a three day period exceeded California's subchronic screening level (3,000 ng/m^3) (Figure 4a). At the Perham site, three of the eight samples taken had detectable levels of MITC. On the second day of sampling, the California chronic screening level was exceeded (300 ng/m^3) (Figure 4b).

Table 3. MITC Air Monitoring Results

Sample Name	Start Date	Start Time	Stop Date	Stop Time	Total Time (min.)	Total Sample Volume (m^3)	MITC Concentration ($\mu g/m^3$)	Notes a, b
Knee	10/17/15	11:10 AM	10/18/15	12:29 PM	1,264	2.53	53.0	D, S
Laurel	10/18/15	12:58 PM	10/19/15	2:40 PM	1,542	2.93	36.2	E
Roof	10/19/15	3:32 PM	10/20/15	3:34 PM	1,442	2.88	71.8	S
Bread	10/20/15	3:37 PM	10/21/15	3:37 PM	1,440	2.88	2.74	S
Salt	10/21/15	3:41 PM	10/22/15	12:45 PM	1,264	2.53	53.4	S
Dance	10/27/15	5:54 PM	-	-	0	0	None detected[a]	E, Trip
Snow	10/15/15	8:59 AM	10/16/15	5:53 PM	959	1.94	None detected[a]	P
Pony	10/15/15	5:56 PM	10/16/15	9:52 AM	1,977	3.86	None detected[a]	P
Song	10/16/15	6:06 PM	10/18/15	12:38 PM	2,552	5.10	0.590	P
Hand	10/18/15	12:47 PM	10/19/15	9:02 AM	1,215	2.40	None detected[a]	P
Razor	10/19/15	9:12 AM	10/20/15	8:56 AM	1,424	2.85	1.86	P,B
Sky	10/20/15	9:09 AM	10/21/15	8:26 PM	1,409	2.78	None detected[a]	P
Wave	10/21/15	8:34 AM	10/22/15	8:17 AM	1,414	2.83	None detected[a]	P
Mom	10/22/15	8:25 AM	10/23/15	9:07 AM	1,482	3.11	0.740	P
Cat	10/16/15	5:58 PM	-	-	0	0	None detected[a]	P, Trip

[a] Laboratory reporting limit was 0.5 micrograms/tube.
[b] D = duplicate was analyzed and value shown is the average of two duplicate samples; MV = minimum value (see "Methods: Sample Collection" in text). Sites: S = Sazama; E = Enslin; P = Perham; B = Back of airtube (breakthrough reservoir) was analyzed and no residues were detected.

Figure 4a. MITC Concentration, Sazama/Enslin Site

Monitoring was done from 10/17/15 to 10/21/15. Samples were taken for approximately 24 hours. The numbers at the top of each column indicate the concentration of MITC in the air at the time of sampling. Reference exposure levels based on EPA risk assessment and California's screening levels for MITC (subchronic level is for 4 weeks) are shown at the right side of the graph.

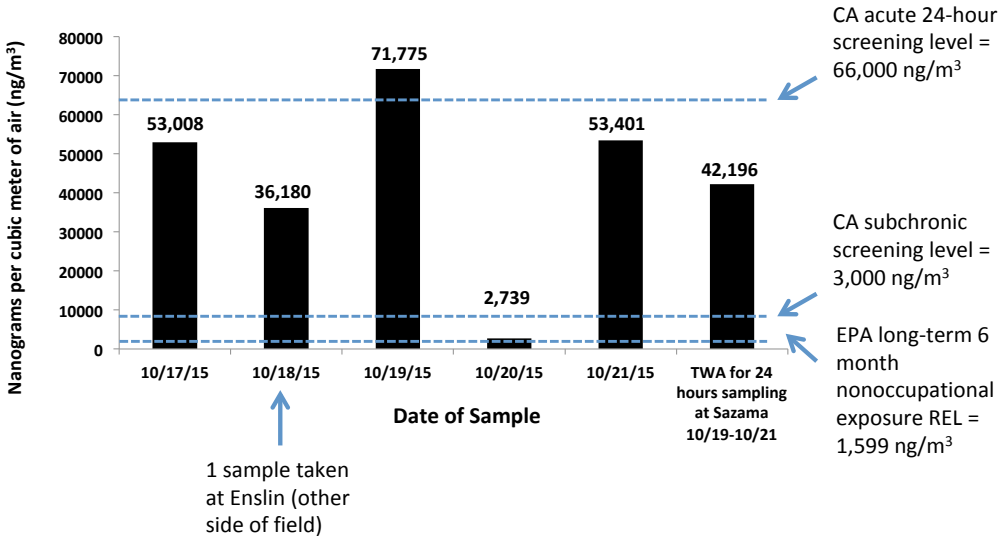
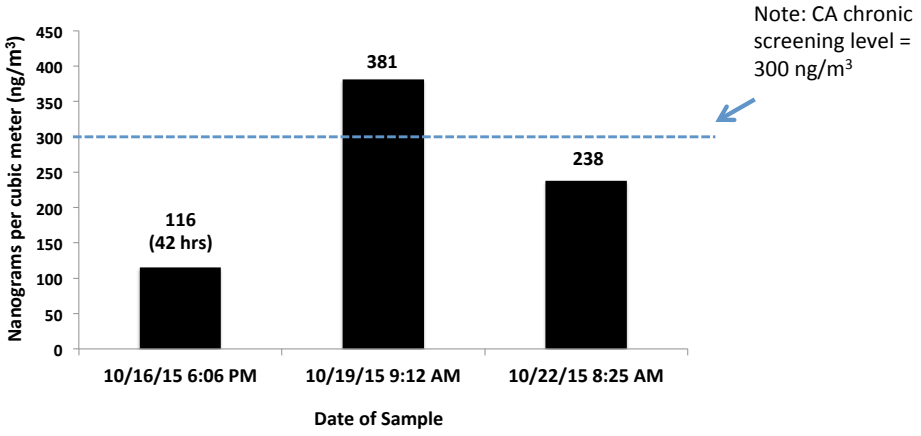


Figure 4b. MITC Concentration, Perham Site

Monitoring was conducted between 10/16/15-10/22/15. One sample was taken for 42 hours where specified at the top of the column in parentheses, the rest are 24 hour samples. The numbers at the top of each column indicate the concentration of MITC in the air at the time of sampling. No time-weighted average was calculated for this sampling period because samples were not taken continuously for the time period of sampling. A state of California chronic screening level (1 year) is shown at right.



Discussion

PAN's ambient air monitoring is targeted, in that the monitoring is initiated when community partners observe a pesticide application taking place. We have often observed residences that are located at the edges of fields. Most of PAN's air monitoring work is done within 300-1,000 feet of a known pesticide application, and usually is done at community partners' residence or at another site relevant to the community. The purpose of this is to learn about peak exposures in places where people live in close proximity to pesticide use. PAN's air monitoring work is done with community partners who are affiliated with a local, organized group. If the data support it, the results can help community groups argue for greater protections against pesticide drift.

At the Melrose site, chlorpyrifos volatilization levels were found that exceeded risk estimates for adult and young child bystanders based on EPA's 2016 HHRA (see Appendix 3, Table 4). It should be noted that the EPA's 2016 proposal to revoke agricultural use was based on the risk of dietary exposures, which EPA had determined was the major route of exposure for the majority of the population. Children and women of childbearing age who live and work near chlorpyrifos applications are thus potentially exposed to the neurotoxic insecticide via inhalation of the volatilized chemical, as well as via dietary exposures.

The levels of MITC found in the air were 100 times greater at the Sazama/Enslin monitoring site than the concentrations found at Perham. The data collected in northern Minnesota at two sites likely indicate the difference between sampling at closer proximity versus sampling at a greater distance from a known pesticide application. The air monitoring done at the field at Sazama/Enslin was 500 or 732 feet from the fumigated field, while the Perham site was noted by the community partner to be about 1.25 miles away from the nearest known fumigated field.

The levels of MITC found in this air monitoring project indicate that there are health concerns for Minnesota residents regarding potential chronic and subchronic exposures for families living at sites located adjacent to metam applications. The Sazama/Enslin site had one sample that exceeded the CA DPR acute 24-hour screening level (Figure 4a).

Chlorpyrifos

In its 2016 revised HHRA, U.S. EPA proposed that chlorpyrifos be banned for all agricultural uses because dietary exposure of children or pregnant women would result in neurotoxic effects.[3] Risks associated with exposure to chlorpyrifos volatilization for residential adult bystanders and children 1 to <2 years old were also assessed. Although EPA scientists proposed a ban of all agricultural uses of chlorpyrifos, the former EPA Administrator Scott Pruitt reversed the proposed ban on April 5, 2017.[21] Since then, EPA has not taken further action on the recommendations of its scientists to reduce chlorpyrifos exposures.[22] [23]

In December 2019, the European Commission (EC) proposed to ban chlorpyrifos and chlorpyrifos methyl, with all uses to expire within three months after the enacting of the regulation.[24] The EC also voted to lower all maximum residue limits (MRL) to the lowest detectable limit for laboratory testing, effectively blocking any residue tolerances for chlorpyrifos. This MRL rule went into effect in October 2020 and applies to food produced in the EU as well as imports.[25]

MITC

The metam sodium product used on the fields during this air monitoring project was VAPAM, registered to the AMVAC Chemical Corporation (Newport Beach, CA).

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[21] Environmental Protection Agency. "Chlorpyrifos; Order Denying PANNA and NRDC's Petition to Revoke Tolerances. EPA-HQ-OPP-2007-1005; FRL-9960-77," April 5, 2017.

[22] LULAC v. Wheeler, No. 111–1, ID 10971132, Case 17-71636 (United States Court of Appeals for the Ninth Circuit August 9, 2018).

[23] "EPA Challenges ban on chlorpyrifos," *Capital Press*, September 26, 2018. https://www.capitalpress.com/nation_world/ap_nation_world/epa-challenges-ban-on-chlorpyrifos/article_992a7972-e19b-52c6-a222-b4e5091ace11.html

[24] Press release, PAN Europe, https://www.pan-europe.info/press-releases/2019/12/victory-future-generations-european-governments-ban-brain-harming-pesticides. Accessed July 1, 2020.

[25] https://ec.europa.eu/food/plant/pesticides/approval_active_substances/chlorpyrifos_chlorpyrifos-methyl_en

US EPA includes consideration of MITC in its risk assessment of metam sodium, as MITC is the primary residue of concern for metam sodium, as well as metam potassium. Metam sodium, a class B2 probable carcinogen, is currently under registration review by US EPA. MITC is formed after the fumigant pesticides metam sodium or metam potassium are hydrolyzed in moist soil and is the chemical that fumigates the soil.[26] MITC is highly volatile, with a vapor pressure of 16 mm Hg at 25°C and a Henry's Law constant of 1.79×10^{-4} atm · m^3/g-mole.[27]

Fumigation patterns vary from year to year, depending on factors like planting and pest pressures. The amount of fumigants residents are exposed to, therefore, also varies from year to year.

California DPR uses screening levels of pesticides in the air as a trigger for conducting a detailed evaluation of health concerns. Some pesticides have regulatory target levels determined by DPR after further evaluation. Once a complete assessment of possible health risks is completed, regulatory targets are established, which supersede screening levels. A regulatory target is based on a more comprehensive evaluation than is done for a health screening level. A specific pesticide and exposure duration will have either a regulatory target or a health screening level, but not both.[28]

MITC has toxic effects similar to metam sodium and dazomet, another fumigant, at low doses administered orally in rats, mice, rabbits, and dogs. Applicators may be exposed dermally to metam sodium when mixing and loading the pesticide. MITC is Acute Toxicity Category II for the oral and inhalation routes, and category I for the dermal route. MITC also causes skin and eye irritation (Acute Toxicity Category I). Dietary exposure to MITC or metam sodium is unlikely to occur due to the very high volatility of these compounds.[29]

In California, an accidental spill of 19,500 gallons of 32.7% metam sodium from a railroad tank car into the Sacramento River occurred on July 14, 1991 near the town of Dunsmuir and caused a number of residents to report symptoms of exposure. There were 848 spill-related hospital visits made by 705 individuals during the month after the accident. Of those visits, 64% reported headache, 49% eye irritation, 42% throat irritations, 46% nausea, 30% dizziness, 27% shortness of breath, 25% diarrhea, 23% nasal irritation and 22% chest tightness. Residents from

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[26] Woodrow, James E., et al. "Determination of Methyl Isothiocyanate in Air Downwind of Fields Treated with Metam-Sodium by Subsurface Drip Irrigation." *Journal of Agricultural and Food Chemistry* 56, no. 16 (August 2008): 7373–78. https://doi.org/10.1021/jf801145v.

[27] California Department of Pesticide Regulation. "Risk Characterization Document: Methyl Isothiocyanate (MITC) Following the Agricultural Use of Metam Sodium." California Environmental Protection Agency, July 25, 2003.

[28] From p. 29 of "Air Monitoring Network: A Comprehensive Evaluation of Results (2011-2016),"California Department of Pesticide Regulation, June 2018

[29] U.S. EPA. "Metam Sodium: HED Human Health Risk Assessment For Phase 1: DP Barcode: DP 308417, Metam Sodium PC Code: 039003, MITC PC Code: 068103." HED Records Center Series 361 Science Reviews- File R102921. Washington, DC, September 30, 2004.

the town of Earlimart, CA were also exposed to MITC after an illegal sprinkler application of metam sodium to a field in 1999. The residents reported symptoms similar to those experienced by the residents near the Dunsmuir spill.[11]

MITC is the main chemical that people would be exposed to after a metam sodium application. An additional area of uncertainty is methyl isocyanate (MIC), which is a breakdown product of MITC that has been measured in the air by California Air Resources Board and in a 2014 air monitoring study in a Washington state residential area near a potato field application of metam sodium.[30] At high air concentrations, MIC has acute toxicity to humans.[31] Risk of exposure to MIC has not been incorporated into California's risk characterization of MITC, but has been cited as an important consideration by California's Office of Environmental Health Hazard Assessment (OEHHA). OEHHA stated that characterizing MIC exposure risk is "necessary to fully and adequately evaluate risks from MITC."[32] Combined MITC and MIC exposure is an important consideration for residential communities.

Further discussion of air monitoring data on chlorpyrifos and MITC, as well as of risk assessments for chlorpyrifos and MITC, is in Appendix 3b.

Conclusions

No state or federal agency has established health standards for pesticides drifting in the air. California DPR has screening levels and regulatory target concentrations, so that air monitoring data can be placed in a health-related context. EPA has also identified risk estimates for volatilization exposures for chlorpyrifos, as well as a few other pesticides.

Chlorpyrifos levels found in the air at the Melrose residence exceeded levels of concern for children and women of childbearing age, according to EPA's 2016 HHRA, which was based on epidemiology data.

For MITC monitored at the Sazama/Enslin and Perham residences, the levels found indicate reasons for concern. On certain days, the levels of MITC exceeded subchronic (4 week) or chronic (1 year) screening levels determined by California DPR. However, these screening levels are determined for a longer period of time than the monitoring done by community partners. In places where more than one fumigant is used on different fields where use patterns vary depending on farmers' needs, the health risks of cumulative impacts are concerning.

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[30] Woodrow JE, LePage JT, Miller GC, Hebert VR. Determination of Methyl Isocyanate in Outdoor Residential Air near Metam-Sodium Soil Fumigations. *Journal of Agricultural and Food Chemistry.* 2014;62(36):8921-8927. doi:10.1021/jf501696a

[31] Mishra, P., et al. "Bhopal Gas Tragedy: Review of Clinical and Experimental Findings after 25 Years." *International Journal of Occupational Medicine and Environmental Health* 22, no. 3 (January 1, 2009). https://doi.org/10.2478/v10001-009-0028-1.

[32] Fan, Anna M. "Comments and Recommendations Regarding the Draft Risk Characterization Document for Methyl Isothiocyanate." California Office of Environmental Health Hazard Assessment, April 9, 2003.

On one of the sampling days, an exceedance of the 24-hour acute exposure screening level for MITC determined by California DPR was observed at a site where monitoring was done at 500 or 732 feet away from a potato field at the Sazama/Enslin site (Figure 4). Exposure to fumigant pesticides like MITC can cause respiratory irritation, and some exposures to MITC have in fact exceeded the acute respiratory irritation level, according to OEHHA. Respiratory irritant exposure "can result in the development of prolonged adverse effects such as reactive airways dysfunction syndrome. In this condition, subsequent exposures to far lower levels of the same or another irritant gas will then trigger respiratory distress symptoms."[33] California Department of Pesticide Regulation has stated that co-exposure to "any combination" of metam sodium breakdown products such as MITC or MIC "could elicit additive or synergistic effects... particularly in respiratory and ocular tissues."[11]

Data gaps for MITC around carcinogenicity and co-exposures to MIC and MITC are areas of concern for communities where metam sodium is used, especially where other fumigants are used as well. According to OEHHA, "Many exposures to MITC have exceeded the acute respiratory irritation level."[32] While the levels found in this Minnesota study have not exceeded acute respiratory irritation levels, exposures at other sites to MITC could still contribute to respiratory problems for residents nearby.

The data collected by community partners with PAN support the idea that families living near sites where agricultural pesticides are applied are at risk. Health standards for pesticide drift should be established to protect those who are living next to fields where pesticides are applied.

Appendix 1: Calculations

Air Concentrations

Pesticide concentrations in air were calculated from the analytical results obtained from the commercial lab as shown in equation (1):

$$\text{Air concentration, ng/m}^3 = \frac{\text{MITC or chlorpyrifos level in tube, } \mu\text{g}}{\text{volume of air sampled, m}^3} \times 1000 \qquad (1)$$

For convenience, all air concentrations reported here are expressed in units of $\mu g/m^3$. In some cases, concentrations from other studies that are quoted herein were converted from units of ppbv (parts per billion by volume, also abbreviated as ppb) according to equation (2):

[33] Fan, Anna M. "Memorandum: Revised Findings on the Health Effects of Methyl Isothiocyanate." California Office of Environmental Health Hazard Assessment, January 31, 2002.

(2)

$$\text{Air concentration, } \mu g/m^3 = \frac{\text{air concentration, ppb x molecular weight, g/mol}}{\text{24.45, L/mol}}$$

Where the molecular weight of MITC = 73.3 g, and the molecular weight of chlorpyrifos = 350.6 g.

Calculation of Reference Exposure Levels

MITC

In its most recent risk assessment of MITC, EPA determined reference concentrations based on a 28-day inhalation toxicity study in rats. The reference concentration (Rfc) methodology EPA used recommended developing array tables that would allow EPA to evaluate inhalation dosimetry and animal to human extrapolation for systemic effects and local effects for the extrathoracic, tracheobronchial, and pulmonary regions of the respiratory tract for MITC. The acute risk assessment for MITC was based on a human exposure study on eye irritation that had exposure durations ranging from four minutes to eight hours.[44]

EPA's target MOE for short- and intermediate-term inhalation risk was an MOE of 30. Human exposure concentrations were estimated for non-occupational and occupational scenarios. The combined uncertainty factor for long-term risk assessment of MITC was 300X.

California DPR used a critical acute NOEL value (NOEL = 220 ppb) for MITC based on a human study on eye irritation.[27] The REL acute was 22 ppb. Occupational exposure estimates by CDPR have indicated a human health concern for one and eight-hour exposures.

Chlorpyrifos

The total uncertainty factor, or level of concern, for chlorpyrifos recommended by US EPA is 100. PAN and Natural Resources Defense Council, in coalition with other groups have recommended in several documents a total uncertainty factor of at least 1000X. [34]

Margin of exposure approach

EPA assessed inhalation exposure by the target "margin of exposure" (MOE) approach for both chlorpyrifos and MITC. In the first part of this approach, an appropriate toxicological endpoint is selected. Typically, the endpoint is a human equivalent concentration (HEC) or No Observed Adverse Effect Level (NOAEL) from an animal study. This is the highest dose that did not cause observable adverse

[34] "Farmworker and Conservation Comments on Chlorpyrifos Issues Paper: Evaluation of Biomonitoring Data from Epidemiology Studies." Natural Resources Defense Council et al., April 2016, Comments to EPA Scientific Advisory Panel, submitted to EPA-HQ-OPP-2016-0062.

effects in the study. In the next stage, a target MOE is determined. MOE is defined as the ratio of the NOAEL from the animal study to the human exposure dosage; a higher MOE corresponds to a greater margin between the anticipated human exposure and the level known to cause adverse effects in animals. An MOE of less than one for a scenario indicates that humans are being exposed at doses that exceed the safe dose in the test animal. A target MOE is the minimum MOE deemed acceptable for humans by the Agency. Usually the target MOE is set to at least 100. This assumes that humans are 10-fold more sensitive than the test animal and that there is 10-fold variability among humans (i.e., some people, e.g. infants, the elderly, or sick people, may be up to 10 times as sensitive as the average person). In setting the target MOE at 100, EPA is attempting to keep human levels of exposures to the chemical at least 100 times lower than the highest dose known to be safe in animals. In the last stage, MOEs are estimated for various human exposure scenarios. Those situations with MOEs less than the target MOE are usually considered to carry unacceptably high levels of risk and require mitigation.

To facilitate comparisons of the MITC levels observed in this study with EPA's target MOE, we calculated reference exposure levels (RELs) according to the equation below. Breathing rate and body weight are not incorporated into this calculation because the short- and intermediate-term effects are port-of-entry effects. CDPR recommended an uncertainty factor of 10-fold for intraspecific variability and 10-fold for interspecies variability.

$$\text{Reference Exposure Level, } \mu\text{g/m}^3 = \frac{\text{critical NOAEL, } \mu\text{g/m}^3}{\text{UF}_{\text{intraspecies}} \times \text{UF}_{\text{interspecies}} \times \text{UF}_{\text{other}}} \quad (3)$$

The REL represents the air concentration corresponding to a MOE equal to the target MOE. Air levels exceeding the REL have MOEs less than the target MOE, and represent situations with unacceptably high levels of risk. Likewise, air levels below the REL correspond to the MOEs greater than the target MOE and represent "acceptable" levels of exposure, according to the agency making the decision.

For the purpose of calculating RELs, we have used the critical toxicological endpoints specified by EPA for MITC and using the most health protective endpoints from the HHRA on chlorpyrifos, from 2016. For MITC, the California DPR's screening levels were used for further human health related context.

Appendix 2: Interpreting Air Monitoring Results

Interpreting air monitoring results requires understanding of how regulatory authorities like the EPA assess the toxicity of pesticides. In this section we answer the following questions.

How Are "Safe" Levels of Pesticides in Air Determined?
Are RELs and RfCs Air Quality Standards?
Are Levels Below the Level of Concern "Safe"?
What Do Air Monitoring Results Tell Us About Exposure?

How Are "Safe" Levels of Pesticides in Air Determined?

It is generally assumed that humans can be exposed to tiny amounts of most chemicals without suffering ill effects. As doses increase, usually both the severity and incidence of adverse effects increase, hence the adage: "the dose makes the poison." In recent years, this assumption has been challenged for a class of toxicants known as endocrine disruptors; [35] nonetheless, this idea forms the basis of modern risk assessment. Thus, rather than trying to prevent any and all exposures to chemicals of concern, regulators instead try to limit exposure to levels that are so small that the risk of harm is negligible.

Risk assessors use a variety of closely related techniques to quantify the risk posed by exposure to chemicals. These techniques go by various names but almost always involve identifying the largest dose that does not cause observable harm to animals in controlled experiments (the "No Observed Adverse Effects Level," or NOAEL), then extrapolating from this dose to an acceptable dose in humans that is anticipated to be without harm. This extrapolation often takes into account physiological differences between the test animal and humans such as body weight, breathing rate, absorption, and metabolism.

The NOAEL usually comes from an experiment that uses only a few dozen animals (usually rats, mice, or rabbits) that are nearly genetically identical. Therefore, the extrapolation also includes factors to account for the inherent uncertainty that arises when extrapolating to a human dose that is supposed to be without risk for all members of an exceedingly large and diverse population. An interspecies factor of 10 is generally used to account for the fact that laboratory animals and humans are different and an intraspecies factor of 10 is used to account for variability among different people. The acceptable human dose calculated with these uncertainty factors is thus often several orders of magnitude smaller than the animal NOAEL that it is based on.

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[35] Myers JP, vom Saal FS. 2007. Time to Update Environmental Regulations: Should public health standards for endocrine-disrupting compounds be based upon sixteenth century dogma or modern endocrinology? *San Francisco Medicine Magazine*, San Francisco Medical Society. April, 2007 and references cited therein. http://www.sfms.org/AM/Template.cfm?Section=Home&TEMPLATE=/CM/HTMLDisplay.cfm &CONTENTID=2506&SECTION=Article_Archives.

In assessing the risk of dietary exposure to pesticides, EPA uses oral dosing studies to establish a "Reference Dose" (RfD) following the procedure described above. The Agency defines a RfD as:

> an estimate, with uncertainty spanning perhaps an order of magnitude, of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects of a lifetime.[36]

An RfD should not, therefore, be considered a threshold level above which adverse effects are guaranteed or even expected. Rather, it should be understood as a level of concern, above which the risk of adverse effects is unacceptably high (although perhaps still quite small in absolute terms), and below which the risk is acceptably small. The agency uses RfDs to determine worker protection rules, mitigations for exposures the general public might experience, and acceptable limits for the maximum amount of pesticide residue permissible in food items. With these regulations, the Agency tries to limit human exposure to an amount less than the RfD.

For a constant dose, the incidence and severity of adverse effects generally increase as the duration of exposure increases. In other words, a dose that does not cause acute toxicity after a single exposure may cause chronic toxicity if exposure occurs repeatedly. For this reason, different RfDs are often calculated for acute and chronic exposure, and for 1-hour and 24-hour exposure, etc.

Reference doses are defined specifically for dietary exposure, but similar levels of concern can be derived for inhalation exposure using analogous methods: usually starting with a NOAEL from an animal study and then applying uncertainty factors to extrapolate to an acceptable human dose. The conversion from an acceptable dose (in units of mg of chemical per kg bodyweight per day) to a level of concern (in units of mg or ng of chemical per a certain volume of air) is complicated by variations in breathing rates among human beings. For example, infants and children have proportionately higher breathing rates than adults, so if an infant and an adult are exposed to the same airborne concentration of a toxicant for the same period of time, the infant will receive a larger dose (measured in mg of pesticide per kg of body weight) than the adult. Similarly, breathing rates vary with physical activity, so, for example, a person exercising in contaminated air would receive a greater dose than a person napping in the same environment for the same length of time. Since the resulting levels of concern are air concentrations rather than doses these are called Reference *Concentrations* or Reference *Exposure Levels,* rather reference *doses*.

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[36] US EPA 2009. *Glossary of Terms. America's Children and the Environment*, US Environmental Protection Agency, http://www.epa.gov/economics/children/basic_info/glossary.htm.

In this air monitoring study, we compare concentrations of pesticides measured in air for acute and short term RfCs and RELs calculated by DPR and OEHHA. We also derive a REL from EPA data as described in the **Calculations** section of this report.

Are RELs and RfCs Air Quality Standards?

No. A REL or RfC is not an enforceable standard like a water quality standard or a worker protection standard. They are analogous to a RfD, a dose that the EPA uses in its dietary assessments as a Level of Concern (LOC). To minimize exposure risk, EPA typically takes action to reduce dietary exposures of the 99.9th percentile person to below the LOC. This means that if even one-tenth of one percent of the people were exposed to a pesticide in their diet at this level, EPA would take action to reduce risk. Unfortunately, there are regulatory gaps for inhalation exposure—EPA does not currently assess bystander inhalation exposures for most pesticides but rather assumes that inhalation is not a significant contributor to total exposure.

Are Levels Below the Level of Concern "Safe"?

Concentrations below the REL do not necessarily indicate that the air is "safe" to breathe. In particular, a number of recent studies evaluating people's capacity to metabolize toxic substances show that the variability among different people can be substantially greater than the variability assumed by EPA in its toxicological analysis.[37] Additionally, as in this study or in past studies, people are often exposed to multiple pesticides simultaneously, or are taking prescription or non-prescription drugs, or are exposed to other chemicals, thus reducing their capacity to detoxify the pesticides to which they are exposed.

What Do Air Monitoring Results Tell Us About Exposure?

Air monitoring data provide exposure estimates that may or may not represent worst-case exposure scenarios, and do not represent the precise exposure individuals may experience. Variables that affect an individual's exposure to airborne pesticides include the amount of time spent in areas with high concentrations of airborne pesticides, body weight and breathing rate.

The breathing rates used to derive the levels of concern in this study (see the **Calculations** section) represent the breathing rates of individuals *averaged over the course of 24 hours*. An individual's breathing rate will vary substantially over the course of 24 hours. For example, the typical breathing rate of a 10-year old child during resting activity (e.g. sleeping, reading or watching television) is 0.4 m^3/hr, while during moderate activity (e.g. climbing stairs) it is 2.0 m^3/hr, and during heavy activity (e.g. playing sports) it is almost ten times greater at 3.9 m^3/hr. The breathing rate of a child at play during recess or exercising during a gym class is best approximated by the moderate or heavy activity breathing rate. Thus, children are outside and maximally exposed to air contaminants precisely when their

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[37] Furlong CE, Holland N, Richter RJ, Bradman A, Ho A, Eskenazi B. 2006. PON1 status of farmworker mothers and children as a predictor of organophosphate sensitivity, *Pharmacogen. Genom.*, **16**(3):183-190.

breathing rates are expected to be the highest. The RELs used in this report are calculated using lower than moderate breathing rates—the daily averages—and assuming 24-hour exposure.

For most pesticides, only a limited number of monitoring studies are available for comparison, and most of the available studies only provide results for applications conducted according to label instructions and for exposure estimates to a single pesticide. PAN's Drift Catcher provides additional monitoring data for comparison, and as we gather more data, a clearer picture of pesticide levels in the air near homes, schools, parks and workplaces will emerge.

Notwithstanding that available monitoring data are not comprehensive, the data indicate that many people are routinely exposed to levels of airborne pesticides that exceed both acute and sub-chronic levels of concern.

Appendix 3: Physical Properties & Further Information

Table A-1: Physical Properties of Chlorpyrifos[38] [39] [40]

Property or Identifier	Chlorpyrifos
CAS Number	2921-88-2
Chemical Formula	CCl_3NO_2
Molecular Weight (g/mol)	350.57
Melting Point (°C)	41.5-42.5
Water Solubility (mg/L)	1.05 @ 25°C
Vapor Pressure (mm Hg)	1.87×10^{-5}
Henry's Law Constant (atm-m^3/mol)	6.3×10^{-6} @ 25 °C
Avg. Hydrolysis Half-life	71 days @ pH 8
Avg. Aerobic Soil Half-life	11-141 days
Avg. Anaerobic Soil Half-life	15 and 58 days

Table A-2: Physical Properties of Metam Sodium and MITC

Property or Identifier	Metam Sodium	MITC
CAS Number	137-42-8	556-61-6
Chemical Formula	$C_2H_4NNaS_2$	C_2H_3NS
Molecular Weight (g/mol)	129.18	73.3

[38] Duirk, Stephen E., and Timothy W. Collette. "Degradation of Chlorpyrifos in Aqueous Chlorine Solutions: Pathways, Kinetics, and Modeling." *Environmental Science & Technology* 40, no. 2 (January 2006): 546–51. https://doi.org/10.1021/es0516615.

[39] U.S. Environmental Protection Agency. "Revised Chlorpyrifos Preliminary Registration Review Drinking Water Assessment." Washington, D.C.: U.S. Environmental Protection Agency, June 30, 2011.

[40] U.S. Environmental Protection Agency. "Chlorpyrifos: Updated Drinking Water Assessment for Registration Review." Washington, D.C.: U.S. Environmental Protection Agency, December 23, 2014.--

Melting Point (°C)	Decomposes without melting	35-36
Water Solubility (g/L)	722 @ 20°C	Poorly soluble in water
Vapor Pressure (mm Hg)	End-use: 21@25 °C	16 @ 25 °C
Henry's Law Constant (atm-m^3/mol)	End-use: 4.3 x 10^{-6} @ 25 °C	1.79 x 10^{-4} @ 25 °C
Avg. Hydrolysis Half-life (hours)	23.8 @25 °C, pH 5 180 @25 °C, pH 7 45.6 @25 °C, pH 9	23 hours @20°C, pH 5
Avg. Aerobic Soil Half-life	--[a]	
Avg. Anaerobic Soil Half-life	--[a]	

[a] Studies on soil half-life reviewed by California DPR found to be unacceptable due to flawed methodologies.
[b] References [27, 41]

Further Information on chlorpyrifos and MITC

Chlorpyrifos

The EPA assessed residential bystander exposure to chlorpyrifos based on data available from one application site and several ambient air monitoring studies, and found that acute ambient air concentrations had the most risk estimates that were of concern. Non-occupational bystander post-application inhalation exposures have a level of concern of 100. EPA's risk estimates of concern are MOEs that are less than 100 and risk estimates described as "not of concern" by EPA are MOEs greater than 100. EPA's assessment found that six of the 11 acute ambient air concentrations were of concern for adult residential bystanders. For children 1 to <2 years old, EPA found that all 11 acute ambient air concentrations had risk estimates of concern. Risk estimates of concern for steady-state MOEs were also exceeded for 10 of 11 ambient air concentrations for adults, and for seven of the 11 ambient air concentrations for children 1 to <2 years old in the EPA analysis. These data are reported in Tables 9.1 and 9.2 (p. 32-34) in EPA's 2016 HHRA. [3]

Chlorpyrifos air monitoring data
The chlorpyrifos air monitoring studies included in Tables 4 and 5 include some of the data referenced by EPA in the 2016 HHRA. PAN's data from Melrose, MN resulted in risk estimates of concern, as did other PAN chlorpyrifos air monitoring data. The only state agency that conducts air monitoring on a regular basis is in the state of California. Washington state has done some air monitoring work in the past.

[41] California Department of Pesticide Regulation. "Metam Sodium Risk Characterization Document." California Environmental Protection Agency, July 21, 2004.

Table 4. Chlorpyrifos Volatilization Risk for Residential Adult Bystanders

Study & Year	Location	Maximum Air Concentration (ng/m³)	Arithmetic Mean Air Concentration (ng/m³)	Acute MOEs (LOC = 100)	Steady State MOEs (LOC = 100)
WA DOH 2008-Ambient Air Data only[a]	North Central District Ambient	21	7	190	31
	North Central District Receptor	606.8	33	6.6	6.4
	Yakima Valley Ambient	30	9	130	23
	Yakima Valley Receptor	243	30	16	6.9
CA DPR, Parlier 2009		150	96	27	2.2
Cowiche, PAN 2006		462	155	8.7	1.4
PAN MN Drift Study (2006-2009)	Browerville Site B	15	2.7	270	78
	Perham Site C	47	1.9	85	110
CA DPR AMN, highest concentration[d]	Shafter	422.5	113.3[e]	9.47	1.85
CA DPR AMN 2014[f]	Ripon	14.1	14.1	280	15
	Salinas	14.1	5.4	280	39
	Shafter	337.9	92.1	12	2.3
Melrose, MN 2013		432[g]	173	9.26	1.21

[a] Ambient and application site air monitoring were done for the Washington State Department of Health study. Only ambient air monitoring data are included in this table. These data are reported in EPA's 2016 HHRA, tables 9.1 and 9.2.
[b] Acute MOE = Acute PoD (4,000 ng/m³) / Study maximum air concentration (ng/m³)
[c] Steady State MOE = Steady State PoD (210 ng/m³) / Study arithmetic mean air concentration (ng/m³)
[d] These air concentrations were from data collected at the Shafter DPR air monitoring site in 2013 and represent the highest air concentrations for chlorpyrifos from the data collected by AMN during 2011-2016.
[e] This value is a maximum rolling 4-week average air concentration reported by DPR.
[f] These 2014 data from California DPR were reported in EPA's 2016 chlorpyrifos human health risk assessment, and included here for comparison.
[g] This sample was a 12 hour sample.

Table 5. Chlorpyrifos Volatilization Risk for Residential Children (1 to <2 Years Old) Bystanders

Study & Year	Location	Maximum Air Concentration (ng/m³)	Arithmetic Mean Air Concentration (ng/m³)	Acute MOEs (LOC = 100)	Steady State MOEs (LOC = 100)
WA DOH 2008-Ambient Air Data only [a]	North Central District Ambient	21	7	62	100
	North Central District Receptor	606.8	33	2.1	21
	Yakima Valley Ambient	30	9	43	73
	Yakima Valley Receptor	243	30	5.3	22
Parlier, CA (CA DPR) 2009		150	96	8.7	7.1
Cowiche PAN 2006		462	155	2.8	4.4
PAN MN Drift Study (2006-2009)	Browerville Site B	15	2.7	87	260
	Perham Site C	47	1.9	28	350
CA DPR AMN Highest Concentration[d]	Shafter	422.5	113.3[e]	3.08	6.00
CA DPR AMN 2014[f]	Ripon	14.1	14.1	92	48
	Salinas	14.1	5.4	92	130
	Shafter	337.9	92.1	3.8	7.4
Melrose, MN 2013		432[g]	173	3.01	3.92

[a] Ambient and application site air monitoring were done for the Washington State Department of Health study, but are not included in this table. These data were reported in EPA's 2016 HHRA, tables 9.1 and 9.2.
[b] Acute MOE = Acute PoD (1,300 ng/m³) / Study maximum air concentration (ng/m³)
[c] Steady State MOE = Steady State PoD (680 ng/m³) / Study arithmetic mean air concentration (ng/m³)
[d] These air concentrations were from data collected at the Shafter DPR air monitoring site in 2013 and represent the highest air concentrations for chlorpyrifos from the data collected by AMN during 2011-2016.
[e] This value is a maximum rolling 4-week average air concentration reported by DPR.
[f] These 2014 data from California DPR were reported in EPA's 2016 chlorpyrifos human health risk assessment, and included here for comparison.
[g] This sample was a 12 hour sample.

MITC

California DPR and EPA levels of concern differ due to the agencies' choice of different starting points for their no observable effect level (NOEL) and no observable adverse effect level (NOAEL), respectively. CDPR relied upon an eye irritation study conducted with human subjects for their NOEL, while EPA used a 28-day inhalation toxicity study conducted in rats for their NOAEL. California OEHHA noted that eye irritation alone does not account for the exposures that

would occur in real-world situations via mouth and nose. The majority of the toxicity studies used by US EPA for MITC risk assessment were exposures via the oral route, even though inhalation is the primary route of exposure.

Data gaps around MITC carcinogenicity
Due to insufficient data for MITC in rat and mouse oral carcinogenicity studies and around inhalation, the primary route of human exposure, U.S. EPA has not been able to assess carcinogenicity.

MITC data are currently inadequate for U.S. EPA to make a determination about carcinogenicity and EPA's workplan for MITC includes requests for data on carcinogenicity. Many of the toxicological studies via the oral route do not meet EPA guidelines, and the inhalation toxicity data are inadequate.[42] The oral route studies are problematic due to the difficulty of determining what dose animals were exposed to. MITC was added to the drinking water of rats, and at higher doses the water was observed to have a strong odor, which was thought to have resulted in the rats drinking less water. As a result, the maximum tolerated dose was not reached.

For metam sodium, U.S. EPA determined it was a B2 probable carcinogen in 1999. The EPA concluded that metam sodium data were inadequate for determining whether MITC is carcinogenic via inhalation, because most of the studies submitted were administered via the oral route.[43] In 2000, the U.S. EPA's Hazard Identification and Assessment Review Committee of the Health Effects Division recommended that the carcinogenic potential of MITC be estimated using the cancer slope factor (Q-1*= 1.98×10^{-1} for metam sodium, converted from animals to humans[44]) for metam sodium. HED's Division Director requested that the HED Science Policy Council evaluate this recommendation.[45]

MIC and MITC co-exposures have not been assessed by US EPA or CA DPR
Data gaps around inhalation exposure to MITC, and co-exposures to MITC and another byproduct from metam sodium applications, MIC, have not been fully assessed by either California DPR or US EPA.

Endpoint for MITC used by California DPR and EPA is not adequate
The eye irritation endpoint used by California DPR relied on special goggles that allowed for eyes-only exposure in a human volunteer study. However, in a real-

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[42] U.S. Environmental Protection Agency. "Methyldithiocarbamate Salts (Metam Sodium, Metam Potassium) and Methyl Isothiocyanate (MITC) Final Work Plan, Registration Review Case Numbers 2390 and 2405." Washington, DC: U.S. Environmental Protection Agency, March 2014. www.regulations.gov.

[43] U.S. EPA. "Memorandum: Quantification of Carcinogenic Potential for MITC with Metam Sodium Cancer Slope Factor," HED Records Center Series 361 Science Reviews- File R100662, May 13, 2004.

[44] U.S. EPA. "Metam Sodium: HED Human Health Risk Assessment For Phase 1: DP Barcode: DP308417, Metam Sodium PC Code: 039003, MITC PC Code: 068103." Washington, D.C., September 30, 2004.

[45] U.S. Environmental Protection Agency. "Addendum to Memo from May 13, 2004 (TXR NO. 0052547): Quantification of Carcinogenic Potential for MITC with Metam Sodium Cancer Slope Factor," May 13, 2004.

world exposure, the nose and mouth would also be exposed to MITC. This may lower the NOAEL, as noted by OEHHA in a 2003 memo.[32] The current endpoint used by CDPR is therefore likely not adequate to protect against exposure to MITC, as real-world exposures would take place via the eyes, nose, and mouth.

For DPR, ambient exposure levels were not of concern according to screening levels, though application site exposure ranges were cited as concerning for human health. For chronic exposure, DPR assessed annual exposure concentrations for occupational scenarios based on data from ambient scenarios. Out of 14 sites where MITC was found in California, 10 registered MOEs below 100, indicating a health concern.

In the most recent EPA HHRA, no chronic inhalation data with MITC were available, though ambient air monitoring data by the state of California clearly indicates that chronic exposures are possible.

Other MITC air monitoring data
Data are collected by the California DPR's Air Monitoring Network on ambient air samples for a number of pesticides, including MITC. Other ambient air monitoring work has found MITC in the air. Ambient air monitoring for MITC by AMN or by Woodrow et al. (2014) found MITC at varying air concentrations that ranged from being significantly lower or somewhat comparable to the data reported here (Table 6).

Table 6. MITC Air Monitoring Data from Other States

Study & Year	Location	Maximum Air Concentration (ng/m^3)	Arithmetic Mean Air Concentration[b] (ng/m^3)	Time-weighted Average (ng/m^3)
Minnesota 2015	Enslin/Sazama	71,775.3	-	43,187.7
	Perham	381.3	-	218.1
CA DPR AMN Highest Concentration[a]	Shafter	930.4	563.5	Not calculated
CA DPR AMN 2016	Ripon	73.2	41.4	"
	Salinas	26.3	8.7	"
	Shafter	108.9	51.0	"
Washington, Woodrow et al. 2014[30]	Site 1	12,300[c]	-	2,191
	Site 3-L	14,900[c]	-	3,698
	Site 3-R	15,600[c]	-	3,571
	Site 5	21,700[c]	-	4,949

[a] This value is the highest concentration of MITC detected among all sites between 2011-2016 and was recorded at the Shafter monitoring site in 2011.

[b] This value is the maximum rolling 4-week air concentration for the year 2015, reported by AMN.

[c] These data are time weighted averages representing 4 hour air concentrations. TWA= ($concentration_1$ * $time_1$) + ($concentration_2$ * $time_2$)…/total time in same units.

Appendix 4: Negative Results from Air Monitoring in Minnesota, 2012-2014*

A number of sites where monitoring took place yielded negative data. From 2012-2014 sampling, a total of 148 samples were taken at 10 sites. Of those samples shown in Appendix 4, 52 were sent to EMA Labs and four were sent to APT for analysis.

A number of possibilities exist as to why we obtained negative results for these sites, some of which are listed here:

- Nothing was applied
- Something was applied, but no spray drift and/or the pesticide was not volatile enough
- Something was applied and drifted, but amounts in the air were not sufficient to be captured, and yet damage was documented
- Something applied and drifted, but the sampling media (the airtube) was no the right type for that particular pesticide
- Something was applied, but the type of chemical caught could not be analyzed with the methods used

In addition, two samples out of five preliminary samples sent in was positive for chlorothalonil at a sampling site in Frazee, MN in 2012. However, the concentrations were much lower than the previously reported data on chlorothalonil from the same area, and the remaining three samples from the project were not analyzed.
*One site was located in North Dakota.

Table 7. Negative Data from Other Sites in Minnesota

Sampling site	Year	No. of samples taken; No. of trip blanks made	Name of samples sent to EMA	Date samples taken	No. of samples sent to EMA	EMA Laboratory Screens	Results	Sent to APT Laboratory?	APT screens	APT lab results
Park Rapids, MN	2014	10;2	Cable-A	7/28/14	4	multiresidue	nondetectable	No		
			Six-A	7/31/14		multiresidue	nondetectable			
			Paper-A	6/29/14		multiresidue	nondetectable			
			Wind-B	7/3/14		multiresidue	nondetectable			
Kilkenny, MN	2013	7;1	River-B	6/8/13	3	multiresidue	nondetectable	Yes; sent duplicate of EMA samples for analysis of diquat dibromide (paraquat breakdown)		
			Winter-B	6/8/13		multiresidue	nondetectable	River-A	diquat	nondetectable <0.085 ug
			Mole-B	6/11/13		multiresidue	nondetectable	Winter-A	diquat	nondetectable <0.085 ug
			APT only: Spider-trip					Mole-A	diquat	nondetectable <0.085 ug
								Spider	diquat	nondetectable <0.085 ug
White Earth Reservation, MN	2013	8;1	Yellow-B	7/26/13	2	multiresidue	nondetectable	No		
			Bear-B	7/27/13						
Hendrum, MN	2013	10;2	Purple-A	6/11/13	3	multiresidue	nondetectable	No		
			Lady-A	6/11/13			nondetectable			
			Dad-B	5/14/13			nondetectable			
Grand Forks, ND	2013	5;1	Bird-A	8/27/13	2	OP; ON only	nondetectable	No		
			Wire-A	8/29/13						
Frazee, MN	2012	8;3	OAT-A	8/22/12	5	multiresidue	positive for chlorothalonil	No		
			LOOP-A	8/23/12		multiresidue	positive for chlorothalonil			
			HAT-A	7/20/12		multiresidue	nondetectable			
			FAN-A	7/19/12		multiresidue	nondetectable			
			GLORY-A	9/5/12		multiresidue	nondetectable			
	2013	5;0	Hand-A	7/3/13	3	multiresidue	nondetectable	No		
			Oval-A	7/12/13		multiresidue	nondetectable			
			Knee-A	7/7/13		multiresidue	nondetectable			
	2014	28;4	Letter-B	7/5/14	9	multiresidue	nondetectable			
			Gruel-B	7/6/14		multiresidue	nondetectable			
			Wilow-B	7/12/14		multiresidue	nondetectable			
			Celery-A	7/17/14		multiresidue	nondetectable			
			Fairy-A	7/19/14		multiresidue	nondetectable			
			Sage-A	8/8/14		multiresidue	nondetectable			
			Lizard-A	8/9/14		multiresidue	nondetectable			
			Forest-B	8/13/14		multiresidue	nondetectable			
			Post-B	8/14/14		multiresidue	nondetectable			
Rochester, MN	2013	27;1	Warm-B	7/3/13	8	dicamba/2,4	nondetectable	No		
			Ear-B	7/4/13		dicamba/2,4	nondetectable			
			House-A	5/15/13		dicamba/2,4	nondetectable			
			Ogre-A	5/6/13		dicamba/2,4	nondetectable			
			Boy-A	6/1/13		multiresidue	nondetectable			
			Rain-A	6/11/13		multiresidue	nondetectable			
			Bug-B	6/25/13		multiresidue	nondetectable			
			Ghost-B	7/5/13		multiresidue	nondetectable			
Perham, MN	2013	16;2	Raccoon-B	7/27/13	6	multiresidue	nondetectable	No		
			Beak-B	7/28/13			nondetectable			
			Man-A	7/29/13			nondetectable			
			Desk-A	8/6/13			nondetectable			
			Screen-A	8/6/13			nondetectable			
			Rug-A	8/7/13			nondetectable			
	2014	24;4	Me-A	8/28/14	7	multiresidue	nondetectable	No		
			Pit-B	5/29/14			nondetectable			
			Opt-B	5/30/14			nondetectable			
			Palm-A	9/2/14			nondetectable			
			New-B	7/3/14			nondetectable			
			Kit-B	6/29/14			nondetectable			
			Mine-B	7/1/14			nondetectable			

Appendix 5: Quality Assurance – Quality Control

Operator Training

A Drift Catcher Operator participates in a hands-on training workshop on the operation of the Drift Catcher at which time a Drift Catcher Users' Manual is provided. Operators are then tested on their knowledge of the procedures and practices by a PAN scientist. Participants are certified if they can successfully demonstrate:

(1) Mastery of the technical set-up and operation of the Drift Catcher
(2) Correct use of Sample Log Sheets and Chain of Custody Forms
(3) Ability to troubleshoot and solve common operational problems
(4) Knowledge of the scientific method

Sample Labels

Sample labels were affixed directly to the sorbent tubes and to the corresponding sample log sheets prior to the start of sampling. The following information was contained on the labels: Sample ID, project name, and project date.

Sample Check-In

On arrival at the PAN office, samples were logged into a sample log notebook kept in the PAN offices.

Leak Check

All monitoring equipment was fully leak-checked prior to use by attaching the tubing-manifold combination to a pump generating a positive airflow and testing for leaks at each connection point with a soap solution.

Trip Blanks

One pair of trip blank tubes was prepared over the course of the sampling period as a negative control. These tubes were stored and transported with the samples from that location, and one from each pair was processed and analyzed as part of the batch on arrival in the lab. No pesticide residues were detected in the trip blank.

Appendix 6: Sample Log Sheet

Drift Catcher Sample Log Sheet

STARTING THE SAMPLE

Project: _____ Location: _____

YOU NEED: A Drift Catcher, a sample bag with pre-labeled tubes, caps, and labels, a tube cracker, a rotameter, two light shields, orange flag material, a compass, and a wind meter.

❒ **1. LABELS:** Make sure the labels included in the sample bag MATCH the labels on the pre-labeled tubes. If they match, affix the labels to this log sheet under Steps 4 & 11.

❒ **2. TUBES:** Break the tips of the glass sample tubes and insert them into the manifold.

❒ **3. PUMP:** Plug in the pump and note the EXACT TIME using the clock on the compass.

Today's Date		Exact Pump START Time	**AM or PM?**

❒ **4. ROTAMETER:** Use the rotameter to measure the flow rate for each tube.

	Tube Name	Starting Flow Rate	
Tube A	[stick label here]	**L/min**	**NOTE: Adjust the flow rates so that they are equal to each other!**
Tube B	[stick label here]	**L/min**	

❒ **5. LIGHT SHIELDS:** Attach both light shields.

❒ **6. COMPASS & ORANGE FLAG:** Use these to find the direction of the wind.

Which direction is the wind blowing FROM?	N NE E SE S SW W NW calm

❒ **7. WIND METER:** Face the wind meter into the wind for 2 minutes.

What is the wind speed?	maximum: mph	average: mph
What is the temperature? **(Remember to wave wind meter back and forth!)**		° F

❒ **8. YOUR SENSES:** Use your own senses to answer the following questions.

What is the weather like?	foggy sunny mix of sun and clouds cloudy rainy humid other:
Do you smell anything?	sweet rotten eggs perfume skunk none other:

There is space for other observations and notes at the bottom of the other side of this page.

Name: _____ Initials: _____

STOPPING THE SAMPLE (cont'd from other side)

❒ **9. PUMP:** Is the pump running? ❒ Yes ❒ No (If not, skip to Step #13)

❒ **10. LIGHT SHIELDS:** Remove both light shields.

❒ **11. ROTAMETER:** Use the rotameter to measure the flow rate for each tube.

	Tube Name	Ending Flow Rate	
Tube A	[stick label here]	L/min	**DO NOT adjust the flow rates. Just measure them.**
Tube B	[stick label here]	L/min	

❒ **12. PUMP:** Unplug the pump and note the EXACT TIME, using the clock on the compass.

Today's Date		Exact Pump STOP Time	**AM or PM?**

❒ **13. TUBES:** Remove the sample tubes, cap them, place them in the sample bag.

❒ **14. COMPASS & ORANGE FLAG:** Use these to find the direction of the wind.

Which direction is the wind blowing FROM?	N NE E SE S SW W NW calm

❒ **15. WIND METER:** Face the wind meter into the wind for 2 minutes.

What is the wind speed?	maximum: mph	average: mph	
What is the temperature? **(Remember to wave wind meter back and forth!)**		° F	

❒ **16. YOUR SENSES:** Use your own senses to answer the following questions.

What is the weather like?	sunny mix of sun and clouds cloudy rainy humid other:
Do you smell anything?	sweet rotten eggs perfume skunk none other:

❒ **17. TRIP BLANK:** If this is the first sample of your sample run in this location, prepare a Trip Blank sample (follow instructions on Trip Blank form).

Name: _____ Initials: _____

- -

OBSERVATIONS AND NOTES

Please record observations or notes below (known pesticide applications nearby, equipment failure, nearby activities that could interfere with the sample, etc.)

Date	Time	Observation/Note

Appendix 7: Freezer Log and Chain of Custody Form

Chain of Custody Form and Freezer Log

This form is used to keep track of where all your samples are and who has been responsible for them at all times.

Name: _____ Phone Number: _____

Project Name: _____

Sample Site (Include full address): _____

_____

Date Sampling Started: _____ Date Sampling Finished: _____

Freezer Log

Sample Name	Sample Placed in Freezer on Date	Time (am/pm)	Notes or Comments	Initials
Ejemplo – A	6/8/05	8:18 pm	This is an example entry.	JD

Pesticide Action Network, 49 Powell Street, Suite 500, San Francisco, CA 94102, (415) 981-1771

Chain of Custody Form

This section tracks who has control of the batch of samples as they are being transported and how they are handled.

When you receive the samples,
- Make sure all samples are accounted for.
- Record the time and date and put your initials in the **Received by** column.
- If you are unpacking samples from a shipping box, note the temperature of the ice packs.

When samples are passed from one person to another, you should record the method of storage (freezer, cooler, dry ice, etc). If you change the method of storage (i.e. from a freezer to a cooler) please also record this along with the date and time of change, even though the samples are still in your custody.

Date Sent	Time Sent	Sent by (Initials)	Storage Before Transfer	Storage During Transfer	Storage After Transfer	Date Received	Time Received	Received by (Initials)	Temperature upon arrival (Circle one)*
6/9/05	2:43 pm	JD	Freezer	Cooler	Freezer	6/10/05	9:08 am	SK	(1) - 2 - 3 - 4
									1 - 2 - 3 - 4
									1 - 2 - 3 - 4
									1 - 2 - 3 - 4
									1 - 2 - 3 - 4

*note the shipping container temperature by choosing the ice pack description that best describes the condition of the ice packs.
1: Fully frozen; 2: Partially frozen; 3: Not frozen but still cold; 4: Room Temperature

Names and signatures of sample handlers:

Each person who handles the samples will need to sign off on this form. Your signature and initials are your verification that the samples were handled as indicated on the form.

	Name (Please print)	Phone Number	Signature	Initials
Example	Juan Diego	(234) 567-8901	Juan Diego	JD
1				
2				
3				
4				

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